



# Dual functional electrochromic and electrofluorochromic network polymer film prepared from two hydrolysable crosslinked siloxane monomers



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## ABSTRACT

Dual electrochromic and electrofluorochromic materials have gained much attention for various intelligent applications, such as sensors, displays, and wearable devices. We report here the synthesis of two hydrolysable crosslinked siloxane monomers via nucleophilic reaction, followed by drop-casted onto the hydrophilic indium-tin oxide substrate. After hydrolysis during cyclic voltammetry, the aforementioned two functional siloxane monomers are transformed into a network polymer film. The resulting polymer film exhibits good electrochromic performance with outstanding stability, due to its inherent robust crosslinking structure and strong adhesion to the ITO substrate. Moreover, a fascinating electrofluorochromic behavior has also been disclosed, due to the interplay between electroactive oligoaniline and fluorescent fluorene groups.

## 1. Introduction

Electrochromic polymers have attracted increasing attention recently because of their potential applications, such as smart windows, low-energy displays, self-dimming rear mirrors for automobiles, intelligent wearable devices and so on [1–6]. Among various electrochromic polymers, polyaniline is considered to be a promising candidate due to its low redox switching potentials, high electroactivity, multicolor behavior, and easy synthesis via both chemical and electrochemical polymerization methods [7–9]. Nevertheless, the poor solubility and brittleness of polyaniline stemmed from the conjugated structure have hampered its electrochromic applications [10]. Although some polyaniline derivatives [11–13], have been prepared to fabricate electrochromic device with improved performance, their solubility and flexibility still can't reach the benchmark of practical applications. Currently a fascinating tactics has been explored to synthesize electrochromic polymer bearing oligoaniline segments serving as the electroactive units [10,14–16]. By virtue of exquisite molecular design and synthesis, these resulting oligoaniline-containing polymers possess tunable electrochromic properties with enhanced processability. To modulate certain parameters of electrochromism (such as color range, switching time, coloration efficiency, optical contrast and stability), some functional groups, including azobenzene, sulfoacid, alkene, and hydrophilic groups, have been introduced into the oligoaniline-containing polymers architecture [17–21].

Electrofluorochromic materials exhibit great potentials in the applications of photoelectric conversion devices, biological information storage, chemical sensors, and intelligent displays [22–27]. Recently, some oligoaniline-containing electrofluorochromic polymers have been designed and synthesized through the introduction of fluorophores [28,29]. The interaction between oligoaniline and fluorophore is responsible for the regulation of fluorescence properties upon applied potentials. Hitherto, copolymerization and post-polymerization functionalization are popular strategies to prepare fluorescent oligoaniline-containing polymers. However, these polymerization methods normally produce polymers with a linear or branched architecture. The synthesis of electrofluorochromic polymers with new architectures based on oligoaniline segments remains rare.

Network polymers have gained much attention in the past decade due to their particular architecture and various potential applications [30]. The possess property of inherent robust from the internal networks are beneficial for the enhancement of stability during their actual utilization. Compared to the direct polymerization method, the induced covalent crosslinking of preformed polymer chains in a secondary step is a facile strategy to synthesize network polymers [31,32]. Thereinto, the crosslinking of siloxane monomers through hydrolysis reaction is regarded as a mild and facile method [33]. Although some organic-inorganic hybrid electrochromic materials containing triarylamine and siloxane have been reported [34,35], more similar electrochromic materials with improved performance need to be explored. Herein, we

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report the synthesis of two hydrolysable crosslinked siloxane monomers bearing oligoaniline and fluorene groups, respectively. A multifunctional network polymer (MFNP) is formed through the hydrolysis reaction of the aforementioned two functional siloxane monomers during cyclic voltammetry, which exhibits dual electrochromic and electrofluorochromic behaviors.

## 2. Experiment section

### 2.1. Materials

9-Fluorenone, *N*-phenyl-*p*-phenylenediamine and aniline hydrochloride were purchased from Aladdin. 3-(Triethoxysilyl)propyl isocyanate was purchased from TCI. FeCl<sub>3</sub> was obtained from Sinopharm Chemical Reagent Co., Ltd. Tetraaniline (TA) and 9,9'-bis(4-aminophenyl) fluorene (BAPF) was synthesized in our lab in accordance with the established method described in our previous paper [15,36]. All the solvents were purchased from commercial sources and used as received without further purification. Optically transparent Indium-Tin Oxide (ITO) glass substrates were purchased from Xiang Science & Technology Co. Ltd. (Shenzhen).

### 2.2. Instruments

The nuclear magnetic resonance spectra (NMR) in deuterated dimethyl sulfoxide (DMSO) were run on a VARIAN-300 spectrometer. UV-vis spectra were recorded on a UV-3101 PC spectrometer (SHIMADZU). Fluorescence data were collected on F97Pro fluorospectro photometer (Lengguang, Shanghai). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) of the polymer were run on a CHI 660C Electrochemical Workstation (CH Instruments, USA). The electrochemical experiments were accomplished in a conventional three-electrode cell, composed of an Ag/AgCl reference electrode, a platinum counter electrode, and the polymer/ITO working electrode. The electrolyte in the electrochemical measurement was 1.0 M hydrochloric acid solution. The field emission scanning electron microscopy (SEM, FEI Nova NanoSEM 450) was used to characterize the morphologies of the films before and after the cyclic voltammetry cycles.

