



# Aggregation induced convertible third-order nonlinear optical absorptions of the phenoxazinium containing films prepared by sol–gel method



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## ARTICLE INFO

### Article history:

Received 13 July 2014

Received in revised form

10 September 2014

Accepted 13 September 2014

Available online 20 September 2014

### Keywords:

Optical film

Sol–gel method

Phenoxazinium

Absorption spectrum

Third-order NLO property

Dye aggregation

## ABSTRACT

The preparation and optical properties of phenoxazinium dye containing optical films by a sol–gel method are reported. The monomer of the phenoxazinium dye substituted with a hydroxyl group, prepared from 3-methoxyaniline by a five-step sequence, can be directly converted to the sol–gel precursor. The preparation and optical properties of phenoxazinium dye containing optical films are reported by *in situ* sol–gel spin coating with different mole ratios of the precursor to tetraethylorthosilicate. The UV–visible absorption spectra of the films were recorded and the dye aggregation phenomena were discussed. The third-order nonlinear optical properties of the films were measured by a picosecond Z-Scan method at 532 nm. The results indicate that the third-order nonlinear optical absorptions of the films are turned from the reverse saturation absorption with lower dye doping ratios to saturation absorption with higher doping ratios, which induced by the dye aggregation.

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## 1. Introduction

Functional dyes containing optical films have great importance for application [1–8]. The optical films are usually prepared by spin coating of the polymers from functional monomers [9–12], functional dye doped polymers [13–15] and sol–gel hybrid inorganic–organic materials [16–20]. The *in situ* sol–gel spin coating films have attracted much attention because of their linkage reaction between the sol–gel precursors and the glass [21–24]. Generally, the preparation of functional dye containing sol–gel materials involves two distinct steps: the chromophore was covalently bonded onto an alkoxy silane, and an amorphous silica network was prepared through hydrolysis and condensation of the alkoxy silane dye [25–27]. In the hybrid system, the choice of the chromophores is

crucial because several key requirements must be satisfied such as high optical and thermal stability, excellent compatibility, and possibility of chemical functionalization for coupling.

In previous work, phenoxazinium and phenothiazinium chloride were found as new third-order nonlinear optical (NLO) candidates with good thermal stability, excellent solubility, high third-order NLO susceptibility ( $10^{-11}$  esu) and second hyperpolarizability ( $10^{-29}$  esu) in acetonitrile solution [28,29]. The third-order NLO properties of these dyes doped with poly(methyl methacrylate) (PMMA) in films can be adjusted from the reverse saturable absorption to the saturable absorption with the increasing dye content [30,31]. Compared to the films doped with PMMA, films prepared by the sol–gel method are more stable due to their reaction with the glass surface. To improve the stability of the optical film, the precursors with a hydroxyl group was synthesized with phenoxazinium as the functional parent structure in this paper. The sol–gel precursors were prepared through a bond forming reaction between 3-isocyanatopropyltriethoxysilane and the heteroaromatic chromophore 3-(diethylamino)-7-((2-hydroxyethyl)(methyl)amino) phenoxazin-5-ium perchlorate; the homogeneous hybrid films were obtained by spin coating of the alkoxy silane dye. The design

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and synthesis of the structure as well as linear and third-order NLO properties of the resulting films are discussed in detail.

## 2. Experimental section

### 2.1. Materials

All reagents and solvents (analytical grade) were purchased from TCI Development Co., Ltd. (Tokyo, Japan) or Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used directly. Chromatography was performed with silica gel (300–400 mesh). The quartz glass ( $25 \times 25 \times 1 \text{ mm}^3$ ) was sequentially washed with distilled water, acetone and ethanol in an ultrasonic bath.

### 2.2. Instruments

UV–visible spectra were recorded on a Shimadzu UV-3600 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer. High resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer ( $\text{ESI}^+$ ). The thickness of the films was obtained by a Hitachi S-4700 scanning electron microscope (SEM). Atomic force microscope (AFM) images were tested with a Bruker dimension icon system.

The third-order NLO properties were measured by the Z-scan technique [32]. An Nd:YAG 532 nm laser (EKSPILA) with a pulse width of 21 ps (fwhm) and repetition rate of 10 Hz was used for picosecond Z-scan measurements.

### 2.3. Synthesis

#### 2.3.1. *N*-(3-methoxyphenyl)formamide (**1**) and 3-methoxy-*N*-methylaniline (**2**)

Compounds **1** and **2** were synthesized using reported methods [33,34].

