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Study on novel second-order NLO azo-based chromophores containing strong electron-withdrawing groups and different conjugated bridges

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Novel NLO azo-based chromophores containing strong electron-withdrawing groups and benzene or thiazole moiety as conjugated bridges were synthesized and characterized. β values were measured by HRS method, they are in the range of 238–1459 × 10^{-30} esu at the fundamental wavelength of 800 nm. For chromopheres 3 and 4, β values at the fundamental wavelength of 1064 nm were also measured, they are 1575 × 10^{-30} esu and 935 × 10^{-30} esu, respectively. Thermal stabilities for these chromophores are reported. We also discuss the effects of different acceptors and conjugating moieties on β.

1. Introduction

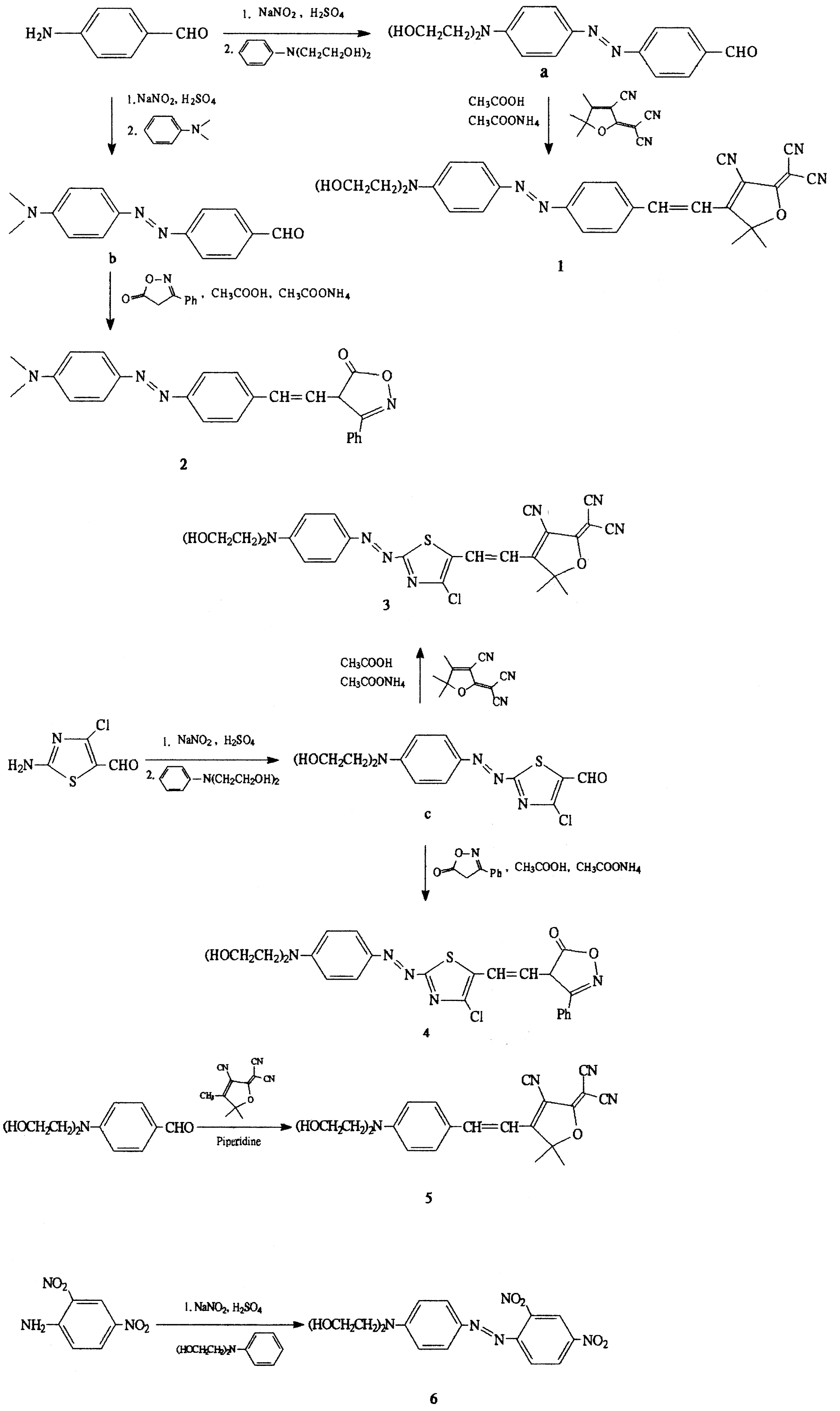
Second-order nonlinear optical (NLO) materials have been investigated extensively because of their potential application in electro-optic (EO) devices [1, 2]. Chromophores containing the donor-π-acceptor (π represent electron conjugated bridge) charge transfer structure usually exhibit large molecular first hyperpolarizability (β). Electron conjugated bridge, donor and acceptor play important role in this kind of system. Azo (N=N) bridge is an efficient π-electron segment. Numerous NLO materials derived from azo compound have been reported, such as the well-known DR-1 [3, 4], in which amino group acts as electron donor group and nitro as acceptor. Strong electron-withdrawing group on the acceptor side can enhance β value. Dalton *et al*. reported some thiophene and polyene based NLO chromophores such as FTC and APTEI, which possess very large β and electro-optic coefficients (γ_{33}) [5, 6]. We noted that the strong electron-withdrawing groups should be responsible for the high $\mu\beta$ values. Although these strong electron-withdrawing groups have attracted much attention recently, and several synthetic methods of preparing their analogues have been developed [5–8], most of the reported chromophores are based on —C=C— conjugating system. Azo chromophores containing these strong electron-withdrawing groups received little attention.

