

# Synthesis, electrochemical properties and inhibition performance of water-soluble self-doped oligoaniline derivative

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## ABSTRACT

A novel water-soluble self-doped oligoaniline derivative (WSOAD) was synthesized by oxidative coupling method. The prepared WSOAD showed expected spectroscopic properties, and also revealed good solubility in strong polar solvents and aqueous media across a pH range of 1–14. WSOAD displayed excellent electroactivity in acid, neutral and even in alkaline solutions (pH = 10) due to self-doping effect between oligoaniline and sulfonic acid groups. Moreover, the inhibition effect of WSOAD on the cold rolled steel in 1.0 M HCl solution was studied by weight loss and potentiodynamic polarization measurements. The results showed that WSOAD was a good inhibitor in HCl medium.

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## 1. Introduction

Conducting polymers have attracted great academic and industrial interest in the areas of chemistry, physics and material science over the past decades because of their high conductivities upon doping [1]. Of these conducting polymers, polyaniline (PANI) has gained extensive attention by virtue of its attributes and applications. These include high conductivity, good environmental stability, simple polymerization, all making available a variety of applications such as sensors, electromagnetic shielding materials, rechargeable batteries, corrosion inhibition and electrochromic devices [2–7]. However, PANI prepared by chemical and electrochemical methods presents the ill-defined molecular structure and ambiguous structure–property correlations [8–10].

Polyaniline oligomers (oligoaniline) not only provide the opportunity to design and synthesize well-defined species with well-defined properties, but is also useful as a model compound to investigate the conducting mechanism and physical properties of PANI [11,12]. Oligoanilines can be mainly divided into three groups based on the identity of the end group: parent oligoaniline (denoted as Ph/NH<sub>2</sub> oligoaniline), amino-capped oligoaniline (denoted as NH<sub>2</sub>/NH<sub>2</sub> oligoaniline), and phenyl-capped oligoaniline (denoted as Ph/Ph oligoaniline). Considerable effort has been devoted toward the syntheses of oligoanilines in the emeraldine base (EB), since

it can be doped by acids to create the conducting form, which can be reversibly dedoped back to the insulating EB form. Zhang et al. reported the syntheses of monodisperse parent oligoanilines such as tetramer and 16-mer by oxidative coupling reaction [13]. By the pseudo-high dilution technique, Zhang and coworkers prepared phenyl-capped aniline tetramer through oxidative coupling of diphenylamine with the acetaldehyde-based Schiff's base of 1,4-phenylenediamine [14]. Phenyl-capped aniline tetramer was also synthesized by MacDiarmid and Kaczorowski using condensation method and a palladium-catalyzed amination strategy [15,16]. The nucleophilic aromatic substitution reaction was utilized to synthesize parent oligoanilines and amino-capped oligoaniline. 4-Fluoronitrobenzene was used to react with the corresponding aromatic amine in the presence of triethylamine [17]. Moreover, an oligoaniline derivative with chiral centers and hydrogen-bonding sites was reported, and the intramolecular interactions were studied in detail [18].

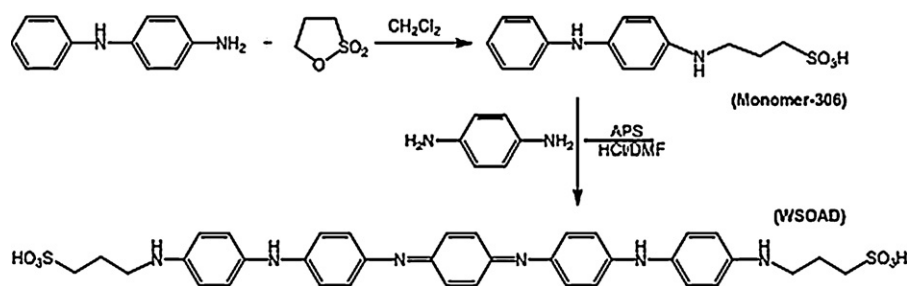
In this work, we report the synthesis of a new water-soluble self-doped oligoaniline derivative by the simple oxidative coupling method. Spectroscopic and electrochemical properties are presented and discussed. The possible application of this material as a corrosion inhibitor is also explored.

