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New nonlinear optical chromophores exhibiting good transparency and large nonlinearity: synthesis and characterization of chromophores with stilbene and ring-locked triene as a combined conjugation bridge

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Two new chromophores employing the combination of stilbene and ring-locked triene as their conjugation bridge were synthesized and found to display blue-shifted absorption and large optical nonlinearity compared with their stilbene-only, triene-only and azobenzene analogues. The two new chromophores with the combined conjugation bridge provide better optimization of the nonlinearity–transparency trade-off.

Introduction

Organic second-order nonlinear optical (NLO) materials have attracted much attention in the past two decades due to their potential applications in telecommunications, optical data storage and optical information processing.[1] The design of NLO chromophores exhibiting large first molecular hyperpolarizability (β) is a requisite for the design of efficient second-order materials.[2–4] In particular, much effort has been concentrated on the optimization of the typical "push–pull" structure, *i.e.*, of molecules that bear an electron-donating group and electron-withdrawing group interacting *via* a π-conjugated system.[5] While from the two-level model,[6] most of this type of chromophore, such as chromophores with conjugated polyene and/or thiophene bridges, possess long wavelength absorption with the λ_{max} up to 600$\sim$900 nm,[7] it can result in unacceptable large optical losses in the wavelength range from 630 to 980 nm for diode-wavelength modulator applications.[8] On the other hand, it should be noted that transparency at both telecommunication wavelength (1300 and 1550 nm) and at their second harmonic (*i.e.* 650 and 775 nm) is an important requirement for applications based on cascading processes.[9] Therefore, the search for blue-shifted chromophores without significant compromising of nonlinearities is one of the major challenges in this area.

One of the crucial factors in tuning the nonlinearity–transparency trade-off has proved to be the nature of the π-conjugated bridge of chromophores.[10,11] In our previous study,[12] it was discovered that two chromophores employing the combination of a 4-aminoazobenzene moiety and a ring-locked triene electron withdrawing group showed large optical nonlinearities and blue-shifted absorption compared with shorter chain analogues. For instance, the chromophore **2b** displays a λ_{max} (Table 1) which is 18 nm and 29 nm blue-shifted and large optical nonlinearity compared with chromophore **2a** (Table 1) and chromophore **5** (Table 1) in chloroform solvent, respectively, though the conjugation bridge of chromophore **2b** is much longer. The experimental results indicate that the combination of different types of conjugation bridge provides a new opportunity for defeating the "nonlinearity–transparency" trade-off.

In light of this, we have designed two new chromophores (**1b** and **1d** in Table 1), in which the conjugation bridge of the isophorone-protected† triene with the terminal acceptors is linked to a alkylamino-substituted stilbene bridge. The stilbene system is used because it has a large similar β value but better transparency in comparison with azobenzene analogues.[13] We hope that two new chromophores with the combined conjugation bridge will exhibit good transparency and large molecular nonlinearities.

Experimental

Materials

4-(*N*-Ethyl-*N*-hydroxyethylamino)benzyltriphenylphosphonium iodide was provided by S. R. Marder. 3-Dicyanomethylene-1,5,5-trimethylcyclohexene (**4a**) and 3-phenyl-4-(3,5,5-trimethylhex-2-en-1-ylidene)-1,2-isoxazol-5-one (**4b**) were prepared following a procedure described in the literature.[14,15] Dichloromethane was dried over anhydrous calcium chloride and distilled before use. All other reagents and solvents were used as received without further purification.

Characterization

^{1}H NMR spectra were obtained with a Varian Mercury 300 spectrometer. FT-IR spectra were recorded on a Shimadzu FT-IR 8000 series in the region of 4000–400 cm^{-1} using KBr pellets. UV–Visible spectra were determined with a Shimadzu 160A spectrometer in chloroform solution. FAB-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. The second-order nonlinear hyperpolarizability of these compounds was determined by Hyper–Rayleigh Scattering in methanol (CH$_3$OH) using the fundamental excitation wavelength of 1064 nm, and in the same solvent, the known hyperpolarizability of *p*-nitroaniline (*p*-NA) was used as an external reference.[16] The thermometer for measurement of the melting point was uncorrected.

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†The IUPAC name for isophorone is 3,5,5-trimethylcyclohex-2-en-1-one.

