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Synthesis and characterization of an alkoxysilane dye for nonlinear optical applications

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Abstract

In order to achieve organic–inorganic hybrid nonlinear optical (NLO) materials with a highly NLO active chromophore covalently bonded into silica networks, an alkoxysilane dye was synthesized from 3-isocyanatopropyl triethoxysilane (ICTES) and NLO active dye 4-nitro-4′-hydroxy-azobenzene (NHA) by a nucleophilic addition reaction. This dye based on a nitro group as an acceptor end of a donor–π-bridge–acceptor chromophore and a hydroxy as the donor end, has a large $\beta\mu$ value measured by solvatochromic method. Compared with C.I. Disperse Red 1, it displayed better transparency and a higher melting point. The resulting products were highly soluble in aprotic polar solvents such as DMF, DMSO, and THF, etc. Molecular structural characterization for the dye (NHA) and alkoxysilane dye (ICTES-NHA) was investigated by elemental analysis, ^{1}H NMR, FTIR, UV–visible spectra and differential scanning calorimetry (DSC).

Keywords: Alkoxysilane dye; Azobenzene; Nonlinear optics; Solvatochromic method; Chromophore; Synthesis

1. Introduction

During the last decade, nonlinear optical (NLO) polymeric materials have continuously drawn interest because of their potential applications in integrated optics, such as frequency doubling, high speed photonic switching and electro-optical (EO) modulation, etc. [1–4]. For the practical application of second-order NLO polymeric materials, high NLO activities plus its temporal and thermal stability are particularly required. However, the ordered state of NLO active molecules obtained by the electric field poling process would normally decay to an equilibrium isotropic state due to thermal motion of polymer chains. Many approaches, including a cross-linking method and the utilization of high glass transition temperature (T_g) polymers, have been used to suppress the relaxation of NLO molecules in the polymeric matrix [5–7].

Recently, NLO sol–gel materials have received significant attention for the inherent properties of the silica matrix [8–13]. These include their excellent optical quality, ease of device fabrication and high temporal and thermal stability of the NLO activity that is attributed to their high T_g. In addition, thin films of the materials can avoid or greatly reduce surface damage induced by corona poling, which is a serious problem in poled polymer based thin films [12].

Basically, NLO sol–gel materials can be divided into two classes, the guest–host matrixes and chromophore-linked hybrids [10]. In the former, the NLO active molecules are physically blended with the inorganic network. Like other guest–host systems, doped sol–gel composites suffer from phase separation and thermal relaxation problems. The performance is limited by the

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chromophore concentration usually to a maximum of 15–20%. To overcome these problems, the chromophore-linked hybrid materials have been developed, in which covalent incorporation of the NLO chromophore with the silica backbone prevents it from aggregating, to achieve high chromophore density and enhanced optical nonlinearity to improve thermal and temporal stability. In addition, the organic molecules impart improved elasticity in the rigid amorphous silica network to prevent the formation of cracks during fabrication of thin films [12].

The chromophore-linked hybrid materials are commonly prepared by attaching the NLO active chromophores into silicon oxide to provide an alkoxysilane dye, followed by a hydrolysis and condensation process to form an amorphous silica network. Therefore, the design and synthesis of new network-forming alkoxysilane dye are of paramount importance and detailed investigation for them offers promise in the fabrication of new materials for second-order nonlinear optics that will eventually meet the basic requirements in building photonic devices.

In this paper, we have synthesized an NLO active dye (NHA) containing azobenzene unit, and then an alkoxysilane dye (ICTES-NHA) for sol–gel NLO materials was synthesized successfully from 3-isocyanatopropyl triethoxysilane (ICTES) with NHA through the reaction of carbamate formation. The composite magnitude ($\beta_{CT}\mu_g$) of the dye was experimentally derived using a solvatochromic method. Compared with C.I. Disperse Red 1, it displayed better transparency and a higher melting point. The synthesized dye and alkoxysilane dye were characterized by elemental analysis, ^{1}H NMR, FTIR, UV–visible spectra and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials and measurements

Tetrahydrofuran (THF, purity > 99%) was purified by refluxing and distilling from calcium hydride. 3-Isocyanatopropyl triethoxysilane (ICTES, purity > 95%) was obtained from Tokyo Chemical Industry Co. All other reagents, of analytical-grade quality, were commercial products and used as received.

Elemental analysis was carried out on an Eager 300 microelemental analyzer. ^{1}H NMR spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethysilane (TMS) as an internal standard and dimethyl sulfoxide-d_6 (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 °C/min.