3-Methoxyaniline (11.08 g, 90.0 mmol) and formic acid (150 mL) was heated at 120 °C overnight. The reaction was cooled to room temperature, saturation  $\text{NaHCO}_3$  solution was added to make the mixture neutral. Then, the solution was extracted with ethyl acetate. The organic layer was combined and washed with brine and dried over  $\text{MgSO}_4$ . The solvent was removed by evaporation to obtain the crude product, which was purified by column chromatography (*n*-hexane/ethyl acetate = 2:1) to give compound **1**. Yield: 73.6%;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.16 (s, 1H), 8.25 (s, 1H), 7.22 (t,  $J = 8.1$  Hz, 1H), 7.10 (d,  $J = 7.9$  Hz, 1H), 6.66 (d,  $J = 7.0$  Hz, 1H), 3.73 (s, 3H); HRMS( $\text{ESI}^+$ )  $m/z$ : calcd for  $[\text{C}_8\text{H}_{10}\text{NO}_2]^+$ : 152.0703, found:  $[\text{M} + \text{H}^+]^+$  152.0706.

$\text{LiAlH}_4$  (5.03 g, 132.3 mmol) and dry ether (100 mL) was added to a 250 mL round-bottomed flask. And compound **1** (10.0 g, 66.16 mmol) dissolving in dry ether (20 mL) was slowly added to the stirring solution at 0 °C. The mixture was gradually raised to room temperature and stirred for 6 h. Then, saturation  $\text{NH}_4\text{Cl}$  solution was added to the mixture and the solution was extracted with ether. The organic layer was combined and washed with brine and dried over  $\text{MgSO}_4$ . The solvent was removed by evaporation to obtain the crude product, which was purified by column chromatography (*n*-hexane/ethyl acetate = 3:1) to give compound **2**. Yield: 65.6%;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  6.96 (t,  $J = 8.0$  Hz, 1H), 6.12 (d,  $J = 4.7$  Hz, 2H), 6.06 (d,  $J = 1.7$  Hz, 1H), 5.59 (s, 1H), 3.66 (s, 3H), 2.64 (d,  $J = 3.7$  Hz, 3H); HRMS( $\text{ESI}^+$ )  $m/z$ : calcd for  $[\text{C}_8\text{H}_{12}\text{NO}]^+$ : 138.0841, found:  $[\text{M} + \text{H}^+]^+$  138.0913.

#### 2.3.2. 2-((3-Methoxyphenyl)(methyl)amino)ethanol (**3**)

Compound **2** (12.00 g, 87.5 mmol) was added slowly to a solution of 60% sodium hydride (3.50 g, 87.5 mmol) in DMF (200 mL). The solution was stirred at room temperature under nitrogen

atmosphere for 1 h, and then 2-iodoethanol (16.50 g, 96.2 mmol) was added to the reaction. After the mixture was allowed to 60 °C and stirred for 48 h, water (80 mL) was added to the reaction, and the solution was extracted with ethyl acetate (40 mL  $\times$  5). The organic layer was combined and washed with brine (15 mL  $\times$  3) and dried over  $\text{MgSO}_4$ . The solvent was removed by evaporation to obtain the crude product, which was purified by column chromatography (*n*-hexane/ethyl acetate = 3:1) to give compound **3**. Pale yellow oil, yield: 50.8%;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.04 (t,  $J = 8.4$  Hz, 1H, Ar–H), 6.29 (d,  $J = 8.2$  Hz, 1H, Ar–H), 6.20–6.18 (m, 2H, 2  $\times$  Ar–H), 4.67 (t,  $J = 4.9$  Hz, 1H, OH), 3.70 (s, 3H,  $\text{OCH}_3$ ), 3.53 (q,  $J = 5.7$  Hz, 2H,  $\text{CH}_2$ ), 3.42–3.34 (m, 2H,  $\text{CH}_2$ ), 2.90 (s, 3H,  $\text{CH}_3$ ); HRMS( $\text{ESI}^+$ )  $m/z$ : calcd for  $[\text{C}_{10}\text{H}_{16}\text{NO}_2]^+$ : 182.1181, found:  $[\text{M} + \text{H}^+]^+$  182.1176.

