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# Multifunctional hyperbranched polyamide: Synthesis and properties



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## ABSTRACT

A novel multifunctional hyperbranched polyamide bearing oligoaniline, azobenzene and triphenylbenzene (PAOAF) has been prepared through a pyridine/LiCl-mediated acylation reaction. The structure of PAOAF was confirmed via nuclear magnetic resonance (NMR), Fourier-transform infrared spectra (FTIR), X-ray diffraction (XRD) and gel permeation chromatography (GPC). The thermal stability was probed via thermogravimetric analysis (TGA). The electrochemical activity of PAOAF was explored by cyclic voltammetry in 1.0 M H<sub>2</sub>SO<sub>4</sub> confirming a surface controlled process. Tunable dielectric property of PAOAF has been accomplished by controlling the isomerization of azobenzene groups using UV/vis irradiation. The electrochromic performance of a PAOAF/ITO electrode was studied by spectrochronoamperometry in detail, exhibiting good electrochromic properties with high contrast value and satisfactory coloration efficiency. Moreover, the fluorescence of PAOAF was modulated by controlling the oxidation degree of oligoaniline segments because of the energy migration occurring between oligoaniline and triphenylbenzene groups.

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## 1. Introduction

The novel properties of multifunctional polymers make them useful for an extensive range of application, including organic fieldeffect transistors, photovoltaic cells, bioengineering materials and sensors [1,2]. Exploring architectures, applications, and fundamental principles of various attributes of multifunctional polymers has recently attracted a significant academic and commercial interest. Among several functions reported for multifunctional polymers, electroactivity, shape-memory, magnetic, biomedical and bioinformatics, are particularly attractive [3–9]. In the Wang research group [3], biodegradable and biocompatible poly(p-dioxanone)-poly(tetramethyleneoxide)glycol multiblock copolymers with excellent shape memory effect and mechanical properties were developed by coupling PPDO-diol and PTMEG-diol with 1,6hexamethylene diisocyanate (HDI). Lendlein and coworkers [6] studied the shape-memory capability as well as the hydrolytic and enzymatic in vitro degradation behavior of electro-spun scaffolds prepared from a multiblock copolymer, containing hydrolytically degradable poly(p-dioxanone) and poly(e-caprolactone) segments. Ma et al. [7] presented cross-linked multifunctional conjugated polymers prepared by in situ electrochemical deposition, which were used as a highly-efficient blue-emitting and electron-transport layer.

Polyaniline (PANI) is one of the most frequently studied functional polymers potential for advanced applications such as eleccoatings, troluminescence. biosensors, anticorrosion electrochemical capacitors, gas separation membranes, and electromagnetic interference shielding materials [10-17] because of its good environmental stability, ease of synthesis and high conductivity [18–21]. Recently, ample work has been conducted on the preparation of multifunctional polymers bearing polyaniline oligomer segments, which could combine the good solubility and processability inherent to the oligoanilines with the functional benefits of other macromolecules. Chen and coworkers prepared and characterized a biodegradable and electroactive polymer blend materials based on PEG/tetraaniline and PLLA, the 20 wt% (PEG/ tetraaniline) blend shows the best biocompatibility and an electroactivity that accelerates the differentiation of rat C6 glioma cells [22]. Albertsson et al. synthesized degradable and electroactive hydrogels based on polylactide, polycaprolactone, and aniline pentamer. Tunable electrical conductivity and swelling behavior were reported [23,24]. Yeh et al. prepared an intrinsically dopable polyimide membrane containing aniline trimer that exhibits excellent gas separation capabilities as well as mechanically and thermally enhanced properties [25]. In our group, we have recently reported a novel poly(aryl ether) containing pendant oligoaniline



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and anthracene moieties. This material exhibits an interesting fluorescent response to redox active species [26]. We also designed and synthesized a multifunctional polyamide containing oligoaniline and azobenzene groups. Taking advantage of surface relief gratings based on azo-chromophores, we have fabricated materials with electrochemically responsive diffraction gratings [27]. In this paper, we describe a versatile post-polymerization modification strategy to prepare multifunctional polyamide bearing oligoaniline, azobenzene and triphenylbenzene groups (PAOAF). The properties of PAOAF, such as thermal stability, electroactivity, electrochromic performance and fluorescence modulating are described in detail.

