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ScienceDirect

Dyes and Pigments 73 (2007) 338–343

DYES and PIGMENTS

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Synthesis and spectroscopic characterization of an alkoxysilane dye containing azo-benzothiazole chromophore for nonlinear optical applications

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Received 5 September 2005; accepted 7 January 2006

Abstract

To form covalent linking between organic and inorganic hybrid materials for nonlinear optical (NLO) applications, an alkoxysilane dye (ICTES–EHNBT) which can be copolymerized via sol–gel process was synthesized from 3-isocyanatopropyl triethoxysilane (ICTES) and an NLO-active chromophore 2-[4′-(*N*-ethyl-*N*-2-hydroxyethyl)-amino-phenylazo]-6-nitrobenzothiazole (EHNBT) by a nucleophilic addition reaction. The azo-benzothiazole chromophore is formed by a donor–π-acceptor system, based on a nitro group connected with benzothiazole as the acceptor and a hydroxyl-functional amino group as the donor. EHNBT and ICTES–EHNBT were characterized by elemental analysis, ^{1}H NMR, FTIR, UV–visible spectra, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Comparing to C.I. Dispersed 1 (DR1), the replacement of benzene ring by a less aromatic heterocycle determines a significant bathochromic shift of the visible absorption band and an increase in molecular hyperpolarizability.

Keywords: Alkoxysilane dye; Benzothiazole; Nonlinear optical; Chromophore; Synthesis

1. Introduction

Over the past few years, there has been increasing interest in sol–gel technology due to its potential for developing a wide variety of material with unique optical properties [1]. The sol–gel process is a method for producing a three-dimensional inorganic network by chemical reaction at low temperature. The basic sol–gel process involves the sequential hydrolysis and polycondensation reactions of metal alkoxide at temperatures that are commonly used to obtain polymeric materials as follows [2].

$$\equiv\text{MOR} + \text{HOH} \rightleftharpoons \equiv\text{MOH} + \text{ROH}$$

$$\equiv\text{MOH} + \text{HOM}\equiv \rightleftharpoons \equiv\text{MOM}\equiv + \text{HOH}(\text{water condensation})$$

$$\equiv\text{MOH} + \text{ROM}\equiv \rightleftharpoons \equiv\text{MOM}\equiv + \text{ROH}(\text{alcohol condensation})$$

where M = Si, Zr, Ti, Al, etc., and R = alkyl. Many organic dyes such as laser-active dyes, photochromic dyes, and NLO dyes have been incorporated in sol–gel matrices to make optical materials [1–6].

Hybridization of organic chromophores and inorganic glasses can be one of the best ways to achieve nonlinear optical (NLO)-active materials with low optical losses. In addition, the use of highly cross-linked metal oxide network, which was formed at low temperature without any thermal

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doi:10.1016/j.dyepig.2006.01.023

decomposition of organic chromophore, can reduce thermal relaxation of the aligned dipoles. NLO chromophores are doped at the molecular level with the metal oxide or grafted to the metal oxide matrix [5–10]. Transparent sol–gel films with large coefficients for second-harmonic generation (SHG) were obtained after corona poling [6].

The first SHG studies concerning hybrid materials prepared through sol–gel process have started by using guest/host (G/H) systems with embedded NLO dyes [7], because such systems can be easily achieved. However, because the chromophore is not efficiently locked in the inorganic matrix, fast reversal to random orientation leads to the relaxation of poling-induced order. And the problem of low chromophore concentration in the composite due to poor solubility of the chromophore in the host matrix still remained [8,9]. To resolve the issues mentioned above, NLO dyes are grafted to the inorganic matrix by covalent bond, allow an easier optimization of the dye concentration and a better control of chemical and processing parameters.

As a consequence, most of the sol–gel work performed on hybrid materials with quadratic NLO properties was devoted to dye-grafted systems in the past years. The grafting of the dyes to sol–gel matrices has been performed by using trialkoxy terminated organic spacers connected to the NLO chromophore. The desired chromophore with optimized molecular structure is linked to the alkoxysilane by a Si–R′ covalent bond, $R'Si(OR)_3$, and then processed by hydrolysis and condensation [10,11]. The design and synthesis of new network-forming alkoxysilane dyes are still challenging and detailed investigation of them will offer great opportunities in the fabrication of new materials for second-order nonlinear optics.