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Table 1 The linear and nonlinear properties of chromophores **1a–d**, **2a–d**, **5** and **6**

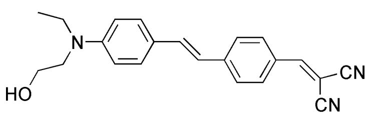
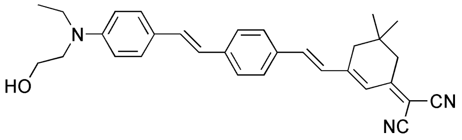
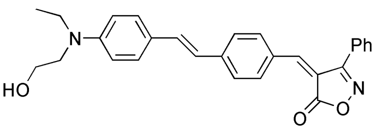
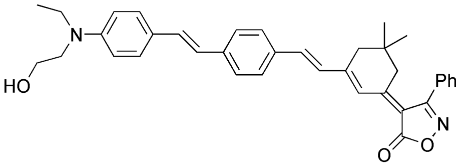
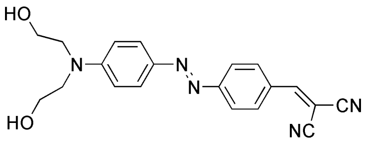
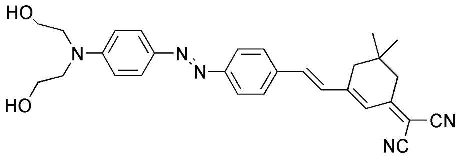
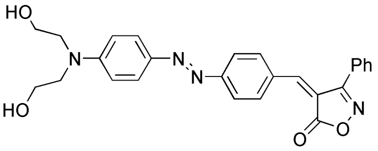
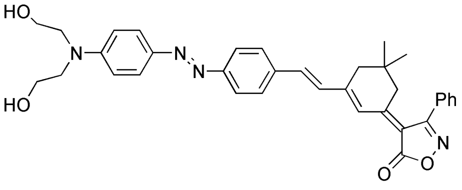
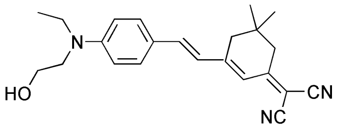
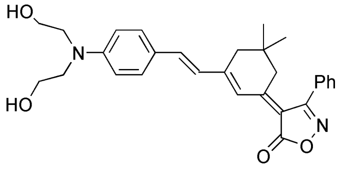
Chromophores	λ_{max} (ε_{max}) (in CHCl$_3$)	β_{HRS}[a]	β_0[b]	β_0[c]	f[17]
 **1a**	493 (48100)	1393	204	43	0.98
 **1b**	474 (69700)	1564	262	52	1.21
 **1c**	519 (16100)	704	27	47	0.4
 **1d**	504 (43700)	3639	224	55	0.87
 **2a**	508	1086	83	43	0.86
 **2b**	490	2890	337	55	1.0
 **2c**	516	1519	47	53	0.82

Table 1 The linear and nonlinear properties of chromophores **1a–d**, **2a–d**, **5 and 6** (*Continued*)

Chromophores	$\lambda_{\max}$ ($\varepsilon_{\max}$) (in CHCl$_3$)	β_{HRS}[a]	β_0[b]	β_0[c]	f[17]
 **2d**	510	3490	198	56	1.1
 **5**	519[d]		60[d]	51	
 **6**	568[d]		27[d]	54	

[a] β values (in unit of 10^{-30} esu) measured by Hyper–Rayleigh Scattering (HRS) technique in methanol using the fundamental excitation wavelength of 1064 nm. [b] Dispersion-corrected β values calculated by using an approximate two-level model. [c] β_0 values calculated by MOPAC in chem3D Pro. [d] Cited from reference 12. $\varepsilon_{\max}$ means molar absorption coefficients at the $\lambda_{\max}$ values.

Synthesis of 4-[4-(*N*-ethyl-*N*-hydroxyethylamino)styryl]benzaldehyde (3)

Benzene-1,4-dicarbaldehyde (0.27 g, 2 mmol) and 4-(*N*-ethyl-*N*-hydroxyethylamino)benzyltriphenylphosphonium iodide (1.14 g, 2 mmol) were dissolved in anhydrous dichloromethane (50 ml), potassium *tert*-butoxide (0.34 g, 3 mmol) and a catalytic amount of 18-crown-6 ether were added, and the mixture was then allowed to stir for 2 h at room temperature under nitrogen. After filtration, the filtrate was evaporated then purified by column chromatography on silica gel (100–200 m) eluting with petroleum (bp 60–90 °C)–ethyl acetate (9 : 10). An orange crystalline compound was then obtained by recrystallization in aqueous ethanol then dried under vacuum. Yield 64%; mp 173–174 °C; IR 1668 (-C=O); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 1.20 (t, J = 7.2 Hz, 3 H), 3.50 (m, 4 H), 3.81 (t, J = 7.2 Hz, 2 H), 6.84 (d, J = 9.0 Hz, 2 H), 6.96 (d, J = 15 Hz, 1 H), 7.16 (d, J = 15 Hz, 1 H), 7.34 (d, J = 9.0 Hz, 2 H), 7.56 (d, J = 9.5 Hz, 2 H), 7.96 (d, J = 9.5 Hz, 2 H), 9.88 (s, 1 H); MS (FAB), *m*/*z*: 295, 100%. Anal. Calcd. For $C_{19}H_{21}NO_2$: C, 77.29; H, 7.12; N, 4.74. Found: C, 77.45; H, 7.32; N, 4.35%.

