

Synthesis and spectroscopic characterization of an alkoxy silane dye containing C. I. Disperse Red 1

Yuanjing Cui, Minquan Wang, Lujian Chen, Guodong Qian*

Department of Materials Science and Engineering, State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, PR China

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Abstract

We describe the synthesis of an alkoxy silane dye (ICTES-DR1) which was copolymerized by sol-gel processing to yield organic–inorganic hybrid materials for use as second-order nonlinear optical (NLO) effect. C. I. Disperse Red 1 (DR1) was attached to Si atoms by a carbamate linkage to provide the functionalized silane *via* the nucleophilic addition reaction of 3-isocyanatopropyl triethoxysilane (ICTES) with DR1 using triethylamine as catalyst. We found that triethylamine and dibutyltin dilaurate were almost equally effective as catalysts. The physical properties and structure of ICTES-DR1 were characterized using elemental analysis, mass spectra, $^1\text{H-NMR}$, FTIR, UV-visible spectra and differential scanning calorimetry (DSC). ICTES-DR1 displays excellent solubility in common organic solvents.

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1. Introduction

Recently, second-order nonlinear optical (NLO) effects of organic molecules have been extensively investigated for their advantages over inorganic crystals [1,2]. These are their large optical non-linearity, ultra fast response speed, high damage thresholds and low absorption loss, etc. Particularly, organic thin films with excellent optical properties have tremendous potential in integrated optics such as optical switching, data manipulation and information processing. Among organic NLO molecules, azo-dye chromophores

have been a special interest to many investigators because of their relatively large molecular hyper-polarizability (β) due to delocalization of the π -electronic clouds [3]. They were most frequently either incorporated as a guest in the polymeric matrix (guest–host polymers) or grafted into the polymeric matrix (functionalized polymers) over the past decade [4–6].

Chromophoric orientation is obtained by applying a static electric field or by optical poling. Whatever the poling process, poled-order decay is an irreversible process which tends to annihilate the NLO response of the materials and this process will be accelerated at higher temperature. For device applications, the most probable candidate must exhibit inherent properties that include: (i) high thermal stability to withstand heating during

* Corresponding author. Tel.: +86-571-8795-2334; fax: +86-571-8795-1234.

E-mail address: gdqian@zju.edu.cn (G. Qian).

poling; (ii) high glass transition temperature (T_g) to lock the chromophores in their acentric order after poling [7].

Most of the polymers, however, have either low T_g or poor thermal stability which makes them unsuitable for direct use. To overcome these problems, one attractive approach is incorporating the nonlinear optical active chromophore into a polymerizable silane by covalent bond to yield an alkoxy silane dye which can be copolymerized via sol-gel processing to form organic–inorganic hybrid materials (Fig. 1). The hydrolysis and condensation of functionalized silicon alkoxydes can yield a rigid amorphous three-dimensional network which leads to slower relaxation of NLO chromophores. Therefore, sol-gel hybrid nonlinear optical materials have received significant attention in the past few years and exhibited the desired properties [8–11]. In this strategy, the design and synthesis of new network-forming alkoxy silane dye are of paramount importance and detailed investigation for them will offer great promise in the fabrication of new materials for second-order nonlinear optics that will eventually meet the basic requirements in building photonic devices [7].

4-Nitro-4'-(*N*-ethyl-*N*-2-hydroxyethyl) aminoazobenzene, known as C. I. Disperse Red 1 (DR1), is a classic azo dye with a terminal hydroxyl group

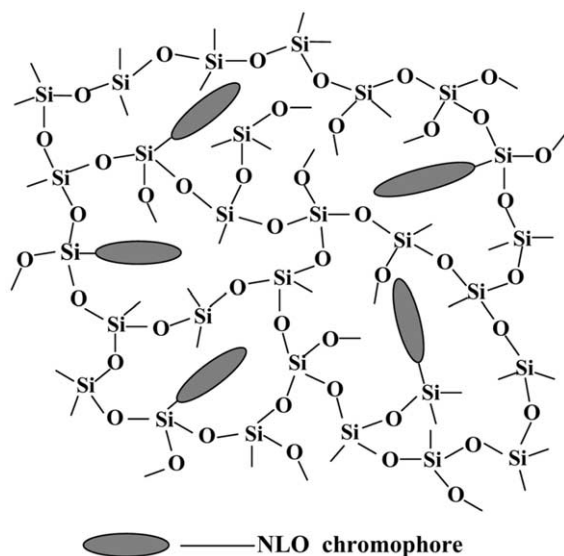


Fig. 1. A structure model of organic–inorganic NLO materials.