In spite of different types of chromophores used for NLO application, the development of more efficient donors, acceptors and conjugating moieties still tempts researchers for the NLO compounds [12,13]. Theoretical NLO studies have revealed that azo-benzothiazole chromophores possess large molecular hyperpolarizability, showing that they are the good choice for the NLO materials [14]. Studies on NLO response properties have shown that the polymers bearing side-chain heteroaromatic azo chromophores possess a larger second-order NLO coefficient than their benzenoid analogues [15]. Despite the importance of azo-benzothiazole dyes [14–17], preparative details corresponding to these dyes derived from benzothiazole coupling components are scarce, and no information concerning alkoxysilane dye containing azo-benzothiazole chromophore has been reported.

The purpose of the present work was to undergo synthesis and characterization of an azo dye containing benzothiazole group (EHNBT) and then its alkoxysilane dye (ICTES–EHNBT) for sol–gel NLO materials. ICTES–EHNBT was synthesized successfully from 3-isocyanatopropyl triethoxysilane (ICTES) with EHNBT 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. Dispersed 1 (DR1), it shows increased molecular hyperpolarizability. The synthesized dye and alkoxysilane dye were characterized by elemental analysis, ^{1}H NMR, FTIR, UV–visible spectra, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials and methods

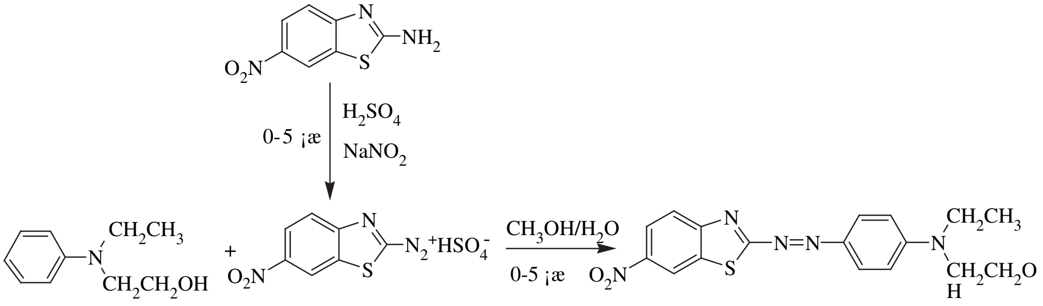
Tetrahydrofuran (THF, purity > 99%) was purified by refluxing and distilling from calcium hydride. 3-Isocyanatopropyl triethoxysilane (ICTES, purity > 95%) was obtained from Tokyo Chemical Industry Co. 2-Amino-6-nitrobenzothiazole and 2-(ethyl(phenyl)amino)ethanol (purity > 98%) were purchased from ACROS Organics. 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 recorded with a Bruker Avance DMX500 spectrometer using tetramethysilane (TMS) as an internal standard and dimethyl sulfoxide-d_6 (DMSO-d_6) as solvent. 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. The decomposition temperature was studied using a TA Instruments SDT Q600 at a heating rate of 10 °C/min under nitrogen atmosphere. Melting point was determined through DSC analysis that was performed using TA Instruments DSC Q100 at 10 °C/min under nitrogen atmosphere.

2.2. Synthesis

2.2.1. 2-[4′-(N-ethyl-N-2-hydroxyethyl)-amino-phenylazo]-6-nitrobenzothiazole (EHNBT)

The diazonium coupling reaction was employed to prepare EHNBT and its reaction scheme is outlined in Scheme 1. Concentrated sulfuric acid (20 mL) containing 2.8 g (40 mmol) of $NaNO_2$ was added dropwise, with stirring, to 56 mL of formic acid, propionic acid, phosphoric acid and acetic acid mixture (1:1:2:3) containing 7.8 g (40 mmol) of 2-amino-6-nitrobenzothiazole in an ice bath. After stirring for 1 h in an ice bath, the reaction mixture was poured into crushed ice to obtain diazonium salt solution, which was then poured into 120 ml of methanol/water (2:1 volume ratio) mixture containing 7.4 g (44 mmol) of 2-(ethyl(phenyl)amino)ethanol in an ice bath with vigorous stirring for an hour. Then the pH of the solution was adjusted to 5–6 by adding ammonia water, and the mixture was stirred for 2 h more. The precipitate formed was filtered, washed with excess of water and purified by column chromatography (silica gel) using petroleum ether/ethylacetate (5/3, v/v) as eluant. Purified product was obtained as black violet powder. Yield: 39%. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 9.02 (d, Ar*H*, 1H), 8.29 (q, Ar*H*, 1H), 8.11 (d, Ar*H*, 1H), 7.88 (d, Ar*H*, 2H), 7.01 (d, Ar*H*, 2H), 4.94 (s, O*H*, 1H), 3.64 (t, C*H*$_2$, 6H), 1.20 (m, C*H*$_3$, 3H). Anal. Calcd for $C_{17}H_{17}N_5O_3S$ (371.4): C, 54.97; H, 4.61; N, 18.86. Found: C, 54.46; H, 4.59; N, 18.72.