## 2. Experimental

## 2.1. Materials

3-Methyl-4-nitrobenzoic acid and *N*-phenyl-*p*-phenylenediamine were purchased from Aldrich.  $\alpha$ -p-Glucose, acetic acid and thionyl chloride were purchased from Shanghai Chemical Factory. 4-Nitroacetophenone, SiCl<sub>4</sub>, hydrazine hydrate and Pd/C catalyst were purchased from Beijing Chemical Factory. All other reagents were obtained from commercial sources and used as received without further purification. Distilled and deionized water was used. Optically transparent ITO glass substrates (Reintech electronic technologies CO., 10  $\Omega$ /square) with dimensions of  $6.0 \times 0.6 \text{ cm}^2$  were used as thin film electrodes.

# 2.2. Synthesis of azo(3-methylbenzoyl)-4,4'-dicarbonyl dichloride (DDBMBC)

The synthesis route was described in Scheme 1. The reaction was conducted in a 500 mL three-necked round-bottom flask equipped with gas inlet and heated in an oil bath.  $\alpha$ -D-Glucose (1250 mmol), dissolved in 500 mL H<sub>2</sub>O, was added dropwise to stirring mixture of 3-methyl-4-nitrobenzoic acid (78 mmol), sodium hydrate (1250 mmol) and H<sub>2</sub>O (250 mL) at 50 °C. Then the reaction carried out readily in an atmosphere with the formation of a brown solution. The pink precipitate obtained by adding acetic acid, was dissolved in 1.0 M K<sub>2</sub>CO<sub>3</sub> aqueous solution, filtered and reprecipitated with hydrochloric acid, followed by drying under dynamic vacuum at room temperature for 24 h. (Yield: 52%).

The obtained acid product was dispersed in 150 mL thionyl chloride. A drop of DMF was added as a catalyst. The reaction



**Scheme 1.** Synthesis of azo(3-methylbenzoyl)-4,4'-dicarbonyl dichloride (DDBMBC), 1,3,5-tri(4-aminophenyl) benzene (TAPB) and parent aniline tetramer (PAT).

mixture was allowed to warm to reflux and stirred for 10 h. The excess thionyl chloride was removed at reduced pressure to give the red product. (Yield: 96%).

FTIR (KBr pellet, cm<sup>-1</sup>): 3081 (m,  $v_{C-H}$  of benzenoid rings), 2972 (m,  $v_{C-H}$  of methyl groups), 1763 (vs,  $v_{C=0}$ ), 1747 (s,  $v_{C=0}$ ), 1593 (m,  $v_{C=C}$  of benzenoid rings), 1421 (m,  $v_{N=N}$ ), 822 (m,  $\delta_{CH}$ ), 760 (w,  $\delta_{CH}$ ), 686 (m,  $\delta_{CH}$ ). <sup>1</sup>H NMR (500 MHz, 25 °C, CDCl<sub>3</sub>, TMS, ppm):  $\delta = 8.13$  (s, 2H, due to H<sub>4</sub> (the protons have been defined in Scheme 1)),  $\delta = 8.02$  (d, 2H, due to H<sub>1</sub>),  $\delta = 7.66$  (d, 2H, due to H<sub>2</sub>),  $\delta = 2.81$  (s, 6H, due to H<sub>3</sub>).