### 2.3. Synthesis of TA-Si

3-(Triethoxysilyl)propyl isocyanate (0.4947 g, 2 mmol), TA (0.732 g, 2 mmol), and DMSO (1.5 mL) were added into a 10 mL three-necked round flask under the nitrogen atmosphere. The reaction was kept with magnetic stirring at room temperature for 3 h. The synthesized tetraaniline-functionalized siloxane compound was defined as TA-Si. Due to its hydrolytic characteristics, TA-Si would be easily cross-linked, yielding a networked polymer with a failed NMR spectrum. So, the deuterated dimethyl sulfoxide (DMSO) was used as the reaction solvent, the resultant solution would be used directly for TA-Si NMR measurement. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, ppm): δ = 8.09 (s, -CONH-), δ = 7.73–7.50 (m, -NH-), δ = 7.28–6.68 (m, Ar-H), δ = 6.02 (m, -CONH-), δ = 3.74 (m, -O-CH<sub>2</sub>-), δ = 3.03 (m, -CH<sub>2</sub>- next to urea group), δ = 1.46 (m, -CH<sub>2</sub>-), δ = 1.14 (m, -CH<sub>3</sub>), δ = 0.54 (m, -CH<sub>2</sub>-Si-(O-)<sub>3</sub>).

### 2.4. Synthesis of BAPF-Si

3-(Triethoxysilyl)propyl isocyanate (3.9579 g, 16 mmol), BAPF (2.7877 g, 8 mmol), and DMSO (6 mL) were added into a 25 mL three-necked round flask under the nitrogen atmosphere. The reaction was kept under magnetic stirring at 85 °C for 3 h. The synthesized BAPF-functionalized siloxane compound was defined as BAPF-Si. Similar to TA-Si, the deuterated DMSO was used as the reaction solvent for BAPF-Si NMR measurement. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, ppm): δ = 8.35 (s,

-CONH-), δ = 7.89 (d, Ar-H), δ = 7.42–7.19 (m, Ar-H), δ = 6.95 (d, Ar-H), δ = 6.09 (m, -CONH-), δ = 3.75 (m, -O-CH<sub>2</sub>-), δ = 3.02 (m, -CH<sub>2</sub>- next to urea group), δ = 1.44 (m, -CH<sub>2</sub>-), δ = 1.14 (m, -CH<sub>3</sub>), δ = 0.53 (m, -CH<sub>2</sub>-Si-(O-)<sub>3</sub>).

### 2.5. Fabrication of MFNP/ITO electrodes

ITO substrates were prepared with 5.5 × 1.0 cm dimension and washed ultrasonically with dichloromethane, ethanol and distilled water for 2 min, respectively, followed by drying with nitrogen flow. Subsequently, the clean ITO substrates were immersed into a mixture of deionized water, 25% ammonium hydroxide and 30% H<sub>2</sub>O<sub>2</sub> (volume ratio 5:1:1) for 30 min at 80 °C, followed by rinsing with deionized water and drying with nitrogen flow [37].

The above TA-Si solution and BAPF-Si solution were mixed under magnetic stirring at room temperature for 0.5 h. Then TA-Si and BAPF-Si were deposited on the hydrophilic ITO substrate by drop-casting method, followed by drying with dynamic vacuum at 40 °C for 2 h. Subsequently, the above decorated ITO substrate was employed as a working electrode to construct a conventional three-electrode cell system, with the assistance of Ag/AgCl reference electrode, and platinum wire counter electrode. The cyclic voltammetry was run between -0.2 V and 0.8 V with a scan rate of 100 mV/s in 1.0 M hydrochloric acid solution.

## 3. Results and discussion

### 3.1. Characterization of MFNP film

As shown in Scheme 1, MFNP film was fabricated by crosslinking reaction of TA-Si and BAPF-Si with ratio of 1:4. During cyclic voltammetry process, the repetitive insertion/extraction of hydronium ion through the mixture film was accomplished under the electrokinetic potential. The kinetic hydronium ion would induce hydrolysis reaction between TA-Si and BAPF-Si monomers. As shown in Fig. 1a, only one pair of redox peaks at 0.53 V/0.33 V are found in the cyclic voltammetry curves, which demonstrates one transition between reduced state and oxidized state in the oligoaniline segment. With the crosslinking reaction proceeded, the more oligoaniline segments were involved in MFNP architecture, resulting in an increasing peak current. No increase of peak current was observed after 50 cyclic voltammetry cycles, which indicates that the MFNP film was accomplished. As shown in Fig. 1b, the FTIR spectra of MFNP film and the mixture of siloxane monomers display characteristic N-H stretching vibration in the range of 3360–3250 cm<sup>-1</sup>, and C-H stretching vibration of alkyl groups around 2900 cm<sup>-1</sup>. The stretching vibrations of C=C groups in the aryl groups are found around 1600 and 1500 cm<sup>-1</sup>. The characteristic carbonyl groups stretching vibration appears around 1650 cm<sup>-1</sup>. The Si-C bonds are verified by the deformation vibration at 1236 cm<sup>-1</sup> and stretching vibration at 750 cm<sup>-1</sup>. In the FTIR spectrum of the siloxane monomers mixture, the characteristic stretching vibration of Si-O-C are found at 1074 and 1022 cm<sup>-1</sup>. After the crosslinking reaction, the resultant Si-O-Si bonds reveal stretching vibration at 1110 and 1020 cm<sup>-1</sup>, which indicates the formation of crosslinked network polymer. Furthermore, the morphology of as-prepared MFNP film was characterized by SEM. The inset of Fig. 1c shows the SEM image of TA-Si and BAPF-Si coated on ITO substrate before the cyclic voltammetry operation. The drop-casting film appears to be uniform and flat with a few irregular particles. After 50 cyclic voltammetry cycles, the film becomes porous, attributed to the molecule aggregation and release of small molecules during the crosslinking reaction through hydrolysis.

### 3.2. Electrochemical properties

Firstly, the electrochemical activity of MFNP was investigated by cyclic voltammetry with different scan rates from 10 to 50 mV/s. The

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