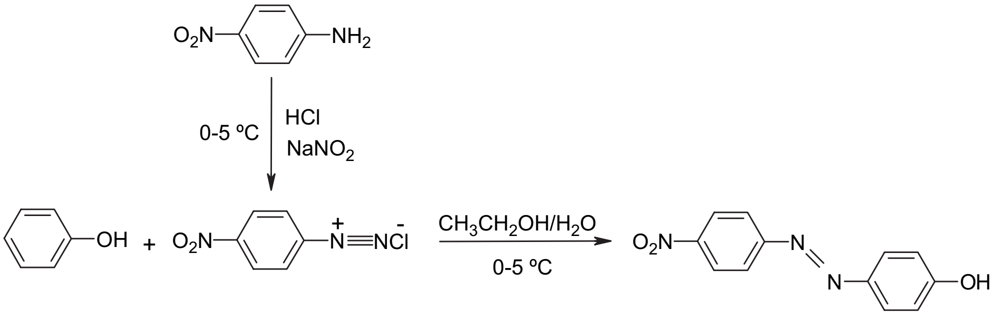
2.2. Synthesis

2.2.1. 4-Nitro-4′-hydroxy-azobenzene (NHA)

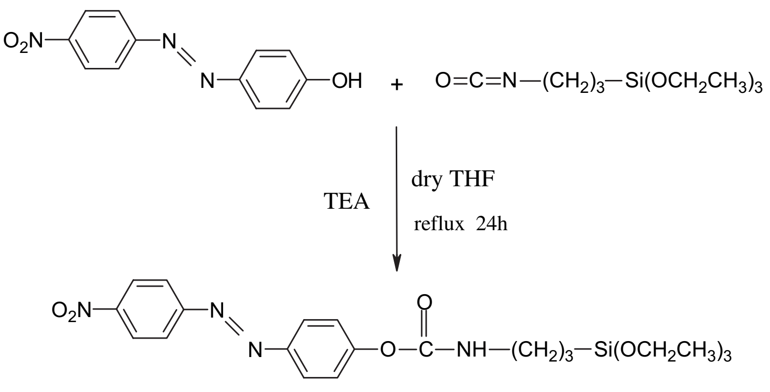
The diazonium coupling reaction was employed to prepared NHA and its reaction scheme is outlined in Scheme 1. A solution of sodium nitrite (1.38 g, 20 mmol) in water was added dropwise, with stirring, to a solution of *p*-nitroaniline (2.76 g, 20 mmol) in 20 cm^3 distilled water and 18 cm^3 concentrated HCl in an ice bath. After 15 min stirring, phenol (1.98 g, 20 mmol) and NaOH (7 g) dissolved in 50 cm^3 methanol/water (2:1) was added with vigorous stirring for half an hour. The precipitate formed was filtered and washed repeatedly with water to remove any remaining reactants. The product was recrystallized from ethanol/water (1:3) and dried under vacuum at 40 °C for 6 h. Yield: 86%. Anal. Calcd for $C_{12}H_9O_3N_3$ (243.1): C, 59.26; H, 3.70; N, 17.28. Found: C, 59.13; H, 3.69; N, 17.03.

2.2.2. Alkoxysilane dye (ICTES-NHA)

Scheme 2 shows the synthesis procedure of ICTES-NHA. To a three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and reflux condenser, 1.22 g, 5 mmol of NHA, 1.5 g, 6 mmol of ICTES, 20 cm^3 of THF and 5 drops of triethylamine (TEA) as catalyst were introduced. The mixture was stirred and refluxed for 12 h under nitrogen atmosphere.



Scheme 1. Synthesis of NHA.



Scheme 2. Synthesis of ICTES-NHA.

The solution was poured into dried hexane, the resulting orange precipitate was collected by suction filtration, washed repeatedly with hexane/THF (9:1) until no NHA was detected by thin-layer chromatography (TLC), and the product was dried under vacuum at 40 °C for 6 h and stored in a desiccator. Yield: 69%. Anal. Calcd for $C_{22}H_{30}O_7N_4Si$ (490.3): C, 53.88; H, 6.12; N, 11.43. Found: C, 53.67; H, 6.05; N, 11.53.

3. Results and discussion

3.1. Characterization

The NLO dye NHA was synthesized by the diazonium coupling reaction of *p*-nitroaniline with phenol in good yield (86%). Through a coupling reaction between the ICTES and NHA, the alkoxysilane dye ICTES-NHA was obtained with 69% yield. The elemental analysis values of the compounds are generally in good agreement with the calculated values for the proposed structures. The synthesized products have good solubility in many common organic solvents, such as THF, DMF, DMSO, ethanol, and chloroform, etc. They are insoluble in nonpolar solvents such as hexane, heptane, etc. The melting points of NHA and ICTES-NHA were determined to be 219 °C and 123 °C, respectively, by means of DSC at a heating rate of 3 °C/min, as presented in Fig. 1.