Synthesis of chromophore 1a

4-[4-(*N*-Ethyl-*N*-hydroxyethylamino)styryl]benzaldehyde (0.29 g, 1 mmol) and malononitrile (0.07 g, 1.1 mmol) were dissolved in pyridine (3 ml), and the mixture stirred for 2 h at room temperature. It was then poured into anhydrous diethyl ether. A dark precipitate was obtained. The crude condensation products were collected by filtration, followed by rinsing with ethanol, diethyl ether and hexane. The pure product was crystallized by ethanol. Yield 82%; mp 144–145 °C; IR 2224 (-C≡N); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 1.12 (t, J = 6.9 Hz, 3 H), 3.42 (m, 4 H), 3.78 (t, J = 5.4 Hz, 2 H), 6.74 (d, J = 8.7 Hz, 2 H), 6.92 (d, J = 15 Hz, 1 H), 7.08 (d, J = 15 Hz, 1 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.56 (d, J = 9.0 Hz, 2 H), 7.81 (s, 1 H), 7.85 (d, J = 9.0 Hz, 2 H); MS (FAB), *m*/*z*: 343,100%. Anal. Calcd. For $C_{22}H_{21}N_3O$: C, 76.96; H, 6.12; N, 12.24. Found: C, 76.56; H, 5.79; N, 12.46%.

Synthesis of chromophore 1b

4-[4-(*N*-Ethyl-*N*-hydroxyethylamino)styryl]benzaldehyde (0.29 g, 1 mmol) was dissolved in freshly distilled dimethylformamide (3 ml), 3-dicyanomethylene-1,5,5-trimethylcyclohexene (0.2 g, 1.1 mmol) and piperidine (0.03 ml) were added, and the solution was stirred for 1 h at room temperature. The stirred mixture was then heated to 90 °C for 2 h. A purple solution was obtained. It was then poured into water. The crude dark precipitate was collected by filtration, followed by rinsing with ethanol, diethyl ether and hexane. The product was purified by column chromatography on silica gel (100–200 m) eluting with petroleum–ethyl acetate (1 : 1). Yield 53%; mp 156–157 °C; IR 2219 (-C≡N); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 1.09 (s, 6 H), 1.22 (t, J = 6.9 Hz, 3 H), 2.48 (s, 2 H), 2.60 (s, 2 H), 3.50 (m, 4 H), 3.82 (t, J = 5.4 Hz, 2 H), 6.76 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 16.5 Hz, 1 H), 6.98 (d, J = 15 Hz, 1 H), 7.01 (d, J = 16.5 Hz, 1 H), 7.06 (d, J = 15 Hz, 1 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.45 (m, 4 H), 7.48 (s, 1 H); ^{13}C (CDCl$_3$, 75 MHz) δ = 162.06, 154.39, 148.63, 140.33, 137.22, 134.26, 130.49, 128.56, 128.39, 128.32, 126.82, 125.74, 123.69, 123.53, 113.87, 113.11, 112.85, 60.40, 52.56, 45.71, 43.06, 39.33, 31.99, 28.02, 12.01; MS (FAB), *m*/*z*: 463, 100%. Anal. Calcd. For $C_{31}H_{33}N_3O$: C, 80.34; H, 7.12; N, 9.07. Found: C, 79.86; H, 7.61; N, 9.42%.

