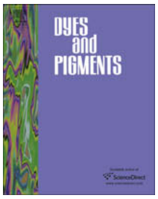
Dyes and Pigments 81 (2009) 53–57

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



An indanone-based alkoxysilane dye with second order nonlinear optical properties

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ARTICLE INFO

Article history:
Received 11 July 2008
Received in revised form 4 September 2008
Accepted 4 September 2008
Available online 19 September 2008

Keywords:
Alkoxysilane dye
Chromophore
Nonlinear optical
Indanone
Thermal stability
Sol–gel

ABSTRACT

An azo-chromophore containing 2-methylidene-3-(dicyano-methylidene)-1-indanone as electronic acceptor group was synthesized via the Knoevenagel condensation between an aldehyde and indanedione derivative, followed by reaction with 3-isocyanatopropyltriethoxysilane. The structures of the chromophore and the synthesized alkoxysilane dye were confirmed by means of elemental analysis, NMR and FTIR analyses. Thermal analysis revealed that both had distinct melting points and thermal stability up to 240 °C. The chromophore and alkoxysilane dye are readily soluble in common solvents such as DMF, THF and DMSO. Compared with the traditional dye C.I. Disperse Red 1, the indanone-based chromophore exhibited larger molecular hyperpolarizability owing to its stronger electron-withdrawing ability.

1. Introduction

Organic and polymeric nonlinear optical (NLO) materials are currently attracting considerable attention because of their large electro-optic coefficients, low dielectric constants, wide response wave band, and ease of fabrication [1–4]. To realize the tremendous potential applications in the fields of optical information processing, high-speed broadband waveguides for optical switches, optical sensing, and data storage, NLO polymers should exhibit good properties such as high thermal and chemical stability, large optical nonlinearity, as well as good transparency [5,6]. For NLO polymers, an electric field is often utilized to achieve the orientation of chromophores. However, the poled order is thermodynamically unstable, especially at elevated temperatures. To enhance the stability of optical nonlinearity, various approaches including a cross-linking after aligning the dipole and an interpenetration polymer network, as well as the use of the highly rigid backbone have been reported [7–11].

Recently, it appears that the sol–gel material has received much attention and has been considered to be one of the most potential matrix candidates for stabilizing poled dipole orientation [12–14]. The sol–gel process offers an attractive route to fabricate inorganic–organic hybrid NLO materials with high thermal stability, excellent optical quality and high stability of dipole alignment by locking the chromophore in the silica networks. The chemical bond between the chromophore and the silicon network will allow incorporation of higher concentrations of NLO chromophores and restrict the randomization of poled NLO chromophore alignment. Generally, the chromophore-linked NLO hybrids are prepared by incorporating NLO chromophores into silicon oxide to provide an alkoxysilane dye, and followed by hydrolysis and condensation to form an amorphous silica network. Therefore, it is crucial to design and synthesis new alkoxysilane dyes for preparation of hybrid NLO materials, especially on how to optimize its structure to achieve excellent optical nonlinearity.

For traditional chromophores with D-π-A structure, electron conjugated bridge, electron donor and electron acceptor play an important role in the variation of molecular hyperpolarizability (β). According to synthetic and theoretical studies on push–pull chromophores, it is shown that increasing the donor and acceptor strength and using easily delocalized five-membered heteroaromatic ring instead of the benzene ring will result in a pronounced increase in β-value [15]. Thus, a NLO chromophore containing 2-methylidene-3-(dicyano-methylidene)-1-indanone as electron acceptor was synthesized, and then an new alkoxysilane dye was successfully synthesized through a coupling reaction between the resulting chromophore and 3-isocyanatopropyltriethoxysilane (ICTES). In this paper, we present in detail the synthesis, structural characterization, thermal properties and nonlinear optical properties of the indanone-based chromophore and the corresponding alkoxysilane dye.

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doi:10.1016/j.dyepig.2008.09.002

2. Experimental

2.1. Materials and measurements

Tetrahydrofuran (THF) was dried over and distilled from calcium hydride. 3-Isocyanatopropyltriethoxysilane (ICTES), 4-fluorobenzaldehyde and indane-1,3-dione were obtained from Tokyo Chemical Industry Co. and Alfa Reagent. All other reagents, of analytical grade quality, were commercial products and used as received.