In this work, we synthesized a series of NLO azo chromophores containing these strong electron-withdrawing groups, and benzene or thiazole were chosen to act as conjugating moieties. A non-azo compound with the strong electron-withdrawing group and a two-nitro-azo compound were also synthesized in order to compare electron-withdrawing abilities between acceptors. β values for these chromophores were measured and the influence of acceptors and conjugating moieties on β value are discussed. We will also discuss the thermal stabilities for these chromophores.

2. Results and discussion

2.1. Synthesis

Scheme 1 shows the synthetic routes and structures for the chromophores. *p*-Aminobenzaldehyde was diazotized and then coupled with N,N-dimethylaniline or N,N-dihydroxyethylaniline to give azo compounds **a** or **b**, which contains formyl group. **a** or **b** was reacted with 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran or 3-phenyl-2-isoxazolin-5-one by condensation reaction to afford the chromophore **1** or **2**. **c** was prepared by diazotizing of 2-amino-4-chloro-5-formylthiazole in nitrosylsulphuric acid and then coupling of the diazonium compound with N,N-dihydroxyethylaniline. **c** was condensed with 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran or 3-phenyl-2-isoxazolin-5-one in the presence of catalyst to give **3** or **4**, **5** was prepared by the condensation reaction of



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Scheme 1 The synthetic routes of the chromophores.

N,N-di-hydroxyethyl-4-benzaldehyde and 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran with piperidine as catalyst. The above condensation reactions are sensitive to catalyst. **a**, **b** and **c** can be easily condensed with 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran or 3-phenyl-2-isoxazolin-5-one in the presence of acetic acid and ammonium acetate, but when acetic acid and ammonium acetate were replaced by piperidine, chromophore **2**, **3** and **4** cannot be obtained in the above conditions. chromophore **1** can also be obtained with piperidine/acetic acid(1:3 by volume) as catalyst. The condensation of N,N-di-hydroxyethyl-4-benzaldehyde and 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran in the presence of piperidine occurs very rapidly. 6 was synthesized according to a similar procedure described in our previous work [9]. The chromophores were characterized by means of HMR, IR and MS spectroscopies.

2.2. Linear and nonlinear optical properties

The absorption maxima (λ_{max}) for the chromophores in chloroform and DMSO are given in Table I. All of them show large bathochromic shift relative to DR-1. The two-nitro-compound 6 has a red shift of 30 nm, and the others are more bathochromic than 6. Chromophore 3, which has thiazole and three cyano group, causes largest red shift (in chloroform) of 179 nm relative to DR-1. Generally, for the donor-π-acceptor system, strong electron-withdrawing ability and more effective conjugating moiety can cause large bathochromic shift and this large bathochromic shift is beneficial to give large NLO response.