Synthesis of chromophore 1c

4-[4-(*N*-Ethyl-*N*-hydroxyethylamino)styryl]benzaldehyde (0.29 g, 1 mmol) was dissolved in hot anhydrous ethanol (10 ml), 3-phenylisoxazol-5-one (0.17 g, 1.1 mmol) was added. The reaction mixture was heated to 70 °C and stirred at this temperature for 2 h. A dark suspension was obtained. The crude condensation products were collected by filtration, followed by rinsing with ethanol, diethyl ether and hexane. The pure product was crystallized by ethanol. Yield 61%; mp 115–116 °C; IR 1745 (-C=O); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 1.03 (t, J = 6.9 Hz, 3 H), 3.43 (m, 4 H), 3.82 (t, J = 5.4 Hz, 2 H), 6.73 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 15 Hz, 1 H), 7.23 (d, J = 15 Hz, 1 H), 7.34–7.60 (m, 11 H), 8.29 (s, 1 H); MS (FAB), *m/z*: 438, 100%. Anal. Calcd. For $C_{28}H_{26}N_2O_3$: C, 76.71; H, 5.93; N, 6.39. Found: C, 76.45; H, 6.25; N, 5.95%.

Synthesis of chromophore 1d

4-[4-(*N*-Ethyl-*N*-hydroxyethylamino)styryl]benzaldehyde (0.29 g, 1 mmol) was dissolved in hot anhydrous ethanol (4 ml), 3-phenyl-4-(3,5,5-trimethylhex-2-en-1-ylidene)-1,2-isoxazol-5-one (0.3 g, 1.1 mmol) and piperidine (0.2 ml) were added, and the mixture was refluxed for 15 min. When the solution cooled to room temperature, 0.4 ml acetic acid was added. The reaction mixture was then stirred for 1 h at room temperature again. The crude dark precipitate was collected by filtration. The product was purified by column chromatography on silica gel (100–200 m) eluting with ethyl acetate. Yield 42%; mp 142–143 °C; IR 1726 (-C=O); ^{1}H-NMR (CDCl$_3$, 300 MHz) δ = 0.87 (s, 6 H), 1.21 (t, J = 6.9 Hz, 3 H), 2.08 (s, 2 H), 2.41 (s, 2 H), 3.49 (m, 4 H), 3.83 (t, J = 5.4 Hz, 2 H), 6.75 (d, J = 8.7 Hz, 2 H), 6.90 (d, J = 16 Hz, 1 H), 6.95 (d, J = 15 Hz, 1 H), 7.01 (d, J = 16 Hz, 1 H), 7.11 (d, J = 15 Hz, 1 H), 7.35–7.45 (m, 6 H), 7.42–7.50 (m, 5 H), 8.25 (s, 1 H); ^{13}C (CDCl$_3$, 75 MHz) δ = 169.49, 155.61, 148.46, 139.94, 136.31, 136.02, 134.36, 131.72, 130.16, 129.08, 128.90, 128.25, 126.71, 125.80, 125.18, 123.76, 119.32, 112.83, 60.59, 52.78, 45.94, 42.86, 39.59, 32.36, 28.36, 12.38; MS (FAB), *m/z*: 557, 100%. Anal. Calcd. For $C_{37}H_{38}N_2O_3$: C, 79.71; H, 6.64; N, 5.02. Found: C, 79.34; H, 6.46; N, 4.61%.

Results and discussion

Synthesis

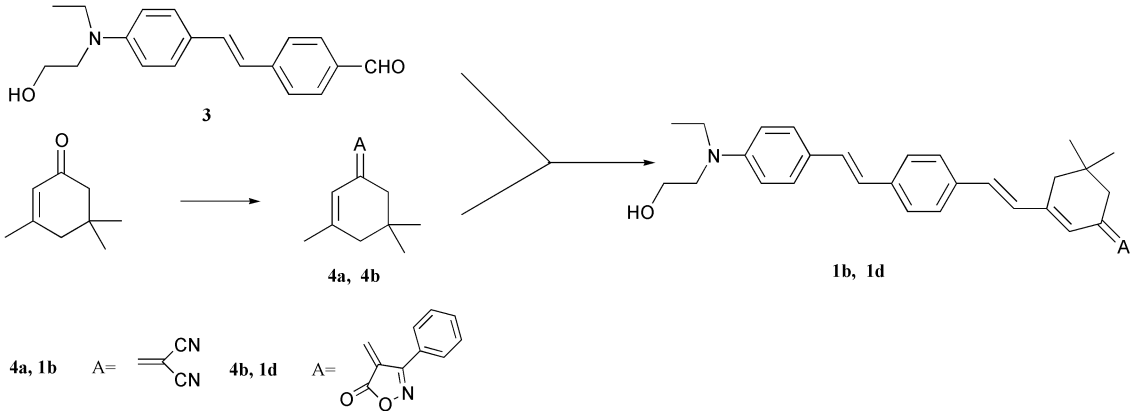
The synthesis of two configuration-locked triene chromophores **1b** and **1d** is shown in Scheme 1. Compound **3** was prepared in 64% yield by the Wittig reaction between 4-(*N*-ethyl-*N*-hydroxyethylamino)benzyltriphenylphosphonium iodide and benzene-1,4-dicarbaldehyde in $\mathrm{Bu^tOK}$–CH_2Cl_2. The key intermediates **4a** and **4b** were made by Knoevenagel condensation, and different reaction conditions have been tested following the literature procedures[14,15] with some modification. Compound **4a** was derived from the condensation of isophorone with malononitrile under the catalysis of piperidine and acetic acid, while compound **4b** was prepared in the presence of ammonium acetate and acetic acid. It should be noted that compound **4b** was obtained as a mixture of *cis* and *trans*-isomers with a ratio of 5 : 1, as determined by ^{1}H-NMR spectroscopy, and it was used in the last step without further separation. Aldehydes **3** had a very high Knoevenagel reactivity and were reacted with various acceptors to give different chromophores. Two ring-locked triene-incorporated stilbene chromophores **1b** and **1d** were obtained by Knoevenagel condensation between compound **3** and **4a** or **4b**, respectively, and the linkage of the carbon–carbon double built in this step was confirmed to be *trans* by detailed ^{1}H-NMR. We also synthesized chromophores **1a** and **1c** to compare the linear and nonlinear properties of chromophores **1b** and **1d** with stilbene-only analogue chromophores. All compounds (**1a–d**) were purified by column chromatography or recrystallization and characterized by ^{1}H-NMR, IR, FAB-MS and elemental analysis.