that can react readily with 3-isocyanatopropyl triethoxysilane (ICTES) in the presence of organotin or tertiary amine catalysts to give carbamate linkage. It has been reported that the organic–inorganic hybrid materials derived from the functionalized silane (ICTES-DR1) exhibit high NLO performance and long-term stability [8,12,13], while physical properties and structural characterization of ICTES-DR1 are scarcely investigated. In this paper, we describe the synthesis of this alkoxy silane dye (ICTES-DR1) in detail and investigate the catalytic activity of triethylamine compared with dibutyltin dilaurate. Characterization of ICTES-DR1 is presented by element analysis, mass spectra, FTIR, $^1\text{H-NMR}$, UV-visible spectra and differential scanning calorimetry (DSC).

2. Experimental

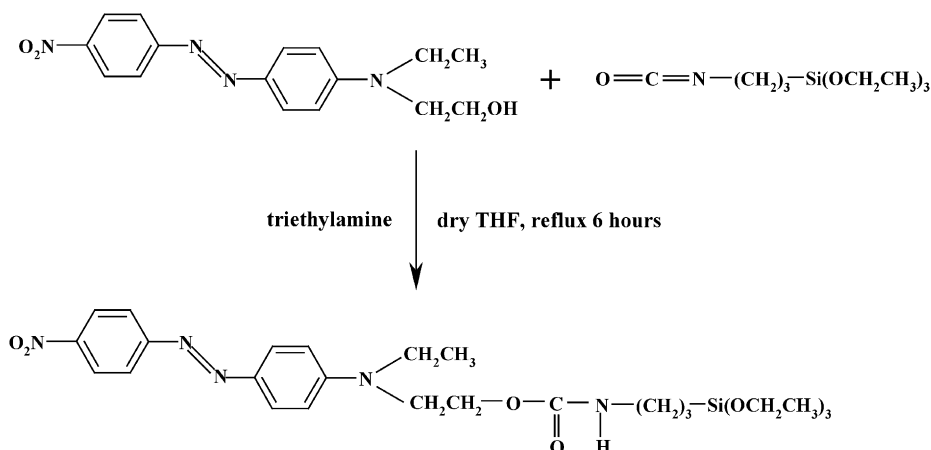
2.1. Materials and measurements

C. I. Disperse Red 1 (DR1, purity >95%) and 3-isocyanatopropyl triethoxysilane (ICTES, purity >95%) were obtained from Aldrich Chem. Co. and Tokyo Chemical Industry Co. respectively, and were used as received. The tetrahydrofuran (THF, purity >99%) was dried prior to use.

$^1\text{H-NMR}$ spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as internal standard and dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) as solvents. FTIR spectra were recorded on a Nicolet Avatar 360 in the region of 4000–400 cm^{-1} using KBr pellets. UV-visible absorption spectroscopic study was performed with a Perkin-Elmer Lambda 20 spectrophotometer. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7 with a heating rate of 3 $^\circ\text{C}/\text{min}$. Element analysis was carried out on a Eager 300 microelemental analyzer. Mass spectrum was measured with Finnigan Trance 2000 mass spectrophotometer by electron ionization (EI).

2.2. Synthesis

The synthesis route of ICTES-DR1 is depicted in Scheme 1. To a three-necked round-bottomed



Scheme 1. Synthesis route of ICTES-DR1.

flask equipped with a mechanical stirrer, a nitrogen inlet and reflux condenser, 1.572 g (5 mmol) of DR1, 2.474 g (10 mmol) of ICTES, 30 cm³ of THF and three drops of triethylamine as catalysts were introduced. The mixture was stirred and refluxed for 6 h under nitrogen atmosphere. The solution was poured into dried hexane, the resulting red precipitated powder was collected by suction filtration, washed again with hexane/THF (9:1) until no DR1 was detected by thin-layer chromatography (TLC), and the product, ICTES-DR1, was dried under vacuum at 30 °C for 24 h and stored in a desiccator. Yield: 77%. Element analysis: Found (%): C, 55.87, H, 7.03, N, 12.69; Calcd (%): C, 55.57, H, 7.00, N, 12.47.

3. Results and discussion

The functionalized sol-gel precursor (ICTES-DR1) was obtained by a carbamate forming reaction between DR1 and ICTES. In this reaction, we substituted triethylamine for dibutyltin dilaurate as catalysts compared with the literature procedures [8]. It was found that triethylamine had almost equal catalytic activity as dibutyltin dilaurate and in contrast to the latter it can be easily removed in purification.

