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Synthesis and nonlinear optical properties of a series of azo chromophore functionalized alkoxysilanes

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Abstract

A series of azo chromophores based on benzene and thiazole moieties as conjugating bridges were synthesized and then reacted with 3-isocyanatopropyltriethoxysilane (ICTES) to give various alkoxysilane dyes. Their structures were confirmed by elemental analysis, ^{1}H NMR, FTIR, and UV–visible spectra; thermogravimetric analysis showed that the compounds displayed high thermal stability. The alkoxysilane dyes had very good solubility in common solvents and their nonlinear optical (NLO) activities were evaluated solvatochromically. The results indicate that the thiazole moiety on the electron acceptor side can significantly enhance molecular hyperpolarizability due to its lower aromatic delocalization energy and auxiliary electron-withdrawing ability.

Keyword: Alkoxysilane dye; Thiazole; Nonlinear optical; Solvatochromic method; Azo chromophore

1. Introduction

Nonlinear optics have been recognized for several decades as a promising field with important potential application in the context of frequency doubling and electro-optic (EO) modulation [1–4]. Hence, various materials including inorganic and organic crystals, poled polymers, organometallic compounds, self-assembled films, and inorganic–organic hybrids have been investigated for their NLO properties [5–12]. Of these, hybrid inorganic–organic materials derived by use of the sol–gel process are considered the most promising NLO materials because of their low optical propagation loss, excellent thermal stability, low-temperature processing capability, and ease of device fabrication [13–15].

Hybrid NLO materials can be made by the doping of organic chromophores inside a sol–gel matrix or by the hydrolysis and condensation of a silicon alkoxide containing chromophore. The former route is limited to a chromophore concentration of 15–20% as a result of phase separation, sublimation at an elevated temperature and thermal relaxation instability [15]. Some of these problems can be resolved by the latter process, in which, NLO-active dyes are covalently incorporated into alkoxysilane. Subsequently, a three dimensional, inorganic network was prepared by the sol–gel processing of an alkoxysilane dye, which is similar to the side-chain NLO polymers. This chemical link will permit the incorporation of a higher concentration of NLO units in the sol–gel matrix, and the rigid silica network can also provide an inert environment for the organic molecule so as to prevent relaxation of the noncentrosymmetry NLO chromophore alignment induced by an electric field [16]. Therefore, the design and synthesis of new alkoxysilane dyes are required for the preparation of hybrid NLO materials.

The choice of chromophore in the case of alkoxysilane dyes is crucial because several requirements must be satisfied, namely high chemical and thermal stability, possibility of chemical functionalization and high hyperpolarizability (β) parameter [17]. Generally, for a push–pull molecule, it is well known that its β value increases with increasing electron donor or acceptor strength and with increasing separation so

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long as there is strong electronic coupling through the conjugated bridge. In addition, it has been demonstrated in previously reported literature that the replacement of a benzene ring by a less aromatic heterocycle in a typical push–pull molecule, will reduce the charge transfer transitional energy and result in a significant enhancement of molecular hyperpolarizability [18].

This work concerns the synthesis of a series of azo chromophores with strong electron acceptors and benzene or thiazole groups as conjugating moieties; three types of alkoxysilane dyes were then obtained via the coupling of the resulting chromophore and 3-isocyanatopropyltriethoxysilane (ICTES). Herein, we present the synthesis, structural characterization, nonlinear optical properties, and thermal stability of the alkoxysilane precursors.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) was dried over and distilled from calcium hydride. 3-Isocyanatopropyltriethoxysilane (ICTES) and 2-amino-5-nitrothiazole were obtained from Tokyo Chemical Industry Co. and were used as received. 2,4-Dinitrobenzenamine, 2-cyano-4-nitrobenzenamine, and *N*-ethyl-*N*-hydroxyethyl-aniline were obtained from Alfa and were used without further purification. Other reagents were of commercial quality and were used as supplied.