The molecular first hyperpolarizabilities (β) were measured by Hyper-Rayleigh Light scattering (HRS) method. At 800 nm measurement, all chromophores only have very small absorption at both fundamental and second harmonic wavelength. There is no fluorescence contribution for them and two—photon fluorescence is excluded. β values for these chromophores at the fundamental wavelength of 800 nm are list in Table I. $\beta(0)$ values are also listed, which are estimated by the two level model [11].

The chromophores exhibit much larger β than DR-1. Compared with DR-1, 6 has the same kind of conjugated bridge and electron-withdrawing group but one more nitro. The $\beta(0)$ value of 6 is about twice that of DR-1. For chromophore 5, which has a three-cyano acceptor, the $\beta(0)$ value is more than twice that of 6, although the conjugated bridge of 5 is very short. That means the electron-withdrawing ability of the three-cyano acceptor is very strong. 3-Phenyl-2-isoxazolin-5-one is a weaker electron-withdrawing group to the three-cyano one, which can be seen by comparing the $\beta(0)$ value of 2 with 1, 4 with 3. But its electron-withdrawing ability is much stronger than that of nitro group, because $\beta(0)$ value of 2 is near to 6, which has two nitro groups.

Conjugating moieties also have effect on NLO properties. Theoretical calculations indicate that lower aromatic delocalization energy and electron-difient moieties on the acceptor side can enhance NLO response, and the latter plays more important role in this enhancement [12]. Thiazole has a lower aromatic delocalization energy (25 kcal/mol [13]) than benzene (36 kcal/mol [14]), but the difference is not very large. From Table I, $\beta(0)$ value of 3 or 4 is much larger than that of 1 or 2, which has thiazole and benzene as conjugating moiety, respectively. That means the conjugating moieties contribute more to the larger β. This meet the theoretical prediction made by Albert [12]. Actually, nitrogen in thiazole is like an electron-withdrawing group on thiophene ring, and Cl substituent on the thiazole ring "pull" electron slightly, so lower aromatic delocalization energy and stronger electron-withdrawing properties on the acceptor side result in the larger β of 3 (compared with 1) and 4 (compared with 2). We can predict that β value will be lower if thiazole moiety is replaced by thiophene in 3 and 4.

From Table I, we noted that the cut-off wavelengths for 3 and 4 are 875 and 805 nm, respectively. It means that resonant enhancement effect exists in 3 and 4 at 800 nm measurement. In order to avoid this effect, measurements at 1064 nm were carried out using nanosecond laser to determine β values for 3 and 4. The results are shown in Table II. It is reasonable that $\beta(0)$ for 3 decreases at 1064 nm comparing the result of 800 nm because the resonant effect is excluded. But for 4, $\beta(0)$ value at 1064 nm is larger than that at 800 nm. This is because the resonant enhancement of 4 at 800 nm measurement is very small, but the absorption (see Fig. 1 and ε in Table II) at its second harmonic wavelength (400 nm) is much larger than that at 1064 nm. The combined factors lead to an increase in $\beta(0)$ values at 1064 nm. In spite of this, the conclusions made by comparing $\beta(0)$ values of the chromophores at 800 nm will not change.

TABLE I Linear and nonlinear optical properties of the chromophores at 800 nm measurement and their thermal stabilities

Compound	$\lambda_{max}/\lambda_{cut\text{-}off}$ (nm) in CHCl$_3$	in DMSO	$\beta \times 10^{30}$ esu	$\beta(0) \times 10^{30}$ esu	T_d (°C)
1	553	567/693	682	343	242
2	529	540/660	252	113	188
3	658	691/875	1549	735	252
4	628	695/805	573	284	221
5	563	602/665	439	241	230
6	509	551/649	238	112	–
DR-1	479	–	–	54	250[a]

[a] Literature 4.