The alkoxy silane dye is soluble in polar aprotic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF),

etc., and chlorinated solvents such as chloroform, methylene dichloride, etc. It is insoluble in non-polar solvents for example hexane, heptane, etc. The melting point of ICTES-DR1 is determined to be 96 °C by DSC at a heating rate of 3 °C/min. The DSC curve is presented in Fig. 2. Mass spectrum was measured by electron ionization (EI), the molecular ion (M^+) was observed at m/z 561.3 which is in a fairly good agreement with the result calculated from $\text{C}_{26}\text{H}_{39}\text{O}_7\text{N}_5\text{Si}$ (561.3).

The infrared spectra of DR1, ICTES and ICTES-DR1 are shown in Fig. 3. The stretching vibration of the hydroxyl group in DR1 is observed around 3288 cm⁻¹. For ICTES, the C–H stretching vibration of CH₃ and CH₂ are observed

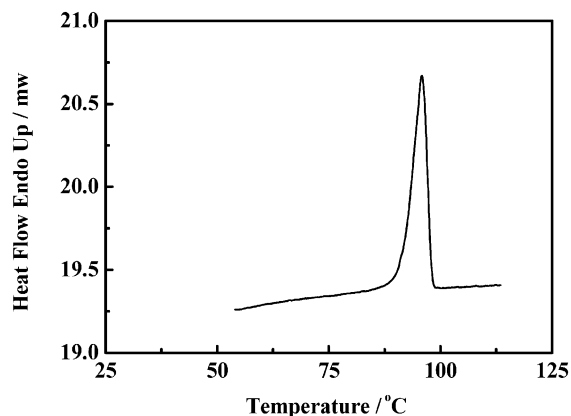


Fig. 2. DSC curve of ICTES-DR1.

at 2888, 2928 and 2976 cm^{-1} , the Si–O–C₂H₅ stretching frequencies of alkoxy silane were located in 1081 and 1167 cm^{-1} , the strong absorption peak corresponding to N=C=O stretching was observed at 2273 cm^{-1} . In spectrum of ICTES-DR1, the absorption bands of N=C=O and OH

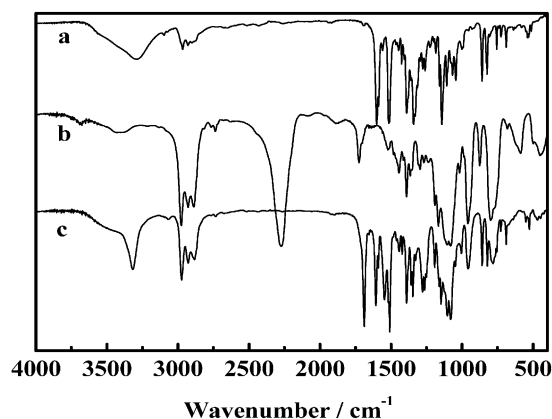


Fig. 3. FTIR spectra of DR1 (a), ICTES (b) and ICTES-DR1 (c).

vanish and new absorption bands at 3317, 1688 and 1546 cm^{-1} emerge, contributed by the NH stretching, carbonyl (C=O) stretching and NH bending respectively. In addition, the C=C stretching of phenylene and asymmetric stretching and symmetric stretching of NO₂ were observed at 1606, 1509 and 1345 cm^{-1} , respectively. These results indicate that the ICTES-DR1 was obtained.

The molecular structure of ICTES-DR1 is also confirmed from the ¹H-NMR spectrum (Fig. 4). Referred to literature [14] we can assign following lines as corresponding to the protons of phenylene: 8.35–8.37, 7.92–7.94, 7.83–7.85 and 6.90–6.92 ppm. The line 7.20 ppm is assigned to the carbamate (–NHCOO, 1H). The lines assigned to the methylene and methyl are as follows: 4.14–4.17 ppm (–CH₂–CH₂–O, 2H), 3.69–3.75 ppm (–O–CH₂–CH₃, 6H), 3.65–3.67 ppm (–N–CH₂–CH₂, 2H), 3.53–3.54 ppm (–N–CH₂–CH₃, 2H), 2.93–2.96 ppm (–NH–CH₂–CH₂, 2H), 1.43–1.46 ppm (–CH₂–CH₂–CH₂, 2H), 0.50–0.53 ppm (–CH₂–Si, 2H), 1.12–1.18 ppm (–CH₂–CH₃, 12H).