## 2.3. Synthesis of 1,3,5-tri(4-aminophenyl) benzene (TAPB)

SiCl<sub>4</sub> (360 mmol) was added dropwise over a period of 1 h to a stirring solution of 4-nitroacetophenone (12 mmol) in 120 mL ethanol. Following the addition of SiCl<sub>4</sub>, the resulting solution was heated to reflux for 10 h. After cooling to room temperature, the mixture was poured into 200 mL saturated NH<sub>4</sub>Cl aqueous solution. The solvent was removed at reduced pressure to give the yellow crude product, followed by drying under dynamic vacuum at 40 °C for 24 h. Then the crude product, Pd/C catalyst and 300 mL ethanol was added into a 500 mL three-necked round-bottom flask equipped magnetic stirring. Hydrazine hydrate (40 mL) was added dropwise to the above mixture, and then was heated to reflux for 10 h. The resulting solution was concentrated and recrystallized twice from ethanol, followed by drying under dynamic vacuum at room temperature for 24 h. (Yield: 81%).

MALDI-TOF-MS: m/z calculated for  $C_{24}H_{21}N_3 = 351.4$ . Found 351.3. FTIR (KBr pellet, cm<sup>-1</sup>): 3434 (s,  $v_{NH}$ ), 3355 (s,  $v_{NH}$ ), 1621 (s,  $v_C=_C$  of benzenoid rings), 1606 (s,  $v_C=_C$  of benzenoid rings), 1513 (vs,  $v_C=_C$  of benzenoid rings), 1473 (m,  $v_C=_C$  of benzenoid rings), 1425 (m,  $v_N=_N$ ), 871 (w,  $\delta_{CH}$ ), 829 (s,  $\delta_{CH}$ ), 707 (m,  $\delta_{CH}$ ), 649 (m,  $\delta_{CH}$ ). <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta$  = 7.48 (s, 3H, due to H<sub>1</sub> (the protons have been defined in Scheme 1)),  $\delta$  = 7.47 (d, 6H, due to H<sub>2</sub>),  $\delta$  = 6.66 (d, 6H, due to H<sub>3</sub>),  $\delta$  = 5.23 (s, 6H, due to H<sub>4</sub>). A typical elemental analysis for  $C_{24}H_{21}N_3$ : Calcd. C 82.02, H 6.02, N 11.96; Found C 82.11, H 5.98, N 11.91.

## 2.4. Synthesis of parent aniline tetramer (PAT)

The synthetic route for the preparation of parent aniline tetramer is depicted in Scheme 1. Firstly, the parent aniline tetramer in emeraldine state was synthesized by oxidative coupling of *N*-phenyl-*p*-phenylenediamine in the presence of ferric chloride according to the literature [28]. The obtained product (5.0 g) was then dispersed into a stirring mixture solution (30 mL of hydrazine hydrate in 400 mL of 1.0 M ammonium hydroxide) and stirred for 12 h. Then it was filtered and washed with distilled water for several times, followed by drying in vacuum. Finally, the PAT was reduced to the leucoemeraldine oxidation state. (Yield: 94%).

MALDI-TOF-MS: m/z calculated for  $C_{24}H_{22}N_4 = 366.5$ . Found 366.6. FTIR (KBr, cm<sup>-1</sup>): 3390 (s,  $v_{NH}$ ), 3020 (m,  $v_{CH}$ ), 1600 and 1527 (s,  $v_{C=C}$  of benzenoid rings), 1305 (s,  $v_{C-N}$ ), 815 (m,  $\delta_{CH}$ ), 746 (m,  $\delta_{CH}$ ), 692 (m,  $\delta_{CH}$ ). <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta = 7.78$  (s, 1H, due to H<sub>4</sub> (the protons have been defined in Scheme 1)),  $\delta = 7.68$  (s, 1H, due to H<sub>3</sub>),  $\delta = 7.43$  (s, 1H, due to H<sub>2</sub>),  $\delta = 7.12$  (t, 2H, due to H<sub>6</sub>),  $\delta = 6.87$  (m, 12H, due to H<sub>8</sub>),  $\delta = 6.65$  (t, 1H, due to H<sub>5</sub>),  $\delta = 6.51$  (d, 2H, due to H<sub>7</sub>),  $\delta = 4.62$  (s, 2H, due to H<sub>1</sub>). A typical elemental analysis for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>: Calcd. C 78.66, H 6.05, N 15.29; Found C 78.49, H 6.01, N 15.50.

