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Synthesis and third-order optical nonlinearity in two-dimensional A-π-D-π-A carbazole-cored chromophores

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Abstract

Novel A-π-D-π-A carbazole-cored chromophores were synthesized and characterized by NMR, IR, UV techniques. The third-order NLO properties of the carbazole chromophores were investigated. The measurements of second-order hyperpolarizabilities were performed using single-beam Z-scan technique with picosecond laser pulses in DMF solutions. Our results indicate that larger second-order hyperpolarizabilities γ can be readily obtained in such carbazole chromophores because of increasing strength of withdrawing group and molecular conjugation length with two aromatic bridges in the two-dimensional conjugated system. Therefore, it is very probable that the increase in the obtained γ values considerably arises from the conjugation path of the delocalized electrons for large third-order nonlinear optical effects.

Keywords: Third-order optical nonlinearity; Z-scan technique; Two-dimensional chromophores; Carbazole derivatives

1. Introduction

The nonlinear optical properties of materials can be used to control the phase, the state of polarization, or the frequency of light beams. With the emergence of photonic technologies in areas such as telecommunications where information is coded, transported, and routed optically, there is a strong technological demand for high-performance NLO materials. Organic molecules are promising candidates for these nonlinear optical applications [1–5]. Multifunctional carbazole derivatives have been recognized as important materials for optical applications as a result of their special photo, electrical, and chemical properties [6–9]. In searches for novel NLO chromophores, we selected carbazole derivatives as the functional basic building block for the molecular design and for the synthesis of NLO materials which are multifunctional materials and have second-order, third-order nonlinear optical and photoconductive properties [10–13].

In second-order nonlinear optics, the relationships between the molecular structure and large first-order hyperpolarizabilities β have been well established. In third-order nonlinear optics, guidelines for the optimization of the second-order hyperpolarizabilities γ of a molecule have been improving, but the understanding is far less developed than for β [14,15]. Most of the attempted chromophores are designed as one-dimensional charge transfer molecules with an extended conjugation in a single direction similar to the case of β in several systems. Particularly, multipolar molecules have attracted increasing attention in recent years [16–18]. In this work, novel two-dimensional A-π-D-π-A

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chromophores were explored. When electron acceptor groups were linked to the electron donor carbazole nucleus, an intramolecular charge transfer was formed. Compared to classical one-dimensional molecules, two-dimensional carbazole chromophores have appeared to show promising properties. We present the synthesis, absorption features and third-order NLO properties of six 3,6-di-acceptor-substituted carbazole azo chromophores, in which two hyperpolarizable bridges were directly connected to form multipolar system.

Fig. 1 shows the base backbone of the multipolar NLO chromophores represented as A-π-D-π-A. Six such compounds were synthesized and characterized by NMR, IR, UV. The third-order NLO properties were determined using Z-scan methods.

2. Experimental section

2.1. Materials

The *N*-ethyl carbazole and 2-amino-6-nitrobenzothiazole were obtained from Aldrich Chemical Co. *N*,*N*-dimethylformamide (DMF) was dried over molecular sieves. All other solvents and chemical reagents were obtained commercially and were used as received without further purification.

2.2. 9-Ethyl-3,6-bis[(6-nitrobenzothiazole-2-yl)azo] carbazole, **C1**

2-Amino-6-nitrobenzothiazole (3.9 g, 20 mmol) was dissolved in concentrated sulfuric acid and glacial acid at 0–5 °C. The reaction flask was immersed in an ice-bath for temperature control. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stirring. Diazonium salt was obtained and used for coupling reaction. Freshly prepared 2-amino-6-nitrobenzothiazole diazonium salt (0–5 °C) was added dropwise for 1 h to the solution of *N*-ethyl carbazole (1.95 g, 10 mmol) in 20 ml acetic acid under vigorous mechanical stirring. After stirring the mixture for a further 5 h, the mixture was neutralized with ammonia water to pH 5–6 while stirring for 0.5 h. The precipitate was filtered and dried after repeatedly washing with water and ethanol. The crude product was recrystallized and purified crystals