Elemental analyses were carried out on Eager 300 microelemental analyzer. ^{1}H NMR spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethysilane (TMS) as an internal standard. 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 Hitachi U4100 spectrophotometer. Melting point was determined through DSC analysis that was performed using TA DSC Q100 at a scan rate of 10 °C/min under a nitrogen atmosphere. The decomposition temperature was studied by TA SDT Q600 thermogravimetric analyzer at the heating rate of 20 °C/min under a nitrogen atmosphere.

2.2. Synthesis

2.2.1. *4-((N-Hydroxyethyl-N-methyl)amino)benzaldehyde (**1**)*

To a solution of 6.4 g of 2-(methylamino)ethanol in dimethyl sulfoxide (DMSO), 3 g of 4-fluorobenzaldehyde, 10 g of anhydrous potassium carbonate, and 0.1 ml aliquat 336 as catalyst were added. The mixture was heated at 98 °C for 3 days and then poured into ice water. The product was extracted with dichloromethane and purified by column chromatography using petroleum ether/ethyl acetate (4/1, v/v) as eluent. Yield: 53%, mp: 69–70 °C.

^{1}H NMR (500 MHz, CD_3COCD_3, δ ppm): 3.13 (CH_3, 3H), 3.60–3.63 (CH_2CH_2OH, 2H), 3.76–3.79 (CH_2CH_2OH, 2H), 3.88–3.90 (CH_2CH_2OH, 1H), 6.83–6.84 (ArH, 2H), 7.67–7.69 (ArH, 2H), 9.70 (CHO, 1H). Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.20; H, 7.29; N, 7.90.

2.2.2. *2-(3-Oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**2**)*

Indane-1,3-dione (4.4 g) and malononitrile (4.0 g) were dissolved in 30 ml absolute ethanol, and then 3.2 g of anhydrous sodium acetate was added while stirring. After 40 min, the mixture was poured into water, and acidified to pH 1–2 by addition of the hydrochloric acid. The precipitate was filtered and recrystallized from acetic acid. Yield: 85%, mp: 231 °C–233 °C.

^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 3.60–3.65 (CH_2, 2H), 7.36–7.44 (ArH, 2H), 7.87–8.04 (ArH, 2H). Anal. Calcd. for $C_{12}H_6N_2O$: C, 74.22; H, 3.11; N, 14.43. Found: C, 73.91; H, 3.20; N, 14.36.

2.2.3. *(E)-2-(2-(4-((2-Hydroxyethyl)(methyl)amino)benzylidene)-3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (**IND**)*

2.2 g of **1** and 1.9 g of **2** were dissolved in 40 ml absolute ethanol, and then stirred for 12 h at room temperature. The precipitate was filtered and washed repeatedly with ethanol to remove any remaining reactants. The product was recrystallized from ethanol. Yield: 80%, mp: 207 °C.

^{1}H NMR (500 MHz, CD_3COCD_3, δ ppm): 3.29 (s, NCH_3, 3H), 3.77 (t, NCH_2CH_2, 2H, $J = 11.2$ Hz), 3.87 (t, CH_2CH_2O, 2H, $J = 16.8$ Hz), 4.05 (t, OH, 1H, $J = 11.1$ Hz), 6.94 (d, ArH, 2H, $J = 9.3$ Hz), 7.81 (t, ArH, 2H,