## 2.5. Synthesis of multifunctional hyperbranched polyamide

A typical polymer synthesis procedure (shown in Scheme 2) is as follows. A mixture of DDBMBC (1.3407 g, 4 mmol), DMAc



Scheme 2. Synthesis of multifunctional hyperbranched polyamide.

(40 mL), toluene (10 mL), anhydrous lithium chloride (7 mmol), pyridine (0.7910 g, 10 mmol) were added to a 100 mL three-necked round-bottom flask and cooled by ice bath under nitrogen with mechanical stirring for 0.5 h. TAPB (0.7029 g, 2 mmol), dissolved in 5 mL DMAc, was added dropwise to the above solution. The reaction proceeded in an ice bath with stirring for 2 h. Then PAT (0.7329 g, 2 mmol) was dissolved in 5 mL DMAc and added to the reaction to cap the hyperbranched polymer. The solution was stirred for another 6 h to ensure the completion of the reaction. The solution was poured into 200 mL water, which yielded a brown precipitate. The precipitate was washed with water, ethanol and dichloromethane several times, filtered and dried under dynamic vacuum at 80 °C for 48 h (90% yield).

FTIR (KBr pellet, cm<sup>-1</sup>): 3386 (s,  $v_{NH}$ ), 2926 (m,  $v_{C-H}$  of methyl groups), 1693 (vs,  $v_{C=0}$ ), 1602 (s,  $v_{C=c}$  of benzenoid rings), 1512 (vs,  $v_{C=c}$  of benzenoid rings), 1429 (m,  $v_{N=N}$ ), 1299 (m,  $v_{C-N}$ ), 823 (m,  $\delta_{CH}$ ), 776 (w,  $\delta_{CH}$ ). <sup>1</sup>H NMR (500 MHz, 25 °C, DMSO- $d_6$ , TMS, ppm):  $\delta = 10.51$  (m, due to -NH-CO-),  $\delta = 8.17-7.49$  (m, due to H-Ar and -NH-),  $\delta = 7.16$  (m, due to H-Ar),  $\delta = 6.97$  (m, due to H-Ar),  $\delta = 6.71$  (m, due to H-Ar),  $\delta = 2.74$  (m, due to  $-CH_3$ ). GPC results:  $M_n$ : 5000,  $M_W$ : 11,000, PDI: 2.2.

## 2.6. Fabrication of electrochromic device

The ITO substrates were washed ultrasonically in acetone for 3 min and then in the deionized water for another 3 min, followed by drying in the air before use. Polymer (0.03 g) was dissolved in 1 mL DMAc to form a solution, and filtered through 0.2- $\mu$ m poly(-tetrafluoroethylene) syringe filter. Then, polymer films were spin-coated onto the ITO substrates using the DMAc solution of polymer. The spin-coating process started at 500 rpm for 5 s and then 1000 rpm for 30 s. A copper tape (1.0 cm  $\times$  0.5 cm) was applied to the top edge of ITO substrates, before electrochromic measurements, as the bus bar.

## 2.7. Characterization techniques

Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 spectrometer. The nuclear magnetic resonance spectra (NMR) were run on a BRUKER-500 spectrometer. The weight percentages of carbon, hydrogen,



Fig. 1. X-ray diffraction pattern (a) and TGA thermogram (b) (under nitrogen atmosphere) of PAOAF.