TABLE II Linear and nonlinear optical properties of 3 and 4 at 1064 nm measurement

Compound	$\beta \times 10^{30}$ esu	$\beta(0) \times 10^{30}$ esu	$\varepsilon_{400\ nm} \times 10^3$ ($l \cdot mol^{-1}\ cm^{-1}$)	$\varepsilon_{532\ nm} \times 10^3$ ($l \cdot mol^{-1}\ cm^{-1}$)
3	1575	626	8.5	7
4	935	379	14	6

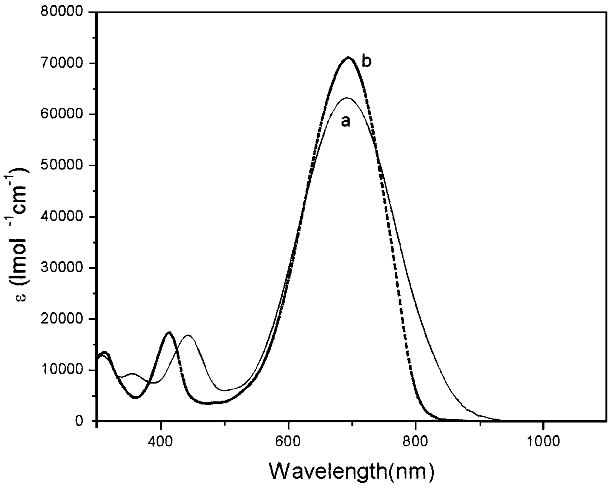

Figure 1 Absorption spectra of 3 (a) and 4 (b) in DMSO.

2.3. Thermal stabilities

Thermal stabilities of the chromophores were studied by means of TGA. The decomposition temperatures (T_d) for the molecules are shown in Table I. Chromophores with the three-cyano group (1, 3) show higher thermal stabilities than the isoxazolinone-containing chromophores (2, 4). We noted that the thermal stabilities of the molecules increase when replacing benzene with thiazole on the acceptor side. For example, T_d for 4 increases by 33°C compared with 2. This result is different from the commonly recognized conclusion, which supports the view of chromophores with lower charge-transfer transitional energies tending to posses lower thermal stabilities [15]. In summary, chromophores 3 has a similar T_d to DR-1, and T_d of 5 and 6 are excess to 220°C, indicating that these chromophores have enough thermal stabilities. Thermal stability of chromophore 2 is slightly lower (T_d is 188°C).

3. Conclusion

NLO azo chromophores based on strong electron-withdrawing groups and benzene and thiazole moieties were synthesized and characterized. β values of them were measured by HRS method. Thiazole moiety on the acceptor side can largely enhance β. Because of the lower aromatic delocalization energy and stronger electron-withdrawing group on the acceptor side, 3 exhibit very large β. TGA data show that most of the chromophores possess enough high thermal stabilities. With both large NLO response and good thermal stability, 3 is a promising NLO molecule. Synthetic design to attach this chromophore and its analogues to polymers is in progress.

4. Experimental

P-aminobenzaldehyde(from Fluka), N,N-dihydroxyethylaniline (from Aldrich), 3-phenyl-2-isoxazolin-5-one and N,N-dimethylaniline (from Aldrich) were purchased and used without further purification. 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, 2-amino-4-chloro-5-formylthiazole and 1-(N,N-dihydroxyethyl)-4-formylaniline were prepared according to the methods described in literatures [16–18]. 6 was synthesized according to a similar procedure described in our previous work [9]. FTIR spectra were taken with a Bio-Rad FTS165 spectrometer. UV-vis spectra were determined on a UV-2001 spectrometer. Mass spectra were recorded with a Trio-2000 spectrometer. ^{1}H-NMR spectra were obtained with a Varian Gemini-300 spectrometer. TGA data were obtained using Unibersal V2.5H TA Instruments at a heating rate of 10°C/min under N^2.