2.2. Characterization

FTIR spectra were recorded on a Nicolet Avatar 360 in the region 4000–400 cm^{-1} using KBr pellets. ^{1}H NMR spectra were obtained with a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as internal reference. Elemental analysis was carried out using an Eager 300 microelemental analyzer while UV–vis absorption spectroscopic study was obtained using a Hitachi U4100 spectrophotometer. Differential scanning calorimetry (DSC) was performed using a TA SDT Q100 with a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed with a TA SDT Q600 thermogravimetric analyzer at 20 °C/min up to 500 °C under nitrogen atmosphere.

*2.3. Synthesis of 2-[4′-(N-ethyl-N-2-hydroxyethyl)-amino-phenylazo]-5-nitrothiazole (**1**)*

2-Amino-5-nitrothiazole (5.8 g, 40 mmol) dissolved in 70 ml of a mixture of formic acid, propionic acid, phosphoric acid and acetic acid (1:1:2:3) was cooled to 0–5 °C, to which was then added, dropwise, nitrosyl sulfuric acid solution which was prepared by slowly adding sodium nitrite (2.8 g, 40 mmol) in small portions to 20 ml concentrated (98%) sulfuric acid under stirring and cooling. After stirring for 1 h in an ice bath, *N*-ethyl-*N*-hydroxyethyl-aniline (7.3 g, 44 mmol) in 120 ml methanol/water (2/1, v/v) was added and the mixture was stirred for 1 h under cooling, followed by neutralization (pH 5–6) with sodium carbonate and was stirred for 2 h more. The precipitate was filtered, washed in plenty of water and purified by flash chromatography using cyclohexane/ethyl acetate (1/1, v/v), then pure chromophore **1** was obtained as a blue powder. Yield: 48%. Mp = 181 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 8.81 (s, Ar*H*, 1H), 7.84 (d, Ar*H*, 2H), 7.04 (d, Ar*H*, 2H), 4.96 (s, O*H*, 1H), 3.66 (t, C*H*$_2$, 6H), 1.21 (t, C*H*$_3$, 3H). Anal. Calcd for $C_{13}H_{15}N_5O_3S$ (321.4): C, 48.59; H, 4.70; N, 21.79. Found: C, 48.64; H, 4.68; N, 21.76.

*2.4. Synthesis of 2-cyano-4-nitro-4′-(N-ethyl-N-hydroxyethyl)aminoazobenzene (**2**) and 2,4-dinitro-4′-(N-ethyl-N-hydroxyethyl)aminoazobenzene (**3**)*

Chromophores **2** and **3** were synthesized in a way similar to **1** by using different intermediates.

*2.4.1. Chromophore **2***

Yield: 58%, Mp = 167 °C. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 8.81 (d, Ar*H*, 1H), 8.52 (q, Ar*H*, 1H), 7.94 (d, Ar*H*, 1H), 7.88 (d, Ar*H*, 2H), 6.97 (d, Ar*H*, 2H), 4.87 (t, O*H*, 1H), 3.64 (t, C*H*$_2$, 6H), 1.18 (t, C*H*$_3$, 3H). Anal. Calcd for $C_{17}H_{17}N_5O_3$ (339.35): C, 60.17; H, 5.05; N, 20.64. Found: C, 60.15; H, 5.05; N, 20.69.

*2.4.2. Chromophore **3***

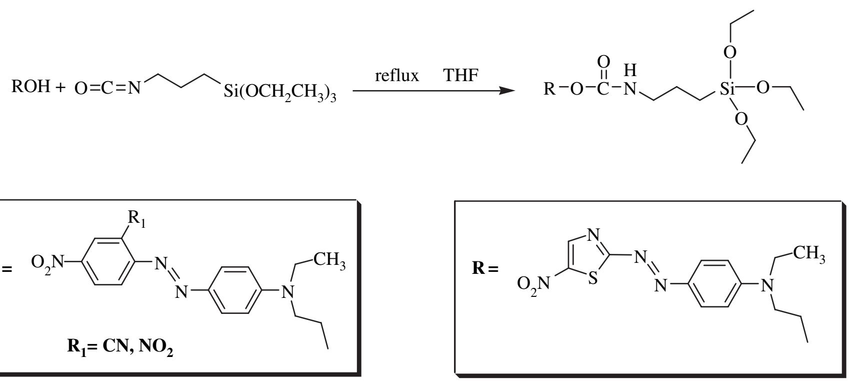
Yield: 68%. Mp = 145 °C. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 8.85 (d, Ar*H*, 1H), 8.52 (q, Ar*H*, 1H), 7.91 (d, Ar*H*, 1H), 7.76 (d, Ar*H*, 2H), 6.93 (d, Ar*H*, 2H), 4.88 (t, O*H*, 1H), 3.62 (t, C*H*$_2$, 6H), 1.17 (t, C*H*$_3$, 3H). Anal. Calcd for $C_{16}H_{17}N_5O_5$ (359.34): C, 53.48; H, 4.77; N, 19.49. Found: C, 53.41; H, 4.79; N, 19.53.