**Fig. 2.** CV of the PAOAF electrode in 1.0 M  $H_2SO_4$  at different potential scan rates: 10–100 mV/s. Inset shows the relationships between the oxidation peaks and reduction current vs. potential scan rate.

nitrogen and oxygen in the samples were measured by a Flash Ea 1112 elemental analysis instrument. The number-average molecular weight  $(M_n)$ , weight-average molecular weight  $(M_w)$ , and molecular weight distribution of the polymer were measured with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector with DMF as an eluant at a flow rate of 1 mL/min. Wide-angle X-ray diffraction (WAXD) measurements were made using a Siemens D5005 diffractometer equipped with a  $CuK_{\alpha}$  radiation source at room temperature. A Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of the polymer. Trans-cis isomerization behavior of PAOAF was investigated by exposing to the UV lamp (365 nm after filter, PHILIPS HPA400S 400 W) and visible lamp (420 nm after filter, CHF-XM 500 W). The CV was investigated on a CHI 660A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using an Ag/AgCl cell as the reference electrode, a platinum wire electrode as the counter electrode, and a glassy carbon electrode ( $\Phi$ 3.0 mm) as the working electrode. Spectroelectrochemical measurements were carried out in a cell built from a 1 cm commercial cuvette using a UV-2501 PC Spectrometer. The ITO-coated glass was used as the working electrode, a Pt wire as the counter electrode, an Ag/AgCl cell as the reference electrode and 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> as the electrolyte. Fluorescence spectra were investigated on a fluorometer of SPEXF212 model (SPEX) in dilute DMAc solution.

The electrical conductivity of the 1 mol/L HCl-doped PAOAF was determined by the standard Van Der Pauw four-probe method.

The conductivity was measured three times at different current values, and the average value was taken as the conductivity. Dielectric spectroscopy was performed using a QuadTech1920 LCR meter. Measurements of the capacitance (*C*) over the range of 100 Hz–1 MHz were carried out with the polymer powder-pressed pellet. Two identical aluminum foil strips were used to clamp the polymer pellet on its two surfaces, which were used as both electrode plates and lead wires. In order to make the aluminum foil well contact with the polymer pellet, two glass plates with two clips were used to clip the aluminum foil strips. The dielectric constant ( $\epsilon'$ ) was calculated from capacitance using the following equation:

$$\varepsilon' = \frac{Cd}{l^2 E_0}$$

where *d* is the thickness and  $E_0$  is the permittivity of the free space, is 8.854 × 10<sup>-12</sup> F m<sup>-1</sup>. The contact part between aluminum foil strip and pellet is an approximate square, *l* is the side length of the square.

## 3. Results and discussion

#### 3.1. Synthesis, structure and thermal properties

The multifunctional hyperbranched polyamide was synthesized by a two-step procedure. The lithium chloride was used as a catalyst and pyridine was used to absorb the hydrochloride acid, which comes from the polycondensation reaction. The reaction proceeded in the ice bath. The structure of PAOAF was confirmed by FTIR, <sup>1</sup>H NMR, GPC and XRD. FTIR spectra of PAOAF displayed the characteristic absorption bonds around 3386 cm<sup>-1</sup> corresponding to N-H stretching vibration, around 1299 cm<sup>-1</sup> based on C–N stretching vibration of amide groups. The vibration at 1602  $cm^{-1}$  and 1512 cm<sup>-1</sup> is attributed to the stretching vibration of C=C in the benzene rings. In the <sup>1</sup>H NMR spectra of PAOAF, the signal at  $\delta = 10.51$  ppm is attributed to the amino protons of the amide groups, and the signal at  $\delta = 2.74$  is ascribed to the methyl protons. Furthermore, aromatic protons appeared at  $\delta = 8.17-6.17$ . According to the integral area ratio of amino protons (amino and amide groups) and methyl protons from the <sup>1</sup>H NMR spectra, the triphenylbenzene, azobenzene and oligoaniline were about 1:1.96:0.92, which almost the same with the feeding ratio (1:2:1) of the reaction. The number average molecular weight and polydispersity index of PAOAF, obtained by GPC, are 5000 and 2.2 respectively.