Scheme 1. Synthesis route of EHNBT.

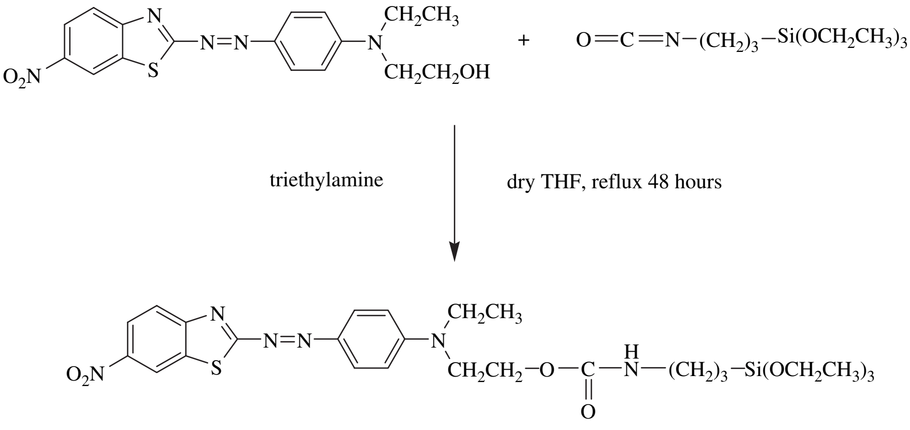
2.2.2. Alkoxysilane dye (ICTES–EHNBT)

The procedure for synthesis of ICTES–EHNBT is shown in Scheme 2. To a three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and a reflux condenser, 1.86 g (5 mmol) of EHNBT, 1.36 g (5.5 mmol) of ICTES, 30 ml of THF and five drops of triethylamine (TEA) as catalysts were introduced. The mixture was stirred and refluxed for 48 h under nitrogen atmosphere. The compound was precipitated into dried hexane, collected by suction filtration and purified by flash column chromatography (silica gel) using petroleum ether/ethylacetate (1:1, v/v) as eluant. The product was dried under vacuum at 40 °C overnight and stored in a desiccator. Yield: 69%. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 11.13 (s, N*H*, 1H), 9.04 (d, Ar*H*, 1H), 8.27 (q, Ar*H*, 1H), 8.14 (d, Ar*H*, 1H), 7.90 (d, Ar*H*, 2H), 7.03 (d, Ar*H*, 2H), 4.20 (s, CH_2CH_2O, 2H), 3.76 (m, OCH_2CH_3, 6H), 3.63 (d, CH_2CH_2O, 2H), 3.16 (d, CH_2CH_3, 2H), 2.26 (d, $CH_2CH_2CH_2$, 2H), 1.53 (d, $CH_2CH_2CH_2$, 2H), 1.15 (m, CH_2CH_3, 12H), 0.59 (t, $CH_2CH_2CH_2$, 2H). Anal. Calcd for $C_{27}H_{38}N_6O_7SSi$ (618.2): C, 52.41; H, 6.19; N, 13.58. Found: C, 52.55; H, 6.22; N, 13.70.