2.5. Synthesis of alkoxysilane dyes

A dry, 50 ml three-necked flask housed in an oil bath and equipped with a mechanical stirrer, nitrogen inlet and reflux condenser was charged with the chromophore (5 mmol), 3-isocyanatopropyltriethoxysilane (ICTES, 1.48 g, 6 mmol), 30 ml of THF and 5 drops of triethylamine (TEA) as catalyst. The reaction mixture was stirred and refluxed for 48 h under a nitrogen atmosphere, and the solvent was then removed under vacuum. The residue was purified by chromatography on silica gel using ethyl acetate/hexane as an eluent to afford the alkoxysilane dyes **A1**, **A2** and **A3**.

*2.5.1. Alkoxysilane dye **A1***

Yield: 59%. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 8.83 (s, Ar*H*, 1H), 7.86 (d, Ar*H*, 2H), 7.18 (s, N*H*, 1H), 7.05 (d, Ar*H*, 1H), 4.18 (s, CH_2C*H*$_2$O, 2H), 3.79 (s, C*H*$_2$$CH_2$O, 2H), 3.65 (t, C*H*$_2$$CH_3$, 2H), 3.45 (t, OC*H*$_2$$CH_3$, 6H), 2.92 (d, C*H*$_2$$CH_2CH_2$, 2H), 1.36 (s, CH_2C*H*$_2$$CH_2$, 2H), 1.20 (t, CH_2C*H*$_3$, 3H), 1.06 (m, OCH_2C*H*$_3$, 9H), 0.45 (t, CH_2CH_2C*H*$_2$, 2H). Anal. Calcd for $C_{23}H_{36}N_6O_7SSi$ (568.7): C, 48.57; H, 6.38; N, 14.78. Found: C, 48.49; H, 6.33; N, 14.81.



Scheme 1. Synthetic routes of alkoxysilane dyes.

2.5.2. Alkoxysilane dye **A2**

Yield: 62%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 8.79 (d, Ar*H*, 1H), 8.51 (q, Ar*H*, 1H), 7.93 (d, Ar*H*, 1H), 7.87 (d, Ar*H*, 2H), 7.20 (s, N*H*, 1H), 6.98 (d, Ar*H*, 2H), 4.18 (s, CH_2CH_2O, 2H), 3.74 (m, OCH_2CH_3, 6H), 3.70 (s, CH_2CH_2O, 2H), 3.59 (d, NCH_2CH_3, 2H), 2.94 (d, $CH_2CH_2CH_2$, 2H), 1.43 (s, $CH_2CH_2CH_2$, 2H), 1.19 (t, CH_2CH_3, 3H), 1.14 (m, OCH_2CH_3, 9H), 0.51 (t, $CH_2CH_2CH_2$, 2H). Anal. Calcd for