The wide-angle XRD pattern of PAOAF (Fig. 1a) shows a broad peak from 10° to 35°, which indicates that the hyperbranched polymer existed in a form of noncrystalline state. This is mainly due to the fact that the branched structure decreases the interchain hydrogen bonding and  $\pi$ – $\pi$  interactions and disturbs the close



Fig. 3. UV-Vis spectra changes of PAOAF during ultraviolet irradiation (a) and visible light irradiation (b).



Fig. 4. Frequency dependence of dielectric constant and dielectric loss of PAOAF in LEB, EB and HCI-doped EB form (a), and under UV/Vis irradiation (b), respectively.

packing and regularity of the polymer chains. The amorphous structure is a basic characteristic for hyperbranched polymers [29]. Moreover, PAOAF exhibited outstanding solubility in polar solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) due to the hyperbranched structure.

The thermal properties of pristine PAOAF were evaluated by TGA (Fig. 1b). An obvious mass loss beginning at 280 °C is observed corresponding to the decomposition of main chain. 5% Weight loss temperatures of the obtained polymer are 300 °C, which indicates that the PAOAF has moderate thermal stability and general degradation temperature the same as typical polyaniline materials [30]. But compared with aramid and copolyaniline material [31,32], the thermal stability of PAOAF is much lower, which due to the weak interchain interaction originated from its hyperbranched structure.

### 3.2. Electrochemical activity

The cyclic voltammetry (CV) was used to study the electrochemical behavior of PAOAF and the results were shown in Fig. 2. The PAOAF DMAc solution was cast on the g-c working electrode and then evaporated to form a thin solid film. The CV of the decorated electrode was performed in 1.0 M H<sub>2</sub>SO<sub>4</sub> at different potential scan rates from 10 to 100 mV/s. The CV of the PAOAF-decorated electrode exhibited two redox processes with the reduction peaks at 200 and 460 mV. The first reduction peak corresponded to the emeraldine base (EB)/leucoemeraldine base (LEB) transition, and the second reduction peak corresponded to the pernigraniline base (PNB)/ emeraldine base (EB) transition. A linear dependence of the peak currents as a function of scan rates in the region of 10-100 mV/s (inset of Fig. 2) confirmed both a surface controlled process and a well-adhered electroactive polymer film. The PAOAF film was found to be very stable with almost no change in its CV diagram after 60 repeated cyclic scans between 0 and 800 mV.

## 3.3. Photoisomerization of PAOAF

Trans-cis isomerization of azobenzene groups was investigated in details by irradiating the PAOAF DMAc solution with UV/visible light. The UV-Vis spectra changes were recorded during the ultraviolet and visible irradiation. As shown in Fig. 3(a), the intensity of the absorption of PAOAF DMAc solution at about 340 nm, associated with the  $\pi$ - $\pi^*$  transition of the trans-azobenzene groups and benzenoid rings, gradually decreased as irradiation time increased. This occurred concurrently with a blue shift, due to the trans-to-cis photoisomerization process of the azobenzene chromophore. The blue shift of the absorption was attributed to the overlap of the  $\pi$ - $\pi^*$ transition of the trans-azobenzene groups and benzenoid rings [33,34]. UV–Vis spectra changes were obtained with time intervals about 2 min and the trans–cis isomerization reached to a steady state 8 min later, and then the above solution was transferred to visible radiation. As shown in Fig. 3(b), the intensity of the absorption, associated with  $\pi$ – $\pi$ \* transition of the trans-azobenzene group, gradually increased with the anticipated red shift. The absorption at about 340 nm nearly reached the intensity of its original value after 16 min. These results confirm that PAOAF retained the photoisomerization characteristics of azobenzene.