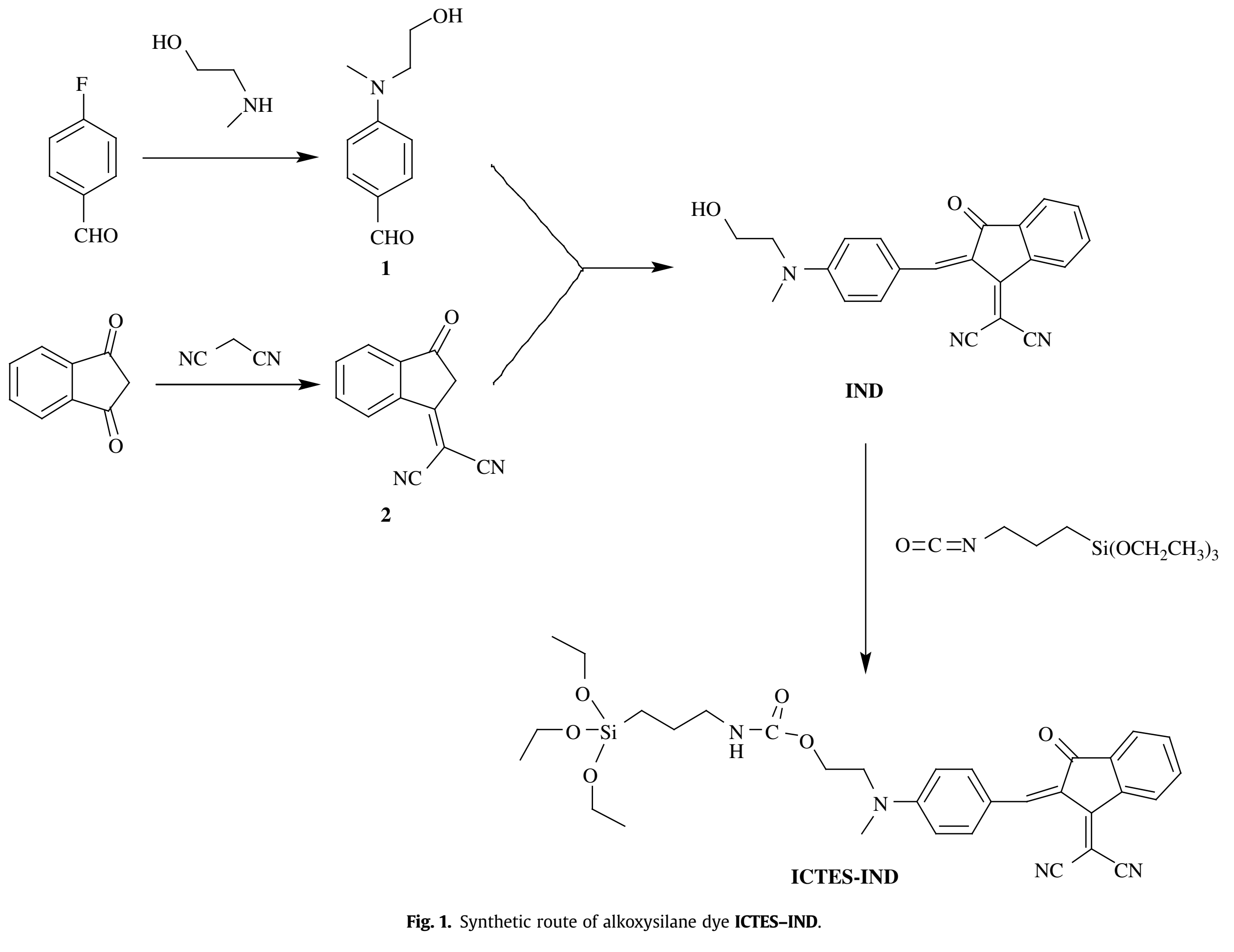

Fig. 1. Synthetic route of alkoxysilane dye **ICTES–IND**.

$J = 7.5$ Hz), 7.84 (q, C*H*=C, 1H, $J = 11.2$ Hz), 8.36 (d, Ar*H*, 2H, $J = 8.9$ Hz), 8.42 (s, Ar*H*, 1H), 8.55 (d, Ar*H*, 1H, $J = 7.7$ Hz). Anal. Calcd. for $C_{22}H_{17}N_3O$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.36; H, 4.79; N, 11.83. IR (KBr, cm^{-1}): 3516 (–OH), 2216 (–CN), 1682 (–C=O), 1614, 1552, 1508 (aromatic ring).

2.2.4. Alkoxysilane dye (***ICTES–IND***)

To a three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and reflux condenser, 2.13 g of **IND**, 2.22 g of ICTES, 20 ml of THF and 5 drops of triethylamine (TEA) as catalyst were mixed. The mixture was stirred and refluxed for 48 h under nitrogen atmosphere, and then the solvent was removed under vacuum. The residue was purified by chromatograph on silica gel using petroleum ether/ethyl acetate (1/1, v/v) as an eluent to provide the alkoxysilane dye **ICTES–IND**. Yield: 30%, mp: 71 °C.