The structures of NHA and ICTES-NHA were confirmed by FTIR and ^1H NMR spectroscopy. Fig. 2 shows FTIR spectra of NHA and ICTES-NHA. For NHA, the stretching vibration of the hydroxy group was observed around 3442 cm^{-1}. The stretching of benzene ring and asymmetric stretching and symmetric stretching of nitro group were observed at 1604, 1504 and 1341 cm^{-1}, respectively. From the spectra of ICTES-NHA, it is noted that the peaks of the characteristic carbamate absorption were at 3319, 1708 and 1530 cm^{-1}, and the absorption of hydroxy group disappeared. In addition, obvious band at 1078 cm^{-1} due to the $Si-O-C_2H_5$ group and the 2884–2974 cm^{-1} bands due to $-CH_2$ and $-CH_3$ group emerged, which means ICTES-NHA was obtained.

In Fig. 3, ^1H NMR spectra of NHA and ICTES-NHA are shown, in which, the peak assigned to the hydroxy group of NHA vanished and several new peaks emerged on going from NHA to ICTES-NHA. According to literature [14], the chemical shifts can be assigned as follow: the lines of 8.43–8.45, 8.06–8.08, 7.99–8.01 and 7.37–7.39 ppm are corresponding to the protons of benzene ring; the line 7.96–7.99 ppm is assigned to the carbamate ($-NH$COO, 1H); the lines assigned to the methylene and methyl are as follows: 3.75–3.79 ppm ($-O-CH_2-CH_3$, 6H), 3.07–3.11 ppm ($-NH-CH_2-CH_2$, 2H), 1.55–1.58 ppm ($-CH_2-CH_2-CH_2$, 2H), 0.59–0.62 ppm ($-CH_2-CH_2-Si$, 2H), 1.15–1.18 ppm ($-O-CH_2-CH_3$, 9H). These assignments clearly support the proposed structures.

The UV–visible absorption spectra of NHA and ICTES-NHA in THF are shown in Fig. 4. It was obvious that the absorption was hypsochromically shifted in ICTES-NHA compared to NHA. This can be explained as follows: the UV–visible absorption

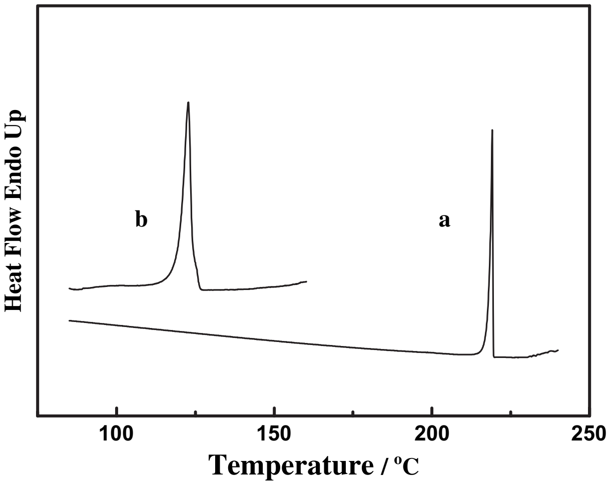


Fig. 1. DSC curves of NHA (a) and ICTES-NHA (b).

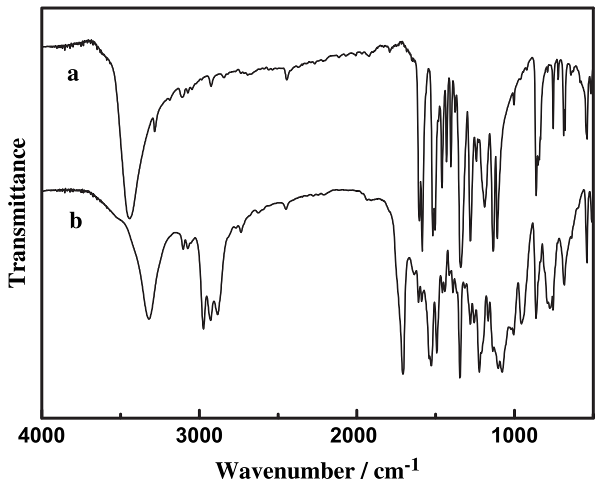


Fig. 2. FTIR spectra of NHA (a) and ICTES-NHA (b).

maximum peak mainly results from π–π* electronic transitions of the NLO chromophore, NHA has a donor group (–OH) and acceptor group (–NO_2) at separated positions, respectively. If the new chemical bond (–NHCOO) is produced between NHA and the silicon oxide, the structure change of the donor can cause a decreased electron-release behavior and change the resonance absorption. As a result, the absorption blue shift can possibly occur. In summary, these analytical results clearly show the formation of alkoxysilane dye by the incorporation of NLO chromophore with the silicon trialkoxide after the coupling reaction.