## 3.4. Electrical and dielectric properties

The electrical conductivity value of PAOAF was determined by the standard four probe method. Firstly, PAOAF in EB was prepared by oxidizing the obtained PAOAF with ammonium persulfate. Then HCI-doped PAOAF in EB was made by dispersing the polymer powder in 1 M HCI solution at room temperature for 8 h. Finally three samples of PAOAF were measured four times at different current values. The average of 12 measurements was about  $7.6 \times 10^{-6}$  S/cm. The electrical conductivity value of PAOAF is much lower than that of HCI-doped PANI, which was attributed to the low conductive percent in the polymer architecture.

Recently, some high dielectric constant materials have been reported by incorporating oligoaniline segment into the polymer architecture, which avoids the drawbacks of agglomeration and phase separation in PANI/insulating polymer blends [35]. Consequently, dielectric response properties of PAOAF were investigated in here.



**Fig. 5.** Optical transmittance of PAOAF electrodes ( $0.6 \times 3 \text{ cm}^2$ ) in 0.5 M H<sub>2</sub>SO<sub>4</sub> at different potentials. Inset shows photographs of PAOAF/ITO electrode at different potentials.



Fig. 6. Current consumption (a) and absorbance changes (b) monitored at 700 nm of PAOAF/ITO electrode in 0.5 mol/L  $H_2SO_4$  for the first 10 cycles.

Dielectric constants and dielectric loss of PAOAF in LEB, EB and HCldoped EB (emeraldine salt) were presented in Fig. 4a. The emeraldine salt of PAOAF possessed a higher dielectric constant than that of EB state from 100 Hz to 1 MHz, and gave a value of 20 detected at the frequency of 100 Hz, then decreased to 5.0, as the frequency was increased to 1 MHz. The frequency dependence of dielectric loss was shown in the inset of Fig. 4a. Due to the enhancement of the polarity of the polymer chains, the dielectric loss of emeraldine salt was higher than that of LEB and EB. The influence of photoisomerization derived from azobenzene groups on the dielectric properties of PAOAF was also investigated. The dielectric properties of emeraldine salt PAOAF exposure to UV/Vis irradiation were shown in Fig. 4b. After exposing to the UV irradiation, the dielectric constant and dielectric loss increased gradually as the time of irradiation increased. When the polymer reached the steady state after 10 min UV irradiation, the dielectric constant increased to 26.5 at 100 Hz, and 5.7 at 1 MHz. After 20 min visible light irradiation, the values of its dielectric constant and dielectric loss went back to its original value, which indicated that the dielectric properties of assynthesized PAOAF could be tuned by controlling the photoisomerization of azobenzene groups using UV/Vis irradiation.

## 3.5. Spectroelectrochemistry and electrochromic performances

Spectroelectrochemical measurements were performed on PAOAF/ITO electrode by increasing the potential from -0.2 to 1.0 V

in conjunction with the acquisition of UV–Vis spectral data (Fig. 5). The optical contrast value ( $\%\Delta T$ ) was obtained from the transmittance difference at 700 nm between its coloring (oxidization) and bleaching (reduction) states. This PAOAF/ITO electrode exhibited good contrast with a high optical transmittance change ( $\%\Delta T$ ) of 25% (69.24% (at –0.2 V)  $\leftrightarrow$  44.69% (at 0.8 V)) at 700 nm. The color of the PAOAF/ITO changed drastically from gray (at 0.0 V), to green (at ca. 0.4 V), and finally to dark blue (at ca. 0.8 V).

Electrochromic switching studies were performed to monitor changes in the optical contrast at 700 nm during repeated potential stepping between reductive state (-0.2 V) and oxidized state at 0.8 V with a residence time of 60 s. Fig. 6 shows the first 10 cycles results. Switching time in this case is the time required to bring the PAOAF to its most reduced state from its most oxidized state or vice versa. It was defined as the time required for reaching 90% of the full change in the coloring/bleaching process. The PAOAF revealed a switching time of 7.8 s at 0.8 V for the coloring process at 700 nm and 3.0 s for bleaching (-0.2 V). The coloration efficiency (CE,  $\eta = \Delta OD/Q$ ) is generally used to measure the power requirements of an electrochromic material. It was calculated by monitoring the amount of ejected charge (Q) as a function of the change in optical density ( $\Delta OD$ ) of the polymer film. The new multifunctional PAOAF exhibited a high CE up to 97.14 cm<sup>2</sup>/C (at 700 nm).