^1H NMR (500 MHz, DMSO-d_6, δ ppm): 0.48 (t, Si–C*H*$_2$CH$_2$, 2H, $J = 8.3$ Hz), 1.09 (m, C*H*$_3$CH$_2$O, 9H, $J = 20.6$ Hz), 1.41 (t, CH$_2$C*H*$_2$CH$_2$, 2H, $J = 7.4$ Hz), 2.91 (t, CH$_2$C*H*$_2$NH, 2H, $J = 14.1$ Hz), 3.16 (s, NC*H*$_3$, 3H), 3.66 (m, CH$_3$C*H*$_2$O, 6H, $J = 20.9$ Hz), 3.78 (d, OCH$_2$C*H*$_2$N, 2H, $J = 5.2$ Hz), 4.17 (t, OC*H*$_2$CH$_2$N, 2H, $J = 10.0$ Hz), 6.89 (d, Ar*H*, 2H, $J = 8.9$ Hz), 7.77 (d, Ar*H*, 2H, $J = 5.9$ Hz), 7.82 (q, C*H*=C, 1H, $J = 11.3$ Hz), 8.23 (d, Ar*H*, 2H, $J = 8.1$ Hz), 8.25 (s, Ar*H*, 1H), 8.39 (d, Ar*H*, 1H, $J = 7.8$ Hz). IR (KBr, cm^{-1}): 3277 (–NH), 2885–2973 (–CH_2CH_3), 2216 (–CN), 1716 (–COO), 1687 (–C=O), 1614, 1556, 1512 (aromatic ring), 1076–1192 (–Si–OR).

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the indanone-based alkoxysilane dye was carried out according to Fig. 1. The key intermediate **1**, 4-((*N*-hydroxyethyl-*N*-methyl)amino)benzaldehyde, was synthesized by following the method previously reported in the literature [16]. The intermediate **2** was prepared through Knoevenagel condensation between indane-1,3-dione and malononitrile in the yield of 85%. In this reaction, the absolute ethanol was selected as solvent due to its strong solubility and polarity. The Knoevenagel reaction of intermediate **1** with **2** produced the chromophore **IND** with a yield of 80% [17]. As mentioned above, chromophore functionalized alkoxysilane is an important step to develop hybrid inorganic–organic NLO materials. In this paper, alkoxysilane dye **ICTES–IND** was prepared by a coupling reaction of the chromophore and 3-isocyanatopropyltriethoxysilane (ICTES) in the presence of triethylamine as catalyst.

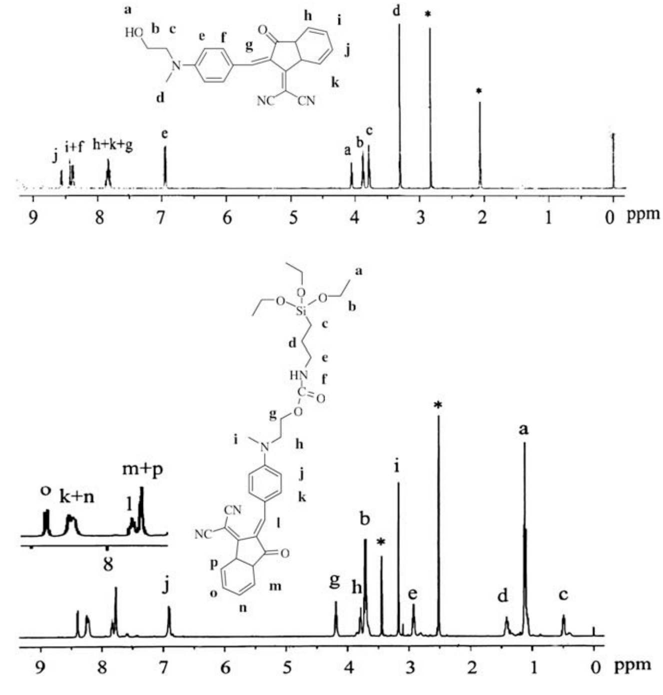

Fig. 2. ^1H NMR spectrum of chromophore and alkoxysilane dye.

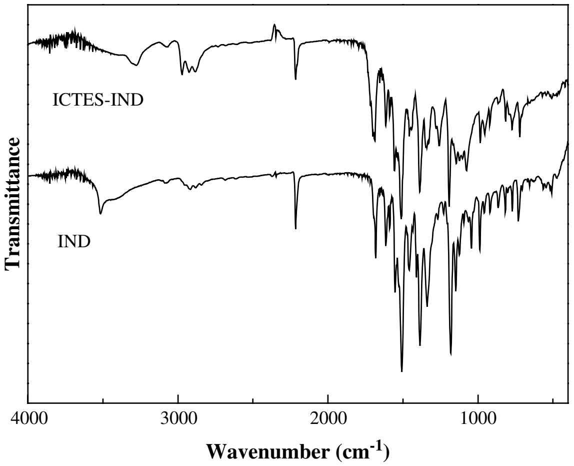

Fig. 3. FTIR spectra of chromophore and alkoxysilane dye.