3.2. Experimental nonlinear optical properties of NHA

Second-order NLO properties of the chromophore were measured by solvatochromic method, which is based on the solvent dependence of the UV–visible absorption spectrum of a molecule. As previously described in literature [15,16], the value for β_{CT} reduces to a simple expression:

$$\beta_{CT}=\frac{3(2\pi)^2}{2\varepsilon_0 h^2}\frac{\omega_{eg}^2}{\left(\omega_{eg}^2-\omega^2\right)\left(\omega_{eg}^2-4\omega^2\right)}(\mu_e-\mu_g)\mu_{eg}^2 \qquad (1)$$

where μ_e–μ_g is the difference between the excited and ground state dipole moment, μ_{eg} is the transition dipole moment between the ground and excited state, ε_0 is dielectric constant in vacuum, h is the Planck constant and ω_{eg} is the transition frequency. Here the ω_{eg} could be obtained simply from the band maximum of the

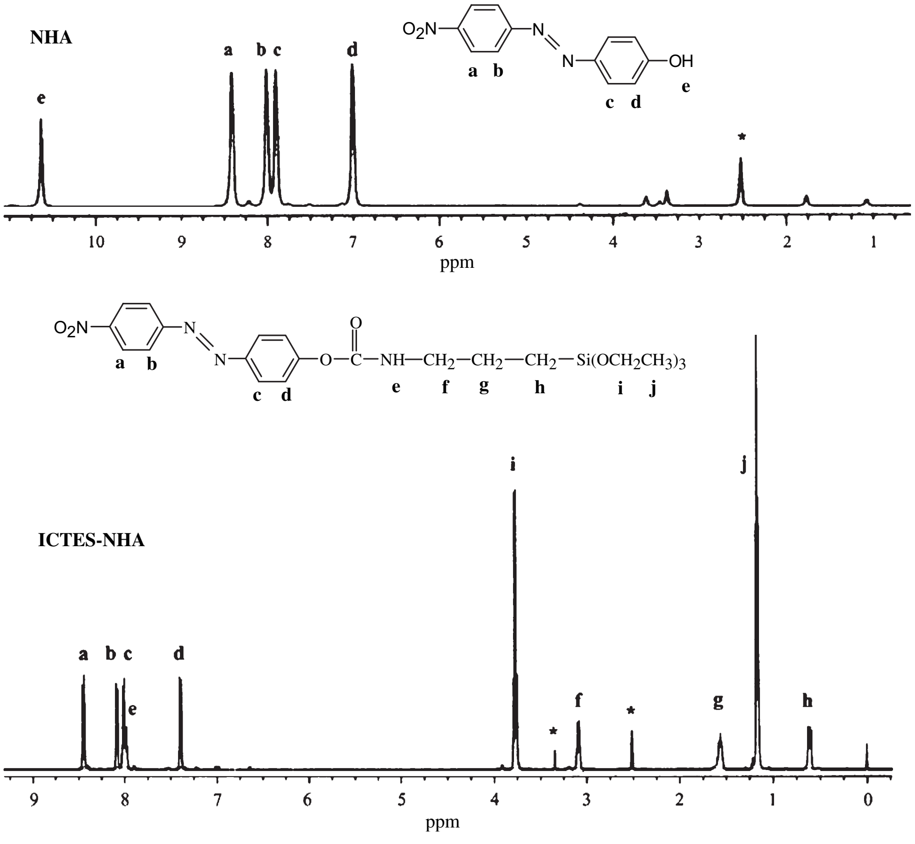


Fig. 3. ^{1}H NMR spectra (500 MHz) of NHA and ICTES-NHA in DMSO-d_6 (the signal marked with * is caused by the solvents) and the assignment of peaks.