### 3.6. Photophysical properties and fluorescence tuning

Photophysical properties of PAT, DDBMBC, TAPB and PAOAF were characterized by UV–Vis spectra and fluorescence emission spectra (Fig. 7). In the UV–Vis spectra, PAT, TAPB and PAOAF in the DMAc are peaked at 322, 300 and 326 nm, respectively, associated with  $\pi - \pi^*$  transition in the conjugated structure. DDBMBC also shows azobenzene's characteristic absorption bands at 341 nm, assigned to the  $\pi - \pi^*$  transition of the trans-azobenzene groups. In the fluorescence spectra, parent aniline tetramer shows blue fluorescence at 440 nm derived from benzenoid units. DDBMBC also exhibits a weak fluorescence at 382 and 405 nm derived from benzenoid units. Moreover, TAPB presents strong emission with maximum at 414 nm, and TAPB units should be the main chromophore in the polymer structure because of the low fluorescent essence of the PAT and DDBMBC [36,37]. As a result, PAOAF displays fluorescence at 420 nm.

Furthermore, to investigate the fluorescence of PAOAF with diverse oxidation degree, the titrations were carried out by adding  $1.0 \times 10^{-3}$  M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> DMAc solution (containing 3 vol% H<sub>2</sub>O) into the reduced PAOAF DMAc solution. Firstly, the as-prepared luminescence solution at LB (0.00 eq S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) exhibits the expected fluorescence signal (Fig. 8). With the increase of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration, the fluorescence intensity of the emission maximum



Fig. 7. UV-Vis spectra (a) and fluorescence spectra (b) of PAT, DDBMBC, TAPB and PAOAF in DMAc solution.



Fig. 8. Monitoring fluorescence spectra of PAOAF in DMAc as it is oxidized from its leucoemeraldine base (LEB) to emeraldine base (EB) and pernigraniline base (PNB).

at 420 nm underwent a dramatic reduction and reached to 30% of its original after the addition of 1.00 eq  $(NH_4)_2S_2O_8$  (PAOAF in EB). However, only tiny change was observed after adding more  $(NH_4)_2S_2O_8$  (1.00–2.00 eq) during transformation of PAT from EB to PNB. In a word, the fluorescence intensity of PAOAF could be modulated by controlling the oxidation degree of oligoaniline (from LEB to EB). Going from EB to PNB has no influence on its fluorescence. We supposed a possible mechanism for the fluorescence tuning that the quinoid structure in the oligoaniline (in EB) will facilitate the interaction between oligoaniline and triphenylbenzene groups, leading to the energy migration between them. Moreover, the quinoid structure in oligoaniline acts as an excitation trap and quenches the polymer's fluorescence [36,37].

## 4. Conclusion

A multifunctional hyperbranched polyamide containing pendant aniline tetramer, azobenzene and triphenylbenzene groups was synthesized and characterized. Based on the synergistic interplay of these three distinct functional groups, the obtained hyperbranched polyamide shows reversible electroactivity, tunable dielectric property and the expected spectroscopic properties. PAOAF displayed good electrochromic performance with high contrast value, outstanding coloration efficiency, and acceptable switching times. Moreover, the fluorescence intensity of PAOAF could be tuned by modulating the oxidation degree of oligoaniline group. Taking into account the molecular diversity and tailoring as well as reversible redox properties, this multifunctional hyperbranched polymer could be competitive material for electrochromic devices, optic devices, sensors, and anticorrosion coatings.

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