4-N,N-dihydroxyethyl-4′-formylazobenzene(a): 1.00 g (14.5 mmol) of sodium nitrite was added in portions to 35 ml of cold sulfuric acid and the mixture was warmed gradually to 70°C. After all sodium nitrite was dissolved, the mixture was cooled to 5°C. 1.75 g (14.5 mmol) of 4-aminobenzaldehyde was added to the solution. The mixture was stirred for 2 h at 5–10°C, then poured into 150 g of ice-water. After filtered, the diazonium solution was added dropwise to a solution of N,N-dihydroxyethylaniline in 30 ml of 0.1 N hydrochloric acid with the temperature maintaining at 10–15°C. 2 g of sodium acetate was added. After addition, the mixture was stirred at 10–15°C for 2 h. The precipitate was collected, washed with water and dried. 2.3 g of orange product was obtained. It was used without further purification. Very pure product can be obtained by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as the eluent. IR: (KBr, cm^{-1}) 3240 (—OH), 1690 (C=O), 1598 (N=N); λ_{max} (acetone): 450 nm.

Chromophore 1: The mixture of 0.92 g (2.9 mmol) of **a**, 0.60 g (3.0 mmol) of 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran and 0.4 ml of piperidine/acetic acid (1:3 by volume) in 20 ml of ethanol was refluxed for 4 h. The precipitate obtained was collected and washed with hot ethanol. 0.8 g of product was obtained. The product was further purified by chromatography on silica gel with chloroform/ethanol (5:1) as the eluent. IR (KBr, cm^{-1}) 3423, 2229, 1600, 1132; ^{1}H NMR (CD_3COCD_3) δ 8.08 (d, 1H), 8.03 (d, 2H), 7.89 (d, 2H), 7.83 (d, 2H), 7.36 (d, 1H), 6.92 (d, 2H), 3.79 (t, 4H), 3.70 (t, 4H), 3.35 (s, 2H), 1.91 (s, 6H); MS: 494 (M^+), 302 ($M^+ - (HOCH_2CH_2)_2\ NC_6H_5N + 2H$).

4-N,N-dimethyl-4′-formylazobenzene(b): This compound was synthesized by a procedure similar to that for **a**, yield: 68%. IR (KBr, cm^{-1}): 1659 (C=O), 1595 (N=N); λ_{max} (acetone): 447 nm.

Chromophore 2: The mixture of **b** (0.60 g, 2.37 mmol), 3-phenyl-2-isoxazolin-5-one (0.39 g, 2.42 mmol), ammonium acetate (20 mg, 0.26 mmol) and acetic acid (30 mg, 0.5 mmol) in 25 ml of toluene was stirred for 4 h at 90°C. After cooled to room temperature, the precipitate was collected, washed with ethanol and then crystallized twice from ethanol to afford 0.61 g (64%) pure product. IR (KBr, cm^{-1}) 3433, 1746, 1604, 1133; ^{1}H NMR (CD_3COCD_3) δ8.58 (d, 2H), 7.92 (s, 1H), 7.88 (d, 4H), 7.72 (d, 2H), 7.64 (d, 2H), 7.33 (m, 1H), 6.86 (d, 2H), 3.13 (s, 6H); MS: 396 (M^+), 264 ($M^+ - (CH_3)_2NC_6H_5N + 2H$).

Compound c: 1.5 g (0.022 mol) of sodium nitrite was added in portions to 15 ml of cold sulfuric acid and the mixture was warmed gradually to 70°C. After all sodium nitrite was dissolved, the mixture was cooled to 5°C and diluted with a mixture of 10 ml of propionic and acetic acid (1:4 by volume). 3.5 g (0.022 mol) of 2-amino-4-chloro-5-formyl thiazole was added in portions to the solution at 5°C. The mixture was stirred at 5°C for 30 min. The diazonium solution was added dropwise to 4.1 g (0.023 mol) of N,N-dihydroxyethylaniline in 4.5 ml sulfuric acid and 200 ml water at 0–5°C. 2 g of sodium acetate was added. After addition, the mixture was stirred at 0–5°C for 1 h. The precipitate was collected, washed with water and dried. 1.5 g of product was obtained and it was used directly in the following steps. It can be further purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as eluent. IR: (KBr, cm^{-1}) 3237 (—OH), 1667 (C=O), 1599 (N=N); $\lambda_{\max}$ (acetone): 568 nm.