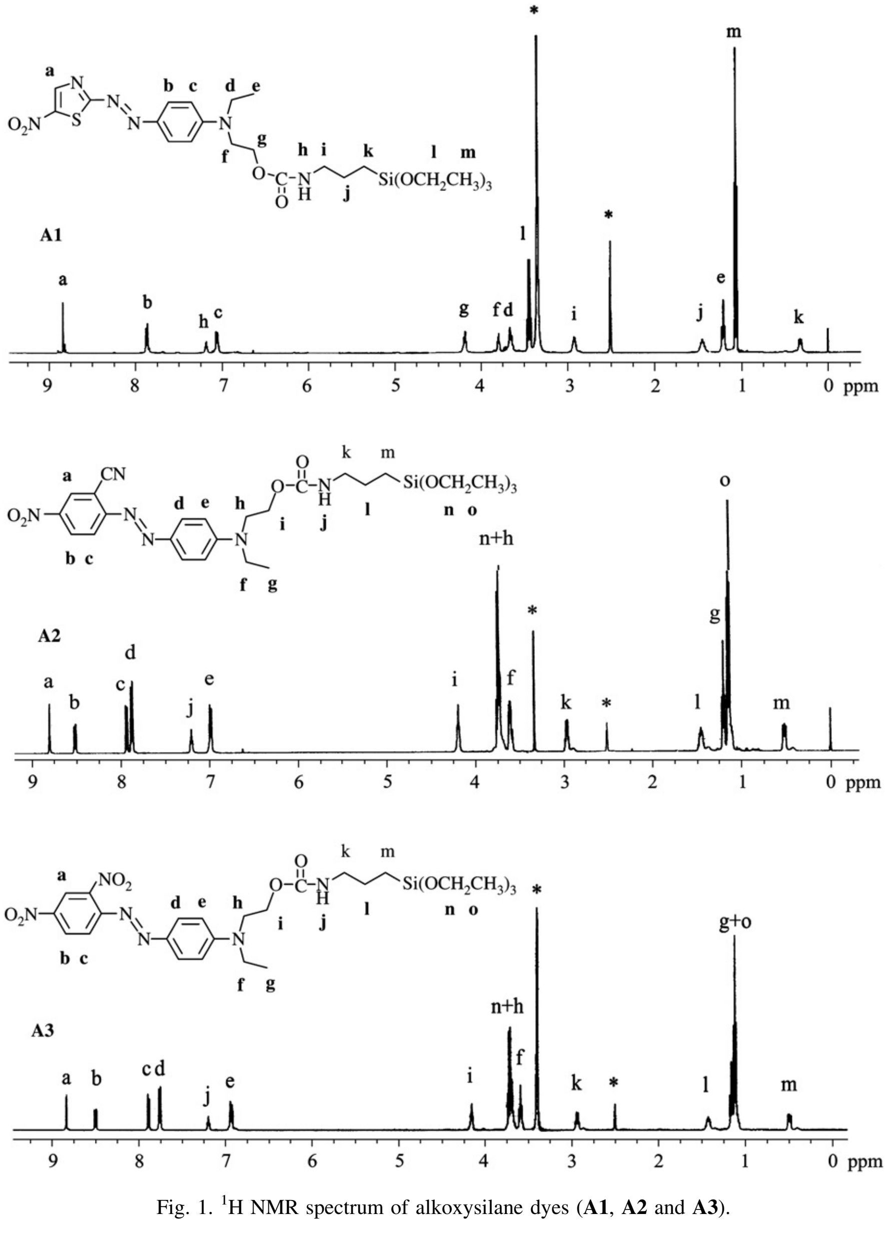


Fig. 1. ^{1}H NMR spectrum of alkoxysilane dyes (**A1**, **A2** and **A3**).

$C_{27}H_{38}N_6O_7Si$ (586.71): C, 55.27; H, 6.53; N, 14.32. Found: C, 55.28; H, 6.54; N, 14.46.

*2.5.3. Alkoxysilane dye **A3**.*

Yield: 47%. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 8.83 (d, Ar*H*, 1H), 8.49 (q, Ar*H*, 1H), 7.88 (d, Ar*H*, 1H), 7.75 (d, Ar*H*, 2H), 7.20 (s, N*H*, 1H), 6.93 (d, Ar*H*, 2H), 4.16 (s, CH_2CH_2O, 2H), 3.71 (m, $OCH_2CH_3 + CH_2CH_2O$, 8H), 3.58 (d, NCH_2CH_3, 2H), 2.93 (d, $CH_2CH_2CH_2$, 2H), 1.43 (s, $CH_2CH_2CH_2$, 2H), 1.16 (t, CH_2CH_3, 3H), 1.11 (m, OCH_2CH_3, 9H), 0.50 (t, $CH_2CH_2CH_2$, 2H). Anal. Calcd for $C_{26}H_{38}N_6O_9Si$ (606.7): C, 51.47; H, 6.31; N, 13.85. Found: C, 51.38; H, 6.34; N, 13.76.

