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Synthesis and NLO properties of hybrid inorganic–organic films containing thiophene ring

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ABSTRACT

A family of second-order nonlinear optical sol–gel films with a pendent thiophene chromophore has been developed. The key step in preparation these hybrids was the syntheses of alkoxysilane dye containing thiophene ring, which was accomplished by utilizing the urethane forming reaction. Molecular structural characterization for the resultant was achieved by FTIR, ^{1}H NMR and UV–Visible spectra. The microscopic optical nonlinearity of the thiophene chromophore was evaluated to be 7646×10^{-30} esu D by solvatochromic method and second harmonic coefficients (d_{33}) of the hybrid film was also calculated to be 41.2 pm/V by second harmonic generation (SHG) measurements, respectively. Furthermore, the stability of optical nonlinearity in poled film was also investigated through a depoling experiment.

1. Introduction

During the past decade, there has been increasing interest in organic–inorganic hybrids due to its unique properties in many fields of applications as they combine the respective characteristics of organic polymers and inorganic glasses [1–4]. The good optical qualities, mechanical strength and thermal stability of these new materials make them very suitable for optical and optoelectronic applications. Recently, a number of second-order nonlinear optical (NLO) hybrid materials have been fabricated through sol–gel process, and significant progress in device design and architecture with implementation of hybrid films into Mach-Zehnder electro-optic modulator has also been reported [5–7]. Generally, the preparation of chromophore-linked NLO hybrid materials involves two district steps: first the NLO chromophore was covalently bonded into alkoxysilane, and secondly an amorphous silica network was prepared through hydrolysis and condensation of the alkoxysilane dye. The chemical bond between the chromophore and the silicon network will allow incorporation of higher concentrations of NLO units and restrict the randomization of poled NLO chromophore alignment [8].

To realize excellent NLO properties in hybrid inorganic–organic materials, the choice and design of the chromophores is crucial because several key requirements must be satisfied, such as high NLO activity, high thermal stability, excellent compatibility, and possibility of chemical functionalization for coupling [9]. At present, the main chromophores employed in inorganic–organic hybrid NLO materials are common push–pull type dyes with benzene ring as the conjugating moiety [10–12]. However, the hybrid systems containing heterocyclic chromophores received little attention. For a common push–pull type NLO chromophore, it is well known that replacing the benzene ring by a less aromatic heterocycle will reduce the charge transfer transitional energy and result in a significantly enhanced molecular hyperpolarizability. Additionally, replacement of benzene ring in chromophores with heterocycle has been shown to improve the thermal stability dramatically [13,14].

With the advantages listed above, we designed and synthesized a chromophore containing thiophene ring as the conjugating moieties, which can be reacted with 3-isocyanatopropyltriethoxysilane to give a chromophore-grafted precursor. Following a sol–gel process of the resultant precursor, a series of transparent NLO films was obtained by spin-coating. Their structures were verified by FTIR, UV–Visible spectra and ^{1}H NMR. The thermal properties as well as linear and second-order nonlinear optical properties of the resulting chromophore and corresponding films are discussed in detail.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from calcium hydride. 3-Isocyanatopropyltriethoxysilane (ICTES) were obtained from Tokyo Chemical Industry Co. and used as received. 2-Amino-3, 5-dinitrothiophene and *N*-ethyl-*N*-hydroxyethylaniline were obtained

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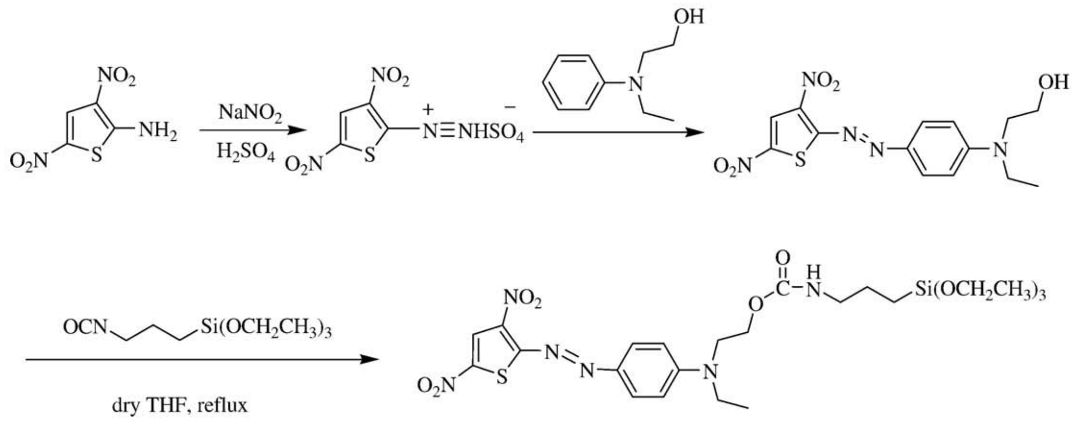

Scheme 1. Synthetic route of alkoxysilane dye containing thiophene ring.

from Alfa and used without further purification. Other reagents were of commercial quality and used as supplied.