All of the chromophore and alkoxysilane dye have good solubility in common organic solvents such as THF, DMF, DMSO, and ethanol, etc. They are insoluble in nonpolar solvents such as hexane, heptane, etc. High optical quality films could be fabricated by spin coating after the hydrolysis and polymerization of alkoxysilane dye.

The molecular structures of the compounds were confirmed by elemental analysis, ^1H NMR, and FTIR. The elemental analyses values of the compounds are in good agreement with the calculated values for the proposed structures. Fig. 2 shows the ^1H NMR spectra of chromophore **IND** and alkoxysilane dye **ICTES–IND**, where the spectral assignments clearly support the proposed structure. Moreover, the ^1H NMR analysis permits monitoring of the systematic structural changes throughout the synthesis of the alkoxysilane dye. In the spectra, the peaks in the range of 6.8–8.5 ppm corresponding to the indene and benzene protons exhibited no significant change. While the peak assigned to the hydroxy group vanished, several new chemical shifts of methylene and methyl groups emerged while going from **IND** to **ICTES–IND**.

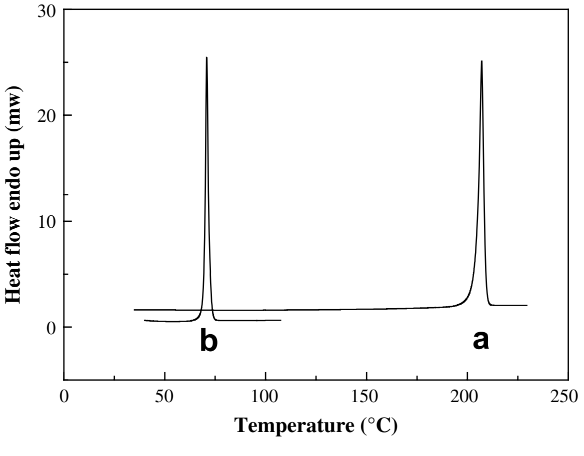

Fig. 4. DSC curves of chromophore (a) and alkoxysilane dye (b).

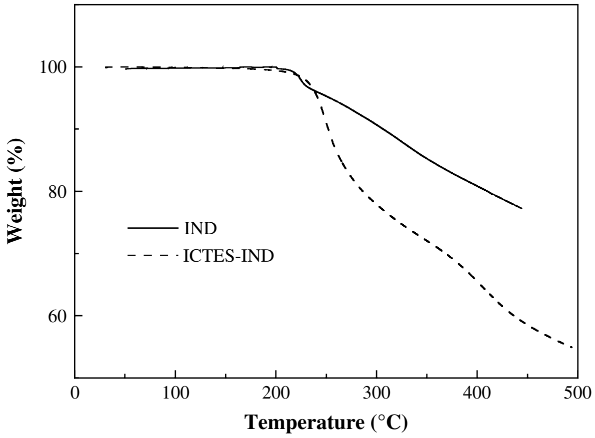

Fig. 5. TGA curves of chromophore and alkoxysilane dye.

The successful incorporation of chromophore into alkoxysilane could be proved once more by FTIR spectra (Fig. 3). Comparing the FTIR spectra of **ICTES–IND** with that of **IND**, a series of new peaks appeared, which including a strong band located at 1070–1100 cm^{-1} attributed to the asymmetric Si–O–C_2H_5 stretching vibration as well as a band at about 2885–2973 cm^{-1} due to a –CH_2CH_3 stretching vibration. Meanwhile, the characteristic strong absorption peaks at 1682 and 2216 cm^{-1} due to the stretching vibration of the carbonyl and cyano group exhibited no significant change. These results clearly show the formation of alkoxysilane dyes through the coupling reaction between **IND** and ICTES.

The analysis of the thermal properties was performed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. DSC results show that both the chromophore and alkoxysilane dye have a distinct melting point around 207 and 71 °C, respectively, as presented in Fig. 4. Fig. 5 gives the thermogravimetric curves of the chromophore **IND** and alkoxysilane dye **ICTES–IND**. Both of them show good thermal stability with the onset decomposition temperature of 248 and 242 °C under nitrogen, respectively, and no weight loss was observed at lower temperatures. The result indicates that the alkoxysilane group incorporated into the chromophore has little impact on the overall stabilities.