3. Results and discussion

3.1. Synthesis and characterization

A series of chromophores were synthesized using traditional, azo coupling [19]. Due to the weak basicity of 2-amino-5-nitrothiazole and the protonation of the heterocycle N-atom in acid, the formation of stable diazonium salts is difficult. In this work, nitrosyl sulfuric acid was selected as diazotizing agent because of its high reactivity. The resulting chromophores were further reacted with 3-isocyanatopropyltriethoxysilane (ICTES) in the presence of triethylamine as catalyst to give the alkoxysilane dyes via a urethane forming reaction (Scheme 1). Flash column chromatography was used to purify the alkoxysilane dye in satisfactory yield. All compounds have good solubility in common organic solvents such as THF, DMF, DMSO, and ethanol, etc. and were insoluble in nonpolar solvents such as hexane, heptane, etc.

The elemental analysis of the compounds was generally in good agreement with the calculated values for the proposed structures. Fig. 1 shows the ^{1}H NMR spectra of the alkoxysilane dyes in DMSO; the chemical shifts of the amino proton in urethane group appear at around 7.20 ppm. All chemical shifts were assignable in the spectrum and clearly showed the formation of alkoxysilane dyes through the coupling reaction between the chromophore and ICTES.

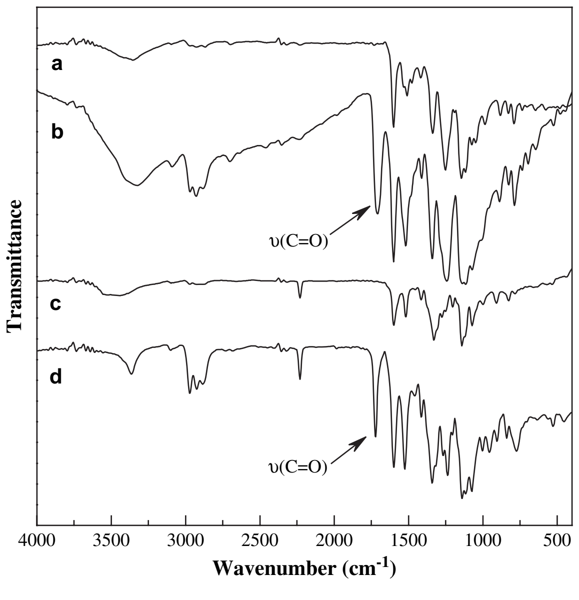


Fig. 2. FTIR spectra of chromophores **1** (a), **2** (c) and alkoxysilane dyes **A1** (b), **A2** (d).

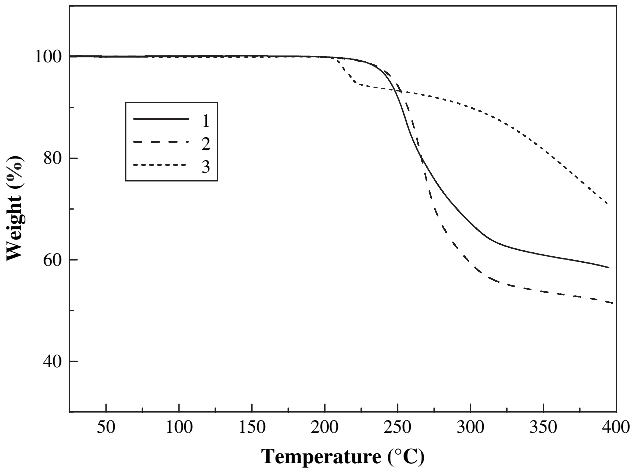


Fig. 3. TGA thermograms of the chromophores **1**, **2** and **3**.

The successful incorporation of the chromophore into the alkoxysilane dye was proven once more by FTIR (Fig. 2). Comparing the IR spectra of the alkoxysilane dyes **A1** and **A2** with that of chromophores **1** and **2**, a series of new peaks appeared which included a strong sharp peak at about 1720 cm^{-1} attributable to the stretching vibration of the carbonyl group in urethane as well as a strong band located at 1072 cm^{-1} due to $Si-O-C_2H_5$ stretching vibration. In addition, the bands of the benzene and nitro groups did not exhibit much change on going from the chromophore to the alkoxysilane dye.