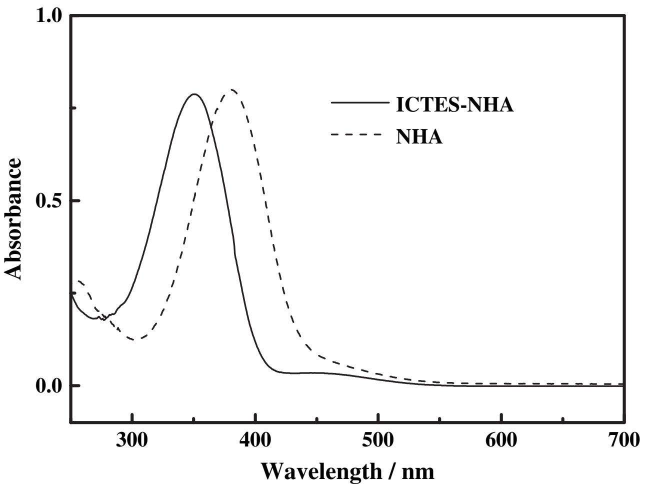


Fig. 4. UV–visible absorption spectra of NHA and ICTES-NHA in THF.

UV–visible absorption spectrum of the molecule, $\omega_{eg} = 2\pi c/\lambda$.

The μ_{eg} is related to the intensity of the transition and could be found from the area under the band by means of Eq. (2) [15].

$$\int \varepsilon \, d\omega = \frac{2\pi\omega_{eg} N n \mu_{eg}^2}{3 \ln 10 \varepsilon_0 c h} \tag{2}$$

where N, n and c are Avogadro's constant, solvent refractive index and speed of light in a vacuum, respectively.

According to Kawski's equation [17], the value of $\mu_e - \mu_g$ is given:

$$\nu_a - \nu_f = A + B\left(\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right) \Bigg/ \left[\frac{1-(n^2-1)}{2n^2+1}\right]^2 \Bigg/ \left[\frac{1-(D-1)}{2D+1}\right]$$

$$B = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{3}$$

where A and B are constants, ν_a and ν_f are wavenumbers of UV–visible absorption and fluorescence emission of molecule, $\nu_a - \nu_f$ is stokes shift; a is the radius of spherical cavity occupied by the molecule, D is dielectric constant of solvent. Measurement of the absorption maximum in a variety of solvents of known dielectric constant and refractive index permits calculation of constant B from Eq. (3).

According to Eq. (4) [16], the values of $\beta_{CT}\mu_g$ can be found:

$$\beta_{CT}\mu_g = 4.612 \times 10^{-5} \times \frac{f(\lambda)\varepsilon \Delta\nu_{1/2} \Delta\nu a^3}{\Delta f(D)}$$

$$f(\lambda) = \frac{\lambda^3 \lambda_0^4}{(\lambda_0^2 - 4\lambda^2)(\lambda_0^2 - \lambda^2)}$$

$$f(D) = \frac{2(D-1)}{2D+1} \tag{4}$$

where λ is the maximum absorption wavelength of molecule in excited state, and here, it is assumed to be the maximum absorption wavelength of molecule in dipolar solvent; ε, $\Delta\nu_{1/2}$, $\Delta\nu$ and λ_0 are maximum of absorption coefficient in dipolar solvent, the difference of the width of peaks at the middle, shift of the maximum absorption in different solvents and wavelength of base frequency, respectively. CGS unit system is adopted, the unit of ε is $\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$ and unit of D is Debye.

The experimental values of NHA and C.I. Disperse Red 1 (DR1) are listed in Table 1, where DR1 data measured under identical experimental conditions, have been enclosed as reference. It can be found that the $\beta\mu$ values of NHA are 141.9×10^{-30} esu D, lower than that of DR1. This may be attributed to the weak electron-donating ability of hydroxy group. Although NHA bears lower $\beta\mu$ values, it possesses a higher melting point (219 °C) and better transparency in the visible region compared with DR1 [18], which make it more suitable for use in second-harmonic generation (SHG) and other parametric processes in the visible spectrum.

4. Conclusions

In summary, an NLO active dye NHA was synthesized with good transparency and a high melting point. With this chromophore, an alkoxysilane dye ICTES-NHA for NLO organic–inorganic hybrid materials was successfully prepared by the coupling reaction. The dye and the alkoxysilane dye are highly soluble in aprotic polar solvents such as DMF, THF, and DMSO, etc. The resulting alkoxysilane dye exhibits acceptable NLO

Table 1
Experimental properties of studied molecules

Compound	λ_{max}[a] (nm)	ε (10^4 mol^{-1} L cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	λ_{max}[b] (nm)	$\Delta\nu$ (cm^{-1})	a (nm)	$\beta_{CT}\mu_g$ (10^{-30} esu D)
NHA	387	2.35	5261	381	407	0.47	141.9
DR1	503	2.87	3819	480	952	0.62	2442.5

[a] Measured in DMF.
[b] Measured in $CHCl_3$.

properties and excellent transparency, indicating its suitability for second-order nonlinear optical applications in the blue and green regions.

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