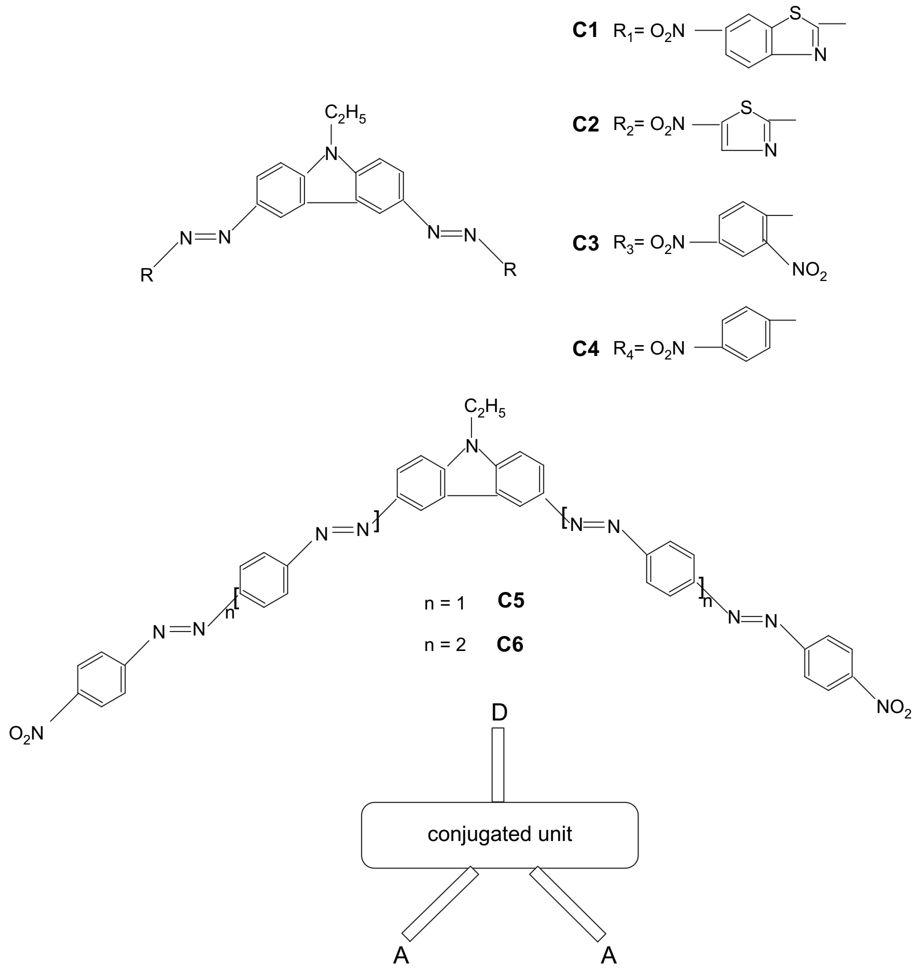


Fig. 1. Series of A-π-D-π-A carbazole-cored NLO-phores **C1–C6**.

were obtained. Further purification was performed by column chromatography.

2.3. 9-Ethyl-3,6-bis(4′-nitrophenyl-1′-azo)carbazole, **C4**

4-Nitroaniline (2.76 g, 20 mmol) was dissolved in 18% hydrochloride solution (20 ml) at 0−5 °C. The reaction flask was immersed in an ice-bath for temperature control. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stirring. Freshly prepared 4-nitroaniline diazonium salt (0−5 °C) was added dropwise for 1 h to the solution of *N*-ethyl carbazole (1.95 g, 10 mmol) in 20 ml acetic acid under vigorous mechanical stirring. After stirring the mixture for a further 4 h, the precipitate was filtered and dried after repeatedly washing with water and ethanol. The crude product was recrystallized and purified crystals were obtained. Further purification was performed by column chromatography.

The chromophores **C1**−**C6** were synthesized by the reaction of *N*-ethyl carbazole and the diazonium salt prepared for the respective amines.

Chromophore **C1** ^{1}H NMR ($CDCl_3$): $\delta = 1.55$(3H, $-CH_{3,}$), 4.45(2H, $-CH_2$), 7.40(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.58(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.49−7.52(2H, carbazole-H *ortho* to *N*-ethyl), 7.54−7.57(2H, carbazole-H *meta* to *N*-ethyl), 8.88(s, 1H, benzothiazole-H *ortho* to nitro group), 8.82(s, 1H, benzothiazole-H *ortho* to nitro group), 8.18(d, 1H, benzothiazole), 8.21(d, 1H, benzothiazole), 8.29(d, 1H, benzothiazole), 8.38(d, 1H, benzothiazole) IR: γ (cm^{-1}) =1625(C=N), 1594 (N=N), 1334, 1513(nitro group), 3060, 1473, 748(benzothiazole group), 621(C−S).