3. Results and discussion

3.1. Characterization

The NLO dye EHNBT has been prepared by coupling 2-(ethyl(phenyl)amino)ethanol with diazotized 2-amino-6-nitrobenzothiazole. Because of the mild acidity of $NaNO_2$/HCl solution resulting in relatively smaller amounts of by-products, most of the mono-substituted carbo-aromatic anilines were diazotized by this reagent, which gave almost quantitative yields of diazonium ions. But heteroaromatic amines are in equilibrium with the respective diazonium ions in the presence of nitrosating agents [18]. In this case, the weak basicity of the 2-amino-6-nitrobenzothiazole was not sufficient to permit the reaction with nitrosyl chloride. The difficulty of forming stable diazonium salts of heteroaromatic amines was caused by the protonation of the ring N-atom in acidic media [19]. Due to the poor solubility of 2-amino-6-nitrobenzothiazole and low stability of the diazonium salt, formic acid, propionic acid, phosphoric acid and acetic acid mixture (1:1:2:3) was used as reaction medium. Although nitrosylsulfuric acid from $NaNO_2$/conc H_2SO_4 was used, a portion of by-products, like the amine sulfate was formed and greatly reduced the rate of diazotization. Subsequent coupling reaction took place readily on adding the resulting diazonium salt continuously to methanol/water mixture containing 2-(ethyl(phenyl)amino)ethanol. Ice flakes were frequently added to keep the coupling temperature below 10 °C and facilitated the precipitation of the resulting dye. To complete the coupling, particularly for this reaction using nitrosylsulfuric acid in the previous diazotization, the pH of the mixture was eventually adjusted to approximately 5–6 and stirred for 2 h more. Thus, an appropriate amount of ammonia water was slowly added below 10 °C. At this stage, the presence of an acid



Scheme 2. Synthesis route of ICTES–EHNBT.

mixture, as a buffer, was very useful to prevent a sudden increase in pH.

The alkoxysilane dye ICTES–EHNBT was obtained with 69% yield through a coupling reaction between the ICTES and EHNBT. Alkoxysilane dyes after coupling reaction were always used directly for sol–gel reaction without further purification. So few experimental data of alkoxysilane dye synthesized were reported previously. Flash column chromatography was found to be useful to purify alkoxysilane dye. The alkoxysilane dye was found to be stable enough to withstand the eluting process. 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, ethanol, DMF, DMSO, and chloroform. They are insoluble in nonpolar solvents such as hexane, heptane.

The infrared spectra of EHNBT, ICTES and ICTES–EHNBT are shown in Fig. 1. The stretching vibration of the hydroxyl group in EHNBT is observed around 3458 cm^{-1}. For ICTES, the C–H stretching vibrations of CH_3 and CH_2 are observed at 2888, 2928 and 2976 cm^{-1}, the Si–O–C_2H_5 stretching frequencies of alkoxysilane were located at 1081 and 1167 cm^{-1}, the strong absorption peak corresponding to N=C=O stretching was observed at 2273 cm^{-1}. In the spectrum of ICTES–EHNBT, the absorption bands of N=C=O and OH vanish and new absorption bands at 3389 and 1699 cm^{-1} emerge, contributed by the NH stretching and carbonyl (C=O) stretching, respectively. In addition, the C=C stretching of phenylene and asymmetric stretching and symmetric stretching of NO_2 were observed at 1600, 1527 and 1335 cm^{-1}, respectively. The Si–O–C_2H_5 stretching frequencies of alkoxysilane were moved to 1105 and 1079 cm^{-1}. These results indicate that ICTES–EHNBT was obtained.

Generally, azobenzene derivatives exhibit a low-intensity n–π* band in the visible region of the spectrum and a high-intensity π–π* band in the UV region. When an electron-donor and an electron-acceptor groups are substituted in the case of chromophores investigated here, the energy of the N=N π-bonding orbital is effectively increased, but the energy of the π*-anti-bonding orbital and the overall energy of the π–π* transition is lowered. The UV–visible absorption spectra of EHNBT, ICTES–EHNBT and DR1 in THF are shown in Fig. 2. The charge-transfer transitional energy is much more reduced in EHNBT than in its analogue DR1 by replacement of benzene ring by a less aromatic heterocycle, resulting in a significant bathochromic shift (51 nm) of the visible absorption band as the color chemistry studies evidenced [20]. EHNBT has its maximum absorption at 540 nm, while ICTES–EHNBT has maximum absorption at 533 nm. It was obvious that when new chemical bond (–O–C=O) was produced in ICTES–EHNBT, the structural change of the donor caused the hypsochromic shift of 7 nm compared to EHNBT. The addition of the ICTES group permits a less polar excited state so that the migration of electrons towards the acceptor ring is hindered, and the resonance absorption peak was changed as a result.