Thermal stabilities of the chromophores were studied by means of TGA; initial decomposition at 230–250 °C can be attributed to the thermal cleavage of the azo group (Fig. 3). All chromophores showed residual mass of >40% at 400 °C in nitrogen atmosphere due to the presence of aromatic rings.

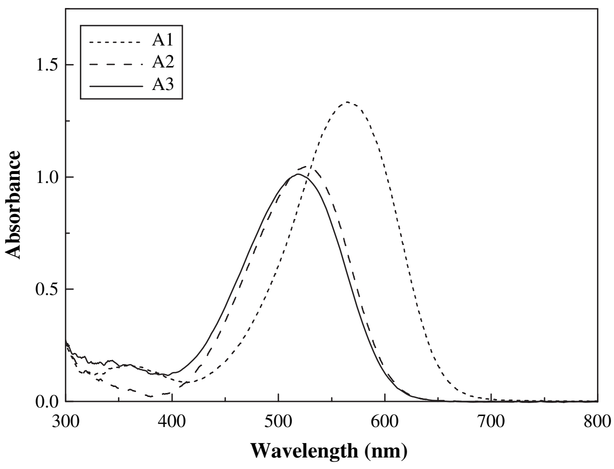


Fig. 4. UV–visible absorption spectra of alkoxysilane dyes in THF.

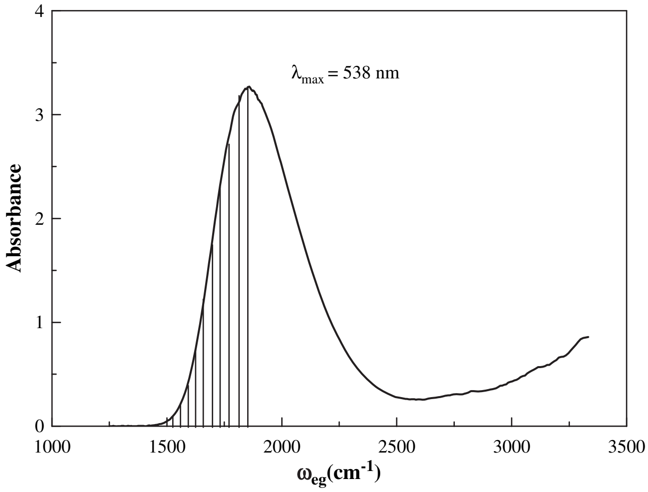


Fig. 5. UV–visible absorption spectra of chromophore **3** in DMF with concentration of 1×10^{-4} M.

3.2. Linear and nonlinear optical properties

The electronic spectra of the alkoxysilane dyes in THF are presented in Fig. 4. All exhibited strong absorption bands in the visible region and showed large bathochromic shifts relative to the analogue containing **DR1** [20]. Generally, azobenzene derivatives exhibit a low-intensity n–π* band in the visible region and a high-intensity π–π* band in the UV region. Strong electron donors and electron acceptors, such as used in the compounds investigated here, effectively reduce the charge transfer transitional energy of the π–π* transition. Consequently, the corresponding band is bathochromically shifted and overlaps the weak n–π* band; this large bathochromic shift is beneficial in terms of obtaining a large NLO response.

The first hyperpolarizability of the chromophores can be calculated by the solvatochromic method based on the two-state model [21,22]:

$$\beta_{\mathrm{CT}}\mu_{\mathrm{g}} = \frac{3}{2\hbar^2}\bullet\frac{\omega_{\mathrm{eg}}^2}{(\omega_{\mathrm{eg}}^2-\omega^2)(\omega_{\mathrm{eg}}^2-4\omega^2)}(\mu_{\mathrm{e}}-\mu_{\mathrm{g}})\mu_{\mathrm{g}}\mu_{\mathrm{eg}}^2 \tag{1}$$

where ω_{eg} is the transition frequency from the ground state to the first excited state, $\mu_{\mathrm{e}}-\mu_{\mathrm{g}}$ is the difference between the excited and ground state dipole moments, μ_{eg} is the transition dipole moment between the ground and excited states, and ω is the laser frequency. The frequency of transition can be found simply from the band maximum of the UV–vis absorption spectrum of the chromophore. The μ_{eg} is related to the intensity of the transition and could be found from the area under the band through Eq. (2).