The linear and nonlinear properties

The first molecular hyperpolarizability of chromophores (**1a–d**) were measured by Hyper–Rayleigh Scattering (HRS) in methanol using a 1064 nm laser light. The technique and the method of analysis for HRS have been described elsewhere.[16] The linear and nonlinear optical properties of various chromophores are summarized in Table 1. Also included are six other chromophores (compounds **2a–d**, **5** and **6** see Table 1) for comparison.

It can be seen that the two chromophores **1b** and **1d** employing the combination of stilbene and ring-locked triene as their conjugation bridge displayed blue-shifted absorption in comparison with the corresponding stilbene-only or triene-only analogues in chloroform, although the length of their conjugation bridge was much longer. For example, the $\lambda_{\max}$ of **1b** was 19 nm and 45 nm blue-shifted compared with **1a** and **5** in chloroform, respectively. Simple MOPAC molecular modeling indicated that the conjugation bridge of chromophores **1b** and **1d** was of poorer co-planarity. For instance, the dihedral angle between the benzene ring and the ring-locked triene of **1b** was approximately 20°. Thus the blue-shifted absorption can be partially accounted for by the limitation of the intramolecular charge transfer (ICT) between the donor and the acceptor of chromophores **1b** and **1d**.

Although the π-electron delocalization efficiency of chromophores **1b** and **1d** is somewhat reduced due to the poorer co-planarity of their conjugation bridge, it should be noticed that the β_0 values of **1b** and **1d** were quite competitive with those of their corresponding stilbene-only and triene-only analogues from the theoretical investigation and the experimental results. The two-level model shows that the β_0 value is a strong function of the oscillator strengths (f) in addition to $\Delta\mu$, the change of the molecular dipole moments between the ground state and the charge-transfer excited state.[16] Thus it can be deduced that the reduction of the ICT efficiency of chromophores **1a–d** does not necessarily accompany a decrease in their f and/or $\Delta\mu$ values, and this has been partially verified by the



Scheme 1 Synthetic route for chromophores **1b** and **1d**.

experimental results. As shown in Table 1, the oscillator strengths of chromophores **1b** and **1d** were significantly high. Full interpretation will require further studies. In addition, comparison of **1a–d** with the corresponding azobenzene (**2a–d**) analogues showed that chromophores **1a**, **1b** and **1d** also exhibited blue-shifted absorption (with the exception of **1c**), while their β_0 values were comparable. All the above results suggest that chromophores employing the combination of stilbene and ring-locked triene as their conjugation bridge exhibit better optimization of the nonlinearity–transparency trade-off.

Conclusions

We have synthesized two new chromophores containing both stilbene and a ring-locked triene as a conjugation bridge and measured their β value and UV–Vis absorption. Comparison with stilbene-only and triene-only analogues showed that these new chromophores display blue-shifted absorption in chloroform and large nonlinearities. This verifies the important role of the combined conjugation bridge, thereby providing a new approach for tuning the nonlinearity–transparency trade-off.

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