## 2. Experimental

### 2.1. Chemicals and instrumentations

All chemicals, including *N*-phenyl-*p*-phenylenediamine, and *p*-phenylenediamine were purchased from Aldrich.

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**Scheme 1.** Synthetic route to water-soluble self-doped oligoaniline derivative.

1,3-Propanesultone, ammonium persulfate (APS, 98%) and hydrochloric acid (37%) were purchased from Beijing Chemical Factory. *N,N'*-Dimethylacetamide (DMAc, 99%), *N,N'*-dimethylformamide (DMF, 99%), dimethyl sulfoxide (DMSO, 99%), *N*-methyl-2-pyrrolidone (NMP, 99%), tetrahydrofuran (THF, 99%), ethanol (99%) and dichloromethane (99.5%) were used as received without further purification. Distilled and deionized water was self-made. Optically transparent ITO glass substrates (Reintech Electronic Technologies Co., 10 Ω/square) with dimensions of 6.0 cm × 0.6 cm were used as thin film electrodes. Inhibition performance were run on the cold rolled steel of the following composition (wt%): C 0.07%, Mn 0.3%, P 0.022%, S 0.01%, Si 0.01%, Al 0.03% and Fe bal.

Fourier-transform infrared spectra (FTIR) measurements were recorded on a Bruker vector 22 spectrometer. The nuclear magnetic resonance spectra (NMR) of samples in deuterated dimethyl sulfoxide (DMSO) were run on a Bruker-500 spectrometer. Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). The composition of monomer-306 and WSOAD were calculated from the results of elemental analysis (EA). The weight percentages of carbon, hydrogen, nitrogen and oxygen in the samples were measured by a Flash Ea 1112 elemental analysis instrument. The cyclic voltammetry (CV) was investigated on a CHI 660A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using a saturated calomel electrode (SCE) as the reference electrode, a platinum wire electrode as the counter electrode, and a glassy carbon electrode (GCE,  $\Phi$  3.0 mm) as the working electrode. Before the experimental tests, the glassy carbon (GC) working electrode was polished carefully with alumina powder to a mirror finish. After sonicating in absolute ethanol and water for 30 s, a thin polymer film was cast onto the GC electrode. The film was cycled in 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution in the range of 0–1000 mV. Solutions of 1.0 mol L<sup>-1</sup> sulfuric acid and 1.0 mol L<sup>-1</sup> KOH solutions with pH ranging from 0 to 12 were prepared and tested at room temperature. UV-vis spectra were recorded on a UV-2501 PC spectrometer (SHIMADZU).

## 2.2. Synthesis of monomer-306

The reaction (Scheme 1) was conducted in a 250 mL three-necked round-bottom flask which was equipped with a magnetic stirrer, a nitrogen inlet. *N*-Phenyl-*p*-phenylenediamine (3.68 g, 20 mmol) and dichloromethane (50 mL) were added in the reaction vessel. A solution of 1,3-propanesultone (2.44 g in 50 mL dichloromethane) was added dropwise over a period of 40 min to the above solution with stirring at room temperature. After the addition, the resulting solution was heated to reflux for 20 h to ensure completion of the reaction, and then it was cooled and filtered to get the product. The crude product was washed with dichloromethane three times, followed by drying under dynamic vacuum at 50 °C for 24 h (yield 80%).

**MALDI-TOF-MS:**  $m/z$  calculated for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S = 306.4. Found 305.8. FTIR (KBr, cm<sup>-1</sup>): 3425 (*s*,  $\nu_{\text{N-H}}$ ), 3028 (*m*,  $\nu_{\text{C-H}}$  of benzene), 2973 (*m*,  $\nu_{\text{C-H}}$  of methene), 1593 (*s*,  $\nu_{\text{C=C}}$  of benzenoid rings), 1520 (*vs*,  $\nu_{\text{C=C}}$  of benzenoid rings), 1308 (*s*,  $\nu_{\text{C-N}}$ ), 1238 (*m*,  $\nu_{\text{S-C}}$ ), 1153 (*m*,  $\nu_{\text{S-O}}$ ), 839 (*m*,  $\delta_{\text{C-H}}$ ), 741 (*m*,  $\delta_{\text{C-H}}$ ), 615 (*m*,  $\delta_{\text{C-H}}$ ). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO, ppm):  $\delta$  = 10.45 (*s*, 2H, due to —NH— and —SO<sub>3</sub>H),  $\delta$  = 8.40 (*s*, 1H, due to —NH—),  $\delta$  = 7.29 (*d*, 2H, due to H—Ar),  $\delta$  = 7.25 (*t*, 2H, due to H—Ar),  $\delta$  = 7.11 (*m*, 4H, due to H—Ar),  $\delta$  = 6.88 (*t*, 1H, due to H—Ar),  $\delta$  = 3.37 (*t*, 2H, due to —CH<sub>2</sub>— adjacent to sulfonic acid),  $\delta$  = 2.67 (*t*, 2H, due to —CH<sub>2</sub>— adjacent to imino group),  $\delta$  = 1.96 (*m*, 2H, due to —CH<sub>2</sub>—). A typical elemental analysis for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S: Calcd. C 58.80, H 5.92, N 9.14, O 15.67; Found C 58.68, H 5.88, N 9.12, O 15.79.