#### 2.3.3. 2-((3-Methoxy-4-nitrosophenyl)(methyl)amino)ethanol (**4**)

A mixture of **3** (16.00 g, 88.3 mmol) and 36% HCl (35.80 g, 353.4 mmol) in  $\text{H}_2\text{O}$  (3.0 mL) was stirred in an ice bath.  $\text{NaNO}_2$  (7.31 g, 106.0 mmol) was slowly added to the mixture within 60 min; then the resulting mixture was stirred in an ice bath for 1 h. The reaction was adjusted to pH 9.0 by  $\text{K}_2\text{CO}_3$  powder. The solid was ultrasonicated in  $\text{Et}_2\text{O}$  and filtrated to give nitroso compound **4**. Green powder, yield: 64.7%; mp: 127.9–128.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  6.82 (d,  $J = 9.7$  Hz, 1H, Ar–H), 6.43 (d,  $J = 9.6$  Hz, 1H, Ar–H), 6.30 (s, 1H, Ar–H), 4.10 (s, 3H,  $\text{OCH}_3$ ), 3.80 (t,  $J = 5.2$  Hz, 2H,  $\text{CH}_2$ ), 3.72 (t,  $J = 5.1$  Hz, 2H,  $\text{CH}_2$ ), 3.26 (s, 3H,  $\text{CH}_3$ ); HRMS( $\text{ESI}^+$ )  $m/z$ : calcd for  $[\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_3]^+$ : 211.1083, found:  $[\text{M} + \text{H}^+]^+$  211.1077.

#### 2.3.4. 3-(Diethylamino)-7-((2-hydroxyethyl)(methyl)amino)phenoxazin-5-ium perchlorate (**5**)

The mixture of 3-(diethylamino)phenol (1.34 g, 8.5 mmol) and 90% *i*-PrOH, 10% water (20 mL) was stirred at 70 °C in a 50 mL two-neck bottle with distilling apparatus filled with argon. A suspended solution of **4** (1.78 g, 8.5 mmol) and 72% perchloric acid (1.22 g, 8.5 mmol) in 90% *i*-PrOH (20 mL) were injected with syringe to the above mixture in four portions during 45 min. The temperature rose to reflux. When about 20 mL solvent was distilled out, 90% *i*-PrOH (20 mL) was added to the reaction mixture; this procedure was repeated three times during 3–4 h. The dark blue solution was evaporated and the residue was purified by column chromatography with silica gel, eluting by  $\text{CHCl}_3/\text{MeOH}$  from 10:1 to 10:3 (v/v) to obtain **5**. Dark green powder, yield: 67.3%; mp: 197.3–199.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  7.79 (d,  $J = 10.0$  Hz, 1H, Ar–H), 7.77 (d,  $J = 9.5$  Hz, 1H, Ar–H), 7.44 (d,  $J = 12.0$  Hz, 1H, Ar–H), 7.40 (dd,  $J = 10.0$  Hz, 1H, Ar–H), 7.01 (s, 1H, Ar–H), 6.97 (d,  $J = 1.8$  Hz, 1H, Ar–H), 3.89 (br, 4H, 2  $\times$   $\text{CH}_2$ ), 3.78 (q,  $J = 7.1$  Hz, 4H, 2  $\times$   $\text{CH}_2$ ), 3.42 (s, 3H,  $\text{CH}_3$ ), 1.35 (t,  $J = 7.1$  Hz, 6H, 2  $\times$   $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  159.61, 157.95, 151.02, 150.59, 135.94, 135.72, 135.53, 135.08, 118.92, 98.01, 97.55, 60.59, 56.85, 47.92, 41.13, 13.24; HRMS( $\text{ESI}^+$ )  $m/z$ : calcd for  $[\text{C}_{19}\text{H}_{24}\text{N}_3\text{O}_2]^+$ : 326.1869, found:  $[\text{M}-\text{ClO}_4]^+$  326.1869.

#### 2.3.5. 3-(Diethylamino)-7-((2-(1-imino-4-(triethoxysilyl)butylperoxy)ethyl)(methyl)amino)phen-oxazin-5-ium perchlorate (**6**)

To the mixture of compound **5** (425.9 mg, 1.0 mmol) and dry  $\text{CH}_2\text{Cl}_2$  (30 mL) in flask, 3-isocyanatopropyltriethoxysilane (247.4 mg, 1.0 mmol) and dibutyltin laurate (126.5 mg, 0.2 mmol) were added. After the reaction mixture was stirred for overnight at 50 °C under a nitrogen atmosphere, the dark blue solution was evaporated and the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 20:1$ ) to give **6**. Dark green powder, yield: 41.8%; mp: 142.6–144.0 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (s, 1H, Ar–H), 7.74 (s, 1H, Ar–H), 7.24 (br, 1H, Ar–H), 7.22 (br, 1H, Ar–H),

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