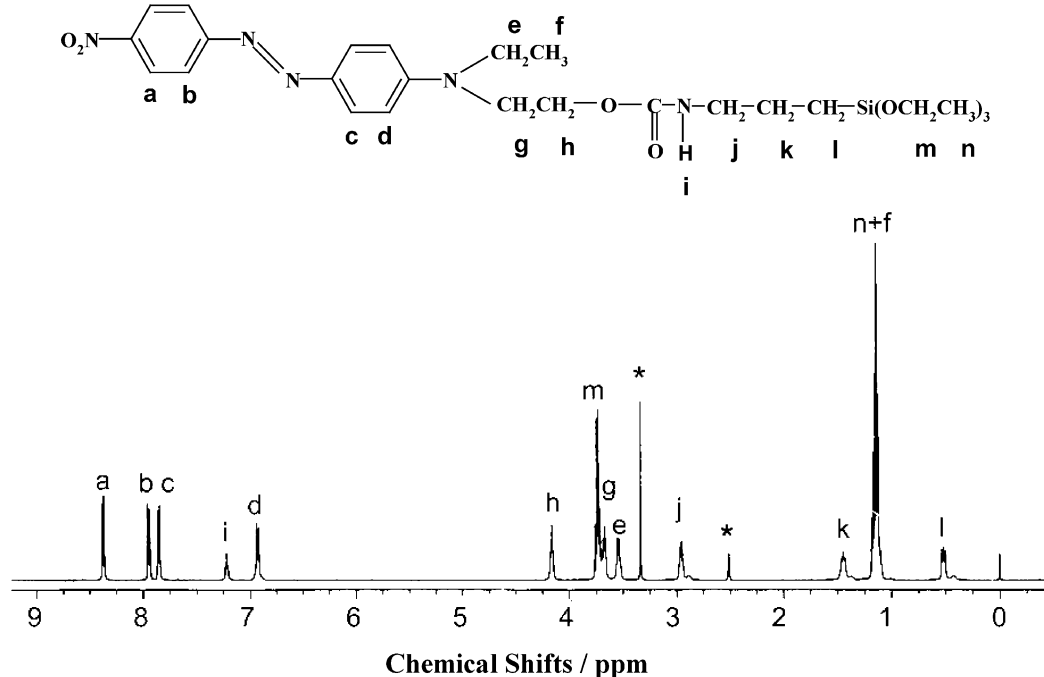


Fig. 4. ¹H-NMR spectrum (500MHz) of ICTES-DR1 in DMSO-*d*₆ (the signal marked with * is caused by the solvents) and the assignment of peaks.

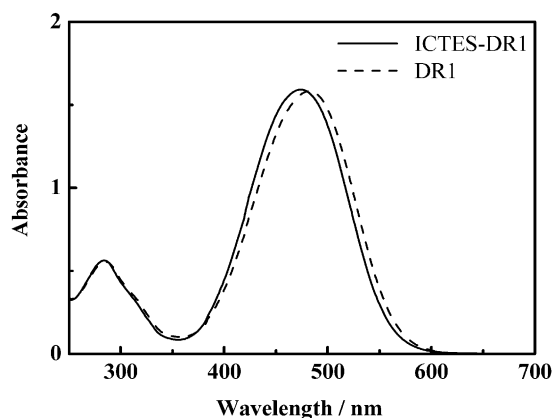


Fig. 5. UV-visible absorption spectra of the DR1 and ICTES-DR1.

The UV-visible of DR1 and ICTES-DR1 in ethanol are shown in Fig. 5. DR1 has its maximum absorption at 482 nm, while ICTES-DR1 has maximum absorption at 474 nm. We can explain the blue shift as follows: DR1 has a donor group $[-N(CH_2CH_3)(CH_2CH_2OH)]$ and an acceptor group $(-NO_2)$ at separated positions, respectively. If the new chemical bound $(-O-C=O)$ is produced, the structure change of the donor will decrease electron-release behavior and change the resonance absorption peak as a result.

4. Conclusions

In this work, we successfully synthesized an alkoxy silane dye containing DR1 (ICTES-DR1) via a nucleophilic addition reaction of 3-iso-cyanatopropyltriethoxysilane (ICTES) and C.I. Disperse Red 1 (DR1), which is confirmed by means of MS, FTIR, 1H -NMR etc. The product (ICTES-DR1) exhibits good solubility in common organic solvents. We also found that triethylamine and dibutyltin dilaurate are almost equally

effective in this reaction and the former can be easily removed in purification.

Acknowledgements

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