2.2. Synthesis of chromophore 2-[4′-(N-ethyl-N-2-hydroxyethyl)-amino-phenylazo]-3, 5-dinitrothiophene (TH)

2-Amino-3, 5-dinitrothiophene (7.6 g, 40 mmol) dissolved in 80 ml of a mixture of phosphoric acid and acetic acid (1:1) was cooled to 0–5 °C, then treated by adding dropwise a nitrosyl sulfuric acid solution which was prepared by slowly adding the sodium nitrite (2.8 g, 40 mmol) in small portions to the 20 ml concentrated (98%) sulfuric acid under stirring and cooling. After stirring for 1 h in an ice bath, *N*-ethyl-*N*-hydroxyethylaniline (7.3 g, 44 mmol) in 120 ml methanol/water (2/1, v/v) was added, then stirred for 1 h under cooling after complete addition, followed by neutralization (pH 5–6) with sodium carbonate and stirred for 2 h more. The precipitate was filtered off, washed by plenty of water and purified by flash chromatography using cyclohexane/ethyl acetate (1/1, v/v), then pure chromophore TH was obtained as a blue powder. Yield: 31%. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 8.32 (s, Ar**H**, 1H), 7.77 (d, Ar**H**, 2H), 7.09 (d, Ar**H**, 2H), 4.91 (s, O**H**, 1H), 3.59–3.63 (m, C**H**$_2$, 6H), 1.18 (t, C**H**$_3$, 3H).

2.3. Synthesis of alkoxysilane dyes (ICTES-TH)

A dry, 100 ml three-necked flask equipped with an oil bath, a mechanical stirrer, a nitrogen inlet and a reflux condenser was charged with chromophores TH (3.65 g, 10 mmol), 3-isocyanatopropyltriethoxysilane (ICTES, 2.96 g, 12 mmol), 40 ml of THF and 0.5 ml of triethylamine (TEA) as catalyst. The reaction mixture was stirred and refluxed for 72 h under nitrogen atmosphere, and then the solvent was removed under vacuum. The residue was purified by chromatograph on silica gel using ethyl acetate/hexane as an eluent to afford the alkoxysilane dyes (ICTES-TH). Yield = 26%. m.p. = 117 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 8.43 (s, Ar**H**, 1H), 7.82 (d, Ar**H**, 2H), 7.22 (s, N**H**, 1H), 7.11 (d, Ar**H**, 1H), 4.21 (s, CH$_2$C**H**$_2$O, 2H), 3.79 (s, C**H**$_2$CH$_2$O, 2H), 3.69–3.71 (m, C**H**$_2$CH$_3$, 8H), 2.91 (d, C**H**$_2$CH$_2$CH$_2$, 2H), 1.36 (s, CH$_2$C**H**$_2$CH$_2$, 2H), 1.22 (t, CH$_2$C**H**$_3$, 3H), 1.13 (m, OCH$_2$C**H**$_3$, 9H), 0.48 (t, CH$_2$CH$_2$C**H**$_2$, 2H).

2.4. Thin film preparation (F-TH)

The alkoxysilane dye was mixed with tetraethoxysilane (TEOS) at a 1:5 molar ratio in THF, then acidic water (HCl, pH = 1) was added, the

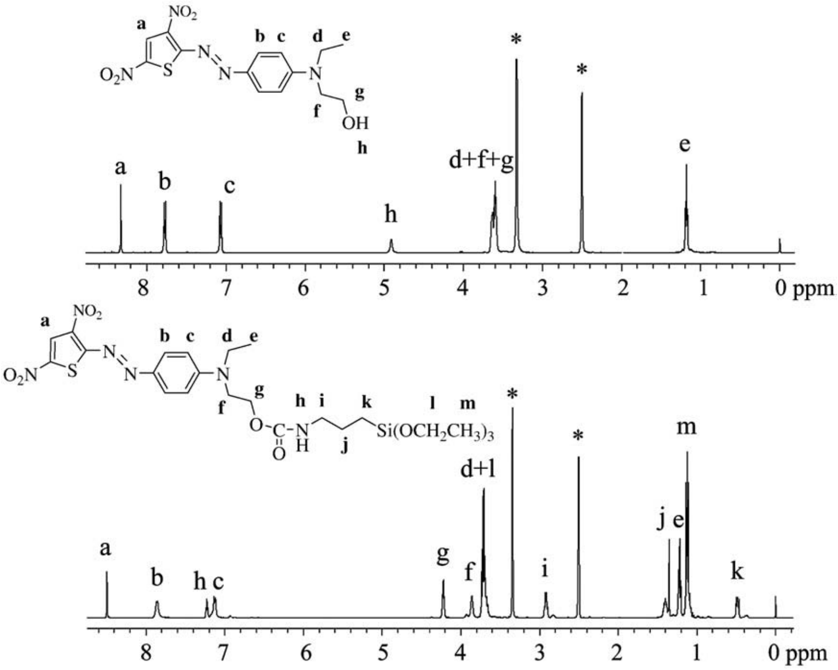

Fig. 1. ^{1}H NMR spectra of chromophore TH and alkoxysilane ICTES-TH (in DMSO, *, solvent).