

Effect of triphenylamine agents as screening moieties for electrostatic interaction in the nonlinear optical response of hybrid organic-inorganic films

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Abstract

A nonlinear optical (NLO) chromophore (2-(3-cyano-4-(4-((2-hydroxyethyl)(methyl)amino) styryl)-5,5-dimethylfuran-2(5H)-ylidene) malononitrile, abbr. FS) and a hole-transporting molecular ((4-(diphenylamino)phenyl)methanol, abbr. TPA) were synthesized and reacted with (3-isocyanatopropyl) triethoxysilane (ICTES) to form two functionalized silicon alkoxide precursors (named ICTES-FS and ICTES-TPA, respectively). Sol solutions were obtained after co-hydrolysis/condensation of tetraethoxysilane, ICTES-FS and ICTES-TPA. Transparent films were only fabricated with the sol containing ICTES-TPA. Thermal stabilities and aggregation behaviors of the NLO chromophores in hybrid films were studied by ultraviolet–visible spectra. ICTES-TPA units with triphenylamine groups at high concentration were found useful to abate dipolar chromophore interactions and consequent aggregation problems. Second-order NLO properties and temporal stabilities of sol–gel films were also investigated by virtue of in-situ second harmonic generation.

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1. Introduction

Second-order nonlinear optics (NLO) continues to be a topical area of research because of its tremendous potential applications in the design of photon-based materials for optical switching, data manipulation, and information processing [1,2]. Functionalized polymers show second-order NLO effects when the NLO-active chromophore is oriented by external electric field poling of a microscopically oriented medium [3]. Moreover, large second-order nonlinearities can be obtained for the NLO polymer containing a push-pull type chromophore which possesses large dipole moments and polarizabilities, consisting of strong electron-donating and-withdrawing groups separated by a π -delocalized moiety. This class of molecules has a distinctive figure of merit given as $\mu\beta/MW$, where μ is the

dipole moment, β is the first hyperpolarizability and MW the chromophore molecular weight [4].

But due to the competition of chromophore–chromophore electrostatic interactions and electric field poling, it is stated that chromophore–chromophore interactions play the dominant role in limiting the translation of microscopic (molecular) optical nonlinearity to macroscopic optical nonlinearity [4,5]. In other words, the chromophore concentration in a polymer matrix plays an extremely important role in the magnitude of these non-linear properties. On the positive side, it is important to investigate chromophore–chromophore interactions, suggesting means of overcoming the limitations of current chromophores by changing the shape of chromophores and by exploiting chromophore–polymer attachment. This approach has already been used to achieve factor of two improvements in macroscopic optical nonlinearity in agreement [4].

Parallel to the polymer development, another chemical way has shown important results as those obtained in polymers. The sol–gel process with silicon multialkoxides can form various

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microstructures as a transparent matrix at low temperature [6–8]. Silicon alkoxide can be hydrolyzed in the presence of water and a catalytic amount of acid or base. The hydrolysis and condensation of organically functionalized metal alkoxides leads to the preparation of organic-inorganic hybrid compounds exhibiting unique properties. Silicon trialkoxide derivatives can be designed to bear a NLO-active chromophore in one arm of silicon through a flexible spacer. The way allows enhancing the temporal stability of the dipolar orientation and then, to increase the molecular concentration, but it also increases the aggregation problems [5]. This fact also means a limitation in the NLO response because of the intermolecular interactions introduced with the molecular aggregation as revealed in polymer system.

Photorefractive materials are of great importance for their potential applications in optical data storage, image processing, and programmable interconnection [9,10]. To be photorefractive, carbazole and triphenylamine units are commonly used as charge-transporting and hole-transporting groups to exhibit photoconductivity, respectively [10]. In the case of the development of photorefractive sol–gel materials, a carbazole unit was chosen and covalently attached to the sol–gel silicon skeleton previously, and acted as screeners for the electrostatic interaction between NLO-active chromophores [5]. This fact allowed increasing the NLO molecule concentration furthermore, avoiding aggregation effect.

In this work, a NLO chromophore with large microscopic polarizabilities and a hole-transporting molecular with triphenylamine unit were synthesized and reacted with (3-isocyanatopropyl) triethoxysilane (ICTES) to form two functionalized silicon alkoxide precursors, named ICTES-FS and ICTES-TPA respectively, and co-hydrolysis/condensation with tetraethoxysilane to fabricate transparent films. The aggregation behavior of the NLO chromophores incorporated in hybrid films were studied by ultraviolet-visible (UV–Vis) spectra and atomic force microscopy (AFM). Second-order NLO properties and temporal stability of poled sol–gel films were also investigated by virtue of in-situ second harmonic generation (SHG).

2. Experimental part

2.1. Materials

All starting materials were obtained from Acros Organics, Fluka, Alfa Aesar, TCI and Aldrich respectively, and were used without further purifications. Tetrahydrofuran (THF) was dried by refluxing, distilling from calcium hydride just before use. Other solvents, of analytical-grade quality, were commercial products and used as received.