The melting points of EHNBT and ICTES–EHNBT were determined to be 210 and 123 °C, respectively, by means of DSC at a heating rate of 10 °C/min. The decomposition temperatures (T_d) are defined as shown in Fig. 3, being 241 °C for EHNBT and 221 °C for ICTES–EHNBT. The reaction of carbamate formation between ICTES and EHNBT tends to be associated with a decrease in melting point and decomposition temperature.

3.2. Experimental nonlinear optical properties

The solvatochromism method was used to determine the first-order hyperpolarizability of the chromophores [21–23]. The method is based on the two-level quantum-mechanical model where only terms that involve either the ground or the first excited singlet state are considered. Typical NLO chromophores have an electron-donor group and an acceptor group linked through a π-electron system. As a consequence, the first excited state is often a low-lying charge-transfer state, usually in the visible or near-UV region of the spectrum. The

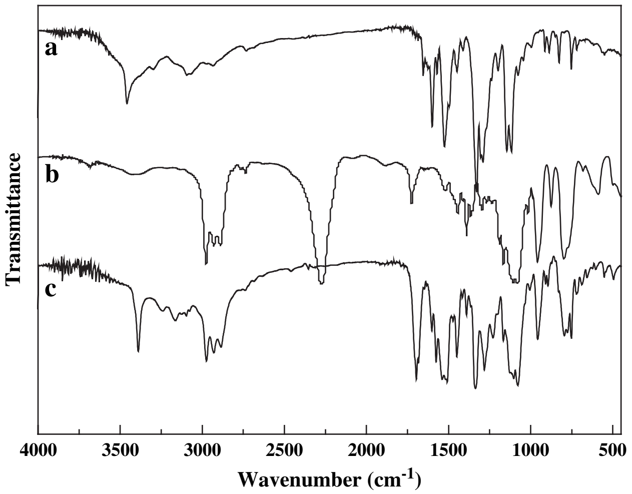


Fig. 1. FTIR spectra of EHNBT (a), ICTES (b) and ICTES–EHNBT (c).

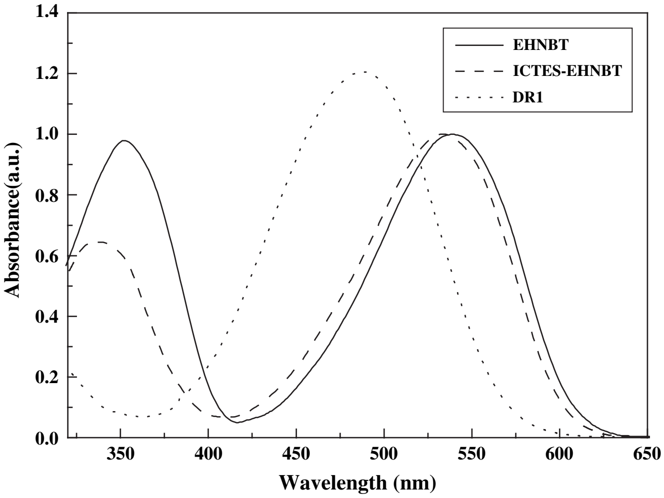


Fig. 2. UV–visible absorption spectra of EHNBT, ICTES–EHNBT and DR1 in THF.

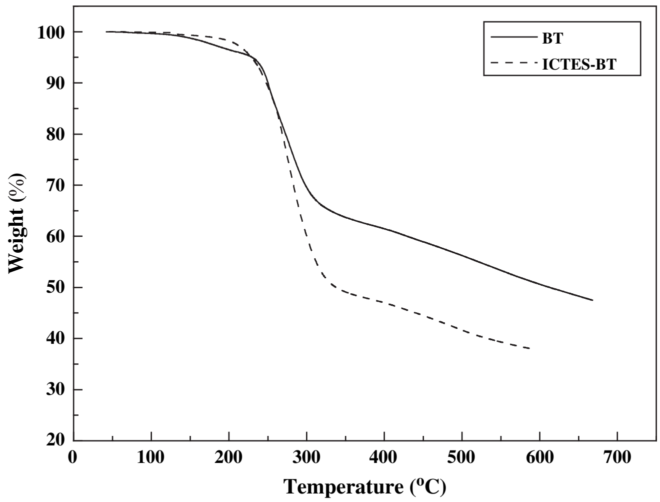


Fig. 3. TGA curves of EHNBT and ICTES–EHNBT.