Chromophore 3: The mixture of 1.3 g (3.7 mmol) of **c**, 1.0 g (5.0 mmol) of 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, 33 mg of ammonium acetate and 50 mg of acetic acid in 40 ml of ethanol was refluxed for 2 h. The precipitate was collected and washed thoroughly with hot ethanol until the color of the filtrate was turned from violet to blue. After dried, pure product was obtained in 90% yield. The product can be further purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:4) as eluent. IR (KBr, cm^{-1}) 3433, 2228, 1603, 1133; ^{1}H NMR (CD_3SOCD_3) δ 8.05 (m, 1H), 7.77 (d, 2H), 7.07 (d, 2H), 6.88 (m, 1H), 3.70 (t, 4H), 3.67 (t, 4H), 3.36 (s, 2H), 1.17 (s, 6H), MS: 535 (M^+), 343 ($M^+ - (HOCH_2CH_2)_2NC_6H_5N + 2H$).

Chromophore 4: The mixture of 1.0 g (2.8 mmol) of **c**, 0.5 g (3.1 mmol) of 3-phenyl-2-isoxazolin-5-one, 25 mg of ammonium acetate and 50 mg of acetic acid in 50 ml of ethanol was refluxed for 2 h. The precipitate was collected, washed with ethanol and dried. 1.0 g (71%) of pure product was obtained. The product can be further purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:4) as the eluent. IR (KBr, cm^{-1}) 3437, 1738, 1596, 1128; ^{1}H NMR (CD_3COCD_3) δ 7.96 (s, 1H), 7.91 (d, 2H), 7.75 (d, 2H), 7.66 (m, 2H), 7.33 (m, 1H), 7.15 (d, 2H), 3.87 (m, 8H), 2.55 (s, 2H); MS: 497 (M^+), 305 ($M^+ - (HOCH_2CH_2)_2\text{-}NC_6H_5N + 2H$).

Chromophore 5: Piperidine (3 drops) was added to a mixture of 0.21 g (1.0 mmol) of 1-(N,N-dihydroxyethyl)-4-formylaniline and 0.230 (1.1 mmol) g of 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran in 6 ml of ethanol. The mixture was refluxed for 3 h, then cooled to room temperature. The solid was collected, washed with cool ethanol. and recrystallized from ethanol twice to afford shining blue-black crystal 0.25 g(65%). The product was further purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:3) as the eluent. IR (KBr, cm^{-1}): 3425, 2975, 2978, 2848, 2228 (—CN); ^{1}H NMR (DMF-d_7): 5.02 (t, 2H), 3.75 (s, 8H), 6.9–7.9 (m, 4H), 7.5 (d, 2H), 1.85 (s, 6H); MS: 390 (M^+), 372 ($M^+ - 18$).

Measurement: The molecular first hyperpolarizabilities were measured by Hyper-Rayleigh Light scattering (HRS) method at the wavelength of 800 nm using a titanium-sapphire laser (Spectra Physics, Model Tsunami®, 100 fs, 80 MHz) [10]. Crystalviolet chloride (CV) was chosen as external reference (β is 338×10^{-30} esu in CH_3OH). A fundamental wavelength of 1064 nm from an injection seeded, Q-switched Nd:YAG laser (Quanta-Ray DCR3, 10 ns, 220 mJ, 10 Hz) was used for the nanosecond Hyper-Rayleigh scattering experiments [19]. The well-studied NLO chromophores p-nitroaniline (PNA) was used as an external reference ($\beta = 32.2 \times 10^{-30}$ esu in DMSO, it is obtained through measuring PNA in DMSO and using $\beta\,(\text{PNA}) = 21.6 \times 10^{-30}$ esu at 1064 nm in CH_2Cl_2 as external reference). Samples were dissolved in DMSO and filtered through a 0.2 μm filters before measuring. A series of different concentrations' solutions of each compound were obtained by serial dilution of a concentrated standard. The concentration of the solution was controlled lower than its absorption at both the fundamental wavelength and second harmonic wavelength which are less than 0.1 during measurements. For these references in different solvents, standard local field correction factors of different solvents were applied $[((n_D^2 + 2)/3)^3$, where n is the refractive index of the solvent at the sodium D line].

Acknowledgments

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