$$\mathrm{Area} = \int \xi M\,\mathrm{d}\omega = \frac{2\pi\omega_{\mathrm{eg}}Nn\mu_{\mathrm{eg}}^2M}{3\ln 10\varepsilon_0 ch} \tag{2}$$

Where M is the concentration of the chromophore, N, n and c are Avogadro's constant, solvent refractive index and speed of light in a vacuum, respectively. Fig. 5 shows the UV–vis absorption spectrum of chromophore **3** in solvent DMF. Typically the band shape is symmetrical and can be treated as a Lorentzian function. However, various interferences contributed from different conjugated absorptions make the band shape asymmetric at high frequency for long conjugated chromophores. To avoid the interference from other conjugated absorptions, the area of half the absorption band, which did not overlap with other absorptions, was calculated.

As previously described [23], the values of $\beta_{\mathrm{CT}}\mu_{\mathrm{g}}$ were estimated (Table 1) and the chromophore **DR1** was taken for comparison. All chromophores exhibited much larger $\beta\mu$ values than **DR1**. When compared with **DR1**, chromophores **2** and **3** had the same kind of conjugated bridge and electron donor but one more cyano or nitro group as acceptor. Their $\beta\mu$ values were more than twice that of **DR1**, indicating that the strong electron acceptor groups should be responsible for the high $\beta\mu$ values. From Table 1, it is seen that $\beta\mu$ value of **3** is larger than that of **2**, which means that the electron-withdrawing ability of the nitro group is larger than that of cyano group.

It has been demonstrated that the conjugating bridge also has an effect on molecular NLO properties. Theoretical calculations indicate that lower aromatic delocalized energy and electron-deficient moieties on the electron acceptor side can significantly enhance molecular hyperpolarizability [24]. As shown in Table 1, the $\beta\mu$ value of chromophore **1** was much greater than that of **2** or **3**, which have thiazole and benzene as conjugating moiety, respectively. This indicates that the conjugating moiety contributes more to the large optical nonlinearity. While the heteroaromatic ring thiazole affects electronic transmission between donor and acceptor substituents, its electron-deficient nature may also play a major role in determining the overall electron-accepting ability of the

Table 1
Solvatochromic data and hyperpolarizabilities of the chromophores

Chromophore	$\lambda_{\max}$[a] (nm)	ε (10^4 mol^{-1} L cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$\lambda_{\max}$[b] (nm)	$\Delta\nu$ (cm^{-1})	$\beta_{\mathrm{CT\ (1907\ nm)}}\mu_{\mathrm{g}}$ (10^{-30} esu D)
DR1	503	2.87	3819	480	952	814
1	605	4.02	3331	570	1014	2302
2	545	3.81	4210	532	448	1632
3	538	3.23	4279	521	607	1739

[a] Measured in DMF.

[b] Measured in $CHCl_3$.

substituents. Indeed, nitrogen in the thiazole moiety behaves like an electron-withdrawing group on a thiophene ring, which acts as an auxiliary acceptor, with the result that the lower aromatic delocalization energy and stronger electron-withdrawing properties on the acceptor side produce the large $\beta\mu$ value of **1**.

4. Conclusions

A series of azo chromophore, functionalized alkoxysilanes were synthesized through a urethane reaction between the chromophore and 3-isocyanatopropyltriethoxysilane (ICTES). Their structures were confirmed by elemental analysis, ^{1}H NMR, FTIR and UV−visible spectra. The nonlinear optical (NLO) activities of the chromophores were evaluated by a solvatochromic method. All chromophores exhibited much larger $\beta\mu$ values than **DR1** and the $\beta\mu$ value of chromophore **1** was three times larger than that of **DR1**, which qualifies the alkoxysilane dyes for further application in NLO sol−gel materials.

Acknowledgements

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