## 2.3. Synthesis of WSOAD

We adopted the one-step synthetic route to obtain WSOAD. The typical procedure is as follows: 3.06 g (10 mmol) monomer-306 and 0.54 g (5 mmol) *p*-phenylenediamine were dissolved in 50 mL mixture solution (including 40 mL DMF, 5 mL distilled water and 5 mL concentrated hydrochloric acid). A solution of ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 2.26 g (10 mmol) in 10 mL 1.0 M HCl aqueous solution) was added dropwise over a period of 40 min to the above solution with stirring at room temperature. After the addition, the resulting solution reacted for another 6 h. Then it was poured into 200 mL ethanol to precipitate the product. The mixture was filtered using a Buchner funnel and water aspirator, and then the filter cake was washed with ethanol three times, followed by drying under dynamic vacuum at 50 °C for 20 h. Finally, the crude product was dissolved in DMAc and filtered to remove the inorganic salt. The product was precipitated in 100 mL ethanol and then washed with ethanol, followed by drying under dynamic vacuum at 50 °C for 12 h. (yield 84%).

**MALDI-TOF-MS:**  $m/z$  calculated for C<sub>36</sub>H<sub>38</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub> = 714.8. Found 714.9. FTIR (KBr, cm<sup>-1</sup>): 3433 (*s*,  $\nu_{\text{N-H}}$ ), 3249 (*s*,  $\nu_{\text{N-H}}$ ), 3087 (*m*,  $\nu_{\text{C-H}}$  of benzene), 2972 (*m*,  $\nu_{\text{C-H}}$  of methene), 1581 (*s*,  $\nu_{\text{C=C}}$  of benzenoid rings), 1506 (*vs*,  $\nu_{\text{C=C}}$  of benzenoid rings), 1315 (*s*,  $\nu_{\text{C-N}}$ ), 1157 (*m*,  $\nu_{\text{S-O}}$ ), 827 (*m*,  $\delta_{\text{C-H}}$ ), 750 (*m*,  $\delta_{\text{C-H}}$ ), 592 (*m*,  $\delta_{\text{C-H}}$ ). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO, ppm):  $\delta$  = 10.55 (*s*, 2H, due to —NH— and —SO<sub>3</sub>H),  $\delta$  = 8.52 (*s*, 1H, due to —NH—),  $\delta$  = 7.68–6.88 (*m*, mH, due to H—Ar),  $\delta$  = 3.37 (*t*, 2H, due to —CH<sub>2</sub>— adjacent to sulfonic acid),  $\delta$  = 2.67 (*t*, 2H, due to —CH<sub>2</sub>— adjacent to imino group),  $\delta$  = 1.96 (*m*, 2H, due to —CH<sub>2</sub>—). A typical elemental analysis for C<sub>36</sub>H<sub>38</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: Calcd. C 60.49, H 5.36, N 11.76, O 13.43; Found C 57.19, H 4.57, N 11.01, O 12.77.

## 2.4. Reduction of WSOAD

The obtained WSOAD (0.2 g) was dispersed into a solution (3 mL hydrazine hydrate in 40 mL 1.0 M ammonium hydroxide) and stirred for 12 h. Then it was precipitated in 200 mL cold methanol and filtered using a Buchner funnel and water aspirator, and the filter cake was washed with cold methanol for several times,

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