dominant component of the first-order hyperpolarizability β_{ijk} is β_{xxx}, often referred as β_{CT}. For practical purpose, the composite magnitude $\beta_{CT}\mu_g$ was adopted. When solvents with similar refractive index were used in measurements, the value of $\beta_{CT}\mu_g$ can be simplified by means of Eq. (1) [22]:

$$\beta_{CT}\mu_g = 4.612 \times 10^{-5} \times \frac{f(\lambda)\varepsilon\Delta\nu_{1/2}\Delta\nu a^3}{\Delta f(D)},$$
$$f(\lambda) = \frac{\lambda^3\lambda_0^4}{\left(\lambda_0^2 - 4\lambda^2\right)\left(\lambda_0^2 - \lambda^2\right)}, \quad f(D) = \frac{2(D-1)}{2D+1} \tag{1}$$

where λ is the maximum absorption wavelength of molecule in the excited state, and here, it is assumed to be the maximum absorption wavelength of the molecule in dipolar solvent; ε, $\Delta\nu_{1/2}$, $\Delta\nu$ and λ_0 are maximum absorption coefficient in dipolar solvent, the difference in 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 $\mathrm{mol^{-1}\,L\,cm^{-1}}$ and unit of D is Debye.

At the present time, 1064 nm was often used as the base frequency in electric-field-induced second-harmonic generation (EFISH) measurement [23]. But most of the organic NLO materials present large linear absorption at the harmonic frequency (532 nm). Unexpected overestimation of β is possible if two-photon absorption induced fluorescence (TPF) [24] and two-photon resonance (TPR) at 1064 nm are not neglected. Furthermore, the assumption of λ_0 to be 1064 nm in the simplified Eq. (2) failed in calculating $\beta_{CT}\mu_g$. So λ_0 in this study was assumed to be 1907 nm which could be obtained by shifting the 1064 nm laser light by stimulated Raman scattering of pressurized H_2 gas [23].

The experimental values of EHNBT and DR1 were determined by spectroscopic measurements and the results are listed in Table 1, where DR1 data measured under identical experimental conditions, have been enclosed as reference. The $\beta\mu$ value of EHNBT was found to be 125.8×10^{-29} esu D, larger than that of DR1 (89.7×10^{-29} esu D). Due to the deficiency of electron density on the ring C-atoms, the benzothiazole ring acts as an auxiliary acceptor strengthening the electron-withdrawing power of NO_2. Moreover, it extends the conjugation length of the π-electron bridge. The large electronegativity and lone electron pairs of S and N-atoms in benzothiazole lead to an increase in molecular hyperpolarizability, showing that they are the good choice for the NLO materials [14].

Table 1
Experimental properties of studied molecules

Compound	λ_{max}[a] (nm)	ε (10^4 $\mathrm{mol^{-1}\,L\,cm^{-1}}$)	$\Delta\nu_{1/2}$ ($\mathrm{cm^{-1}}$)	λ_{max}[b] (nm)	$\Delta\nu$ ($\mathrm{cm^{-1}}$)	a (nm)	$\beta_{CT\ (1907\ nm)}\mu_g$ (10^{-30} esu D)
EHNBT	555	2.05	3494	536	638	0.80	1258
DR1	503	2.87	3819	480	952	0.62	897

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

4. Conclusions

In summary, we synthesized an NLO-active dye EHNBT with large molecular hyperpolarizability. With this chromophore, an alkoxysilane dye ICTES–EHNBT for NLO organic–inorganic hybrid materials was successfully prepared by the coupling reaction. Comparing to commercially available DR1, solvatochromism results indicate that the resulting alkoxysilane dye exhibits a larger molecular hyperpolarizability. The experimental data also indicate that ICTES–EHNBT has a high melting point and an acceptable decomposition temperature insuring that it is a good candidate for electro-optical applications.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from the National Natural Science Foundation of China (under Grant Nos. 50532030 and 50372059), the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 200134) and Education Foundation of FOK Ying Tung (No. 81042).

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