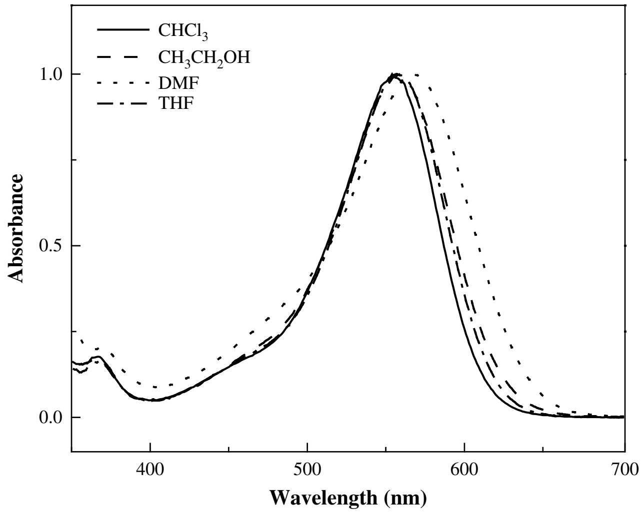

Fig. 6. UV-visible absorption spectra of chromophore **IND** in various solvents.

Table 1
Solvatochromic data and hyperpolarizabilities of the chromophores

Chromophore	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})	$\beta_{CT(1907\ nm)}\mu_g$ (10^{-30} esu·D)
IND	565	5.70	2971	555	351	1558
DR1	503	2.87	3819	480	952	814

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

3.2. Linear and nonlinear optical properties

Fig. 6 illustrates the UV-visible absorption spectra of chromophore **IND** in various solvents. As expected, the absorption spectra of chromophore **IND** undergo a bathochromic shift upon increasing the polarity of the solvent. This solvatochromic behavior is attributed to an intramolecular charge-transfer transition with an increase of the dipole moment upon excitation and is interpreted in terms of predominance of neutral form in the ground-state structure [18]. Demartino et al. correlated high solvatochromic effects with a large molecular hyperpolarizability because both phenomena are associated with a transition from ground state to an excited state [19].

The UV-visible spectra of the chromophore **IND** show an intense lowest energy charge-transfer band in the visible region. The maximum absorption wavelength (λ_{max}) is at 565 nm in the solvent of DMF, which is bathochromically shifted than **DR1**, confirming the stronger electron-withdrawing strength of substituent 2-methylidene-3-(dicyano-methylidene)-1-indanone. In general, the stronger the donor or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. This red shift, suggests an increase of molecular hyperpolarizability, according to theoretical and experimental NLO studies [20,21]. As previously described in literature [22,23], the $\beta_{CT}\mu_g$ values were estimated and listed in Table 1, where **DR1** is the data measured under identical experimental conditions as reference. It can be found that the $\beta_{CT}\mu_g$ value of **IND** is 1558×10^{-30} esu·D, much larger than that of **DR1** (814×10^{-30} esu·D), indicating the powerful electron acceptor group 2-methylidene-3-(dicyano-methylidene)-1-indanone should be responsible for the high $\beta_{CT}\mu_g$ values. In addition, the indene ring may also play a major role in reducing the charge transfer transitional energy between donor and acceptor substituents and result in an enhanced molecular hyperpolarizability.

4. Conclusions

In summary, a new alkoxysilane dye containing 2-methylidene-3-(dicyano-methylidene)-1-indanone as electronic acceptor group was synthesized by the coupling reaction between the chromophore **IND** and 3-isocyanatopropyltriethoxysilane (ICTES). The structures of the chromophore and alkoxysilane dye were confirmed by elemental analysis, ^1H NMR, and FTIR. Thermal analysis by DSC and TGA shows that they have distinct melting point and have high thermal stability up to 240 °C. The result of solvatochromic measurement indicates that the chromophore possesses substantial second order optical nonlinearity, which qualifies the alkoxysilane dye for further application in NLO sol–gel materials.

Acknowledgements

The authors gratefully acknowledge the financial support for this work from PCSIRT, the National Natural Science Foundation of China (under Grant Nos. 50532030, 50625206 and 50802084).

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