2.2. Synthesis of 2-(3-cyano-4-(4-((2-hydroxyethyl)(methyl)amino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile

A push-pull type model chromophore, thereafter referred as FS, was prepared from 2-{3-cyano-4-[2-(10-phenyl-10H-phenothiazin-3-yl)-vinyl]-5,5-dimethyl-5H-furan-2-ylidene}-malononitrile [11] and 4-((2-hydroxyethyl)(methyl)amino)

benzaldehyde[12] via a direct Knoevenagel condensation [13]. Yield: 67%. m. p. 270.8 °C. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm) δ 1.75 (s, 6H, C(CH₃)₂), δ 3.12 (s, 3H, N(CH₃)), δ 3.58–3.59 (d, 4H, NCH₂CH₂), δ 4.78 (s, 1H, OH), δ 6.85–6.87 (d, 3H, ArH, CH=CH), δ 7.75–7.77 (d, 2H, ArH), δ 7.90–7.94 (d, 1H, CH=CH, *J*=15.7). Anal. Calcd for C₂₁H₂₀N₄O₂ (360.41): 69.98; H, 5.59; N, 15.55. Found: C69.76, H5.55, N15.43.

2.3. Synthesis of (4-(diphenylamino)phenyl)methanol

TPA was synthesized via Vilsmeier–Haack reaction, aldehyde reduction as described in a previous literature [14]. Yield: 80%. m. p.: 94.8 °C. ¹H NMR (500 MHz, CDCl₃, δ ppm) δ 1.60 (b, 1H, OH), δ 4.63 (s, 2H, CH₂OH), δ 6.99–7.25 (m, 14H, ArH). Anal. Calcd for C₁₉H₁₇NO (275.34): C82.88, H6.22, N5.09. Found: C82.71 H6.23 N4.89.

2.4. Synthesis of alkoxy silane terminated molecules (ICTES-FS and ICTES-TPA)

General procedure: a dry, 50 ml three-necked flask equipped with an oil bath, a mechanical stirrer, a nitrogen inlet and a reflux condenser was charged with 4 mmol chromophore, 3-isocyanatopropyltriethoxysilane (1.19 g, 4.8 mmol), 15 ml of THF and 5 drops of triethylamine as catalyst. The reaction mixture was stirred and refluxed for 48 h under nitrogen atmosphere. The solution was poured into dried hexane, the resulting orange precipitate was collected by suction filtration, and the product was dried under vacuum at room temperature for 6 h.

ICTES-FS: yield: 67%. m. p.: 125.1 °C. FTIR (KBr pellet, cm⁻¹): 3417 (–NH), 2221 (–CN), 1713 (–C=O), 1562 (–C₆H₄), 1107, 1076 (Si–O–CH₂CH₃). ¹H NMR (500 MHz, CDCl₃, δ ppm) δ 0.59–0.63 (t, 2H, NCH₂CH₂CH₂), δ 1.21–1.26 (m, 9H, Si(OCH₂CH₃)₃), δ 1.59–1.63 (t, 2H, NCH₂CH₂CH₂), δ 1.76 (s, 6H, C(CH₃)₂), δ 3.14 (s, 3H, NCH₃), δ 3.16–3.17 (d, 2H, NCH₂CH₂CH₂), δ 3.73–3.76 (t, 2H, NCH₂CH₂), δ 3.79–3.84 (q, 6H, Si(OCH₂CH₃)₃), δ 4.24–4.27 (t, 2H, NCH₂CH₂), δ 4.96 (b, 1H, NH), δ 6.75–6.78 (s, 1H, CH=CH, *J*=15.9), δ 6.77–6.79 (d, 2H, ArH), δ 7.54–7.56 (d, 2H, ArH), δ 7.59–7.62 (d, 1H, CH=CH, *J*=15.9).

ICTES-TPA: Yield: 73%. m. p.: 73.6 °C. FTIR (KBr pellet, cm⁻¹): 3342 (–NH), 1687 (–C=O), 1589 (–C₆H₄), 1105, 1081 (Si–O–CH₂CH₃). ¹H NMR (500 MHz, CDCl₃, δ ppm) δ 0.61–0.64 (t, 2H, NCH₂CH₂CH₂), δ 1.20–1.24 (m, 9H, Si(OCH₂CH₃)₃), δ 1.58–1.63 (t, 2H, NCH₂CH₂CH₂), δ 3.19–3.21 (d, 2H, NCH₂CH₂CH₂), δ 3.79–3.83 (q, 6H, Si(OCH₂CH₃)₃), δ 4.96 (b, 1H, NH), δ 5.03 (s, 2H, ArCH₂), δ 7.00–7.26 (m, 14H, ArH).

2.5. Films preparation

To prepare the coating solution, ICTES-FS, ICTES-TPA and tetraethoxysilane (TEOS) were mixed in THF with a molar ratio of 0.25: *x*: 1–*x* (*x*=0, 0.25, 0.5, 0.75 and 1). Then acidic water (HCl, pH=2) was added to favor the hydrolysis/condensation process, the molar ratio of H₂O: Si was 20: 1. The solution was

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