Chromophore **C2** ^{1}H NMR ($CDCl_3$): $\delta = 1.61$(3H, $-CH_{3,}$), 4.40(2H, $-CH_2$), 7.45(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.49(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.39(d, 1H, carbazole-H *ortho* to *N*-ethyl), 7.55(d, 1H, carbazole-H *ortho* to *N*-ethyl), 8.10(d, 1H, carbazole-H *meta* to *N*-ethyl), 8.22(d, 1H, carbazole-H *meta* to *N*-ethyl), 8.68(s, 1H, thiazole-H *ortho* to nitro group), 8.81(s, 1H, thiazole-H *ortho* to nitro group). IR: γ (cm^{-1}) = 1625(C=N), 1594 (N=N), 1328, 1513(nitro group), 3050, 1473, 750(thiazole group), 628(C−S).

Chromophore **C3** ^{1}H NMR ($CDCl_3$): $\delta = 1.54$(3H, $-CH_{3,}$), 4.46(2H, $-CH_2$), 7.37(d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.58(d, 2H, carbazole-H to *meta* *N*-ethyl), 7.49(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.51(s, 1H, carbazole-H *meta* to *N*-ethyl), 7.98(d, 1H, benzene-H *ortho* to azo group), 8.17(d, 1H, benzene-H *ortho* to azo group), 8.25(d, 1H, benzene-H *ortho* to nitro group), 8.53(d, 1H, benzene-H *ortho* to nitro group), 8.76(s, 1H, benzene-H in middle of two nitro group), 8.79(s, 1H, benzene-H in middle of two nitro group). IR: γ (cm^{-1}) = 1594 (N=N), 1338, 1517(nitro group).

Chromophore **C4** ^{1}H NMR ($CDCl_3$): $\delta = 1.45$(t, 3H, $-CH_{3,}$), 4.38(q, 2H, $-CH_2$), 7.21(d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.40(d, 2H, carbazole-H *meta* to *N*-ethyl), 7.45(s, 2H, carbazole-H *meta* to *N*-ethyl), 7.48(d, 2H, benzene-H *meta* to NO_2), 8.11(d, 2H, benzene-H *ortho* to NO_2) IR: γ (cm^{-1}) = 1597 (N=N), 1332, 1517(nitro group).

Chromophore **C5** ^{1}H NMR ($CDCl_3$): $\delta = 1.50$(3H, $-CH_{3,}$), 4.45(2H, $-CH_2$), 7.44−7.50(4H, carbazole-H), 7.52(s, 2H, carbazole-H *meta* to *N*-ethyl), 8.02(d, 2H), 8.10(d, 2H), 8.13(d, 2H), 8.18(d, 2H), 8.25(d, 2H), 8.41(d, 2H), 8.76(d, 2H), 9.10(d, 2H). IR: γ (cm^{-1}) = 1595 (N=N), 1341, 1519(nitro group), 3418(*N*-ethyl carbazole group).

Chromophore **C6** ^{1}H NMR ($CDCl_3$): $\delta = 1.49$(t, 3H, $-CH_{3,}$), 4.45(q, 2H, $-CH_2$), 7.21(d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.43(d, 2H, carbazole-H *meta* to *N*-ethyl), 7.46(s, 2H, carbazole-H *meta* to *N*-ethyl), 7.53−7.58(4H, benzene-H), 7.66−7.68(4H, benzene-H), 8.04−8.06(4H, benzene-H), 8.08−8.11(4H, benzene-H), 8.30(4H, benzene-H), 8.40(4H, benzene-H). IR: γ (cm^{-1}) = 1597 (N=N), 1342, 1521(nitro group).

2.4. Characterization

Chemical structures were identified by Fourier transform infrared (FT-IR) spectra and ^{1}H NMR spectra. FT-IR spectra were recorded on a Nicolet 750 series in the region of 4000−400 cm^{-1} using KBr pellets. ^{1}H NMR measurements were determined with a Brucker 500 MHz apparatus, with TMS (tetramethyl silane) as internal standard and chloroform as solvent. Linear optical properties were measured by a Shimadzu UV-2201 UV−visible spectra in solution.

2.5. Nonlinear optical measurements

The Z-scan technique [19,20] was used to measure the nonlinear susceptibility of the carbazole chromophores. The technique relies on the fact that the light intensity varies along the axis of a convex lens and is maximum at the focus. By moving the sample through the focus, the intensity dependent absorption is measured as a change in the transmission through the sample. The nonlinear refraction is determined by the spot size variation at the plane of a finite aperture detector combination, because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

Measurements were performed using a Q-switched, mode-locked Nd:YAG laser source at $\lambda = 1064$ nm emitting $\tau \sim 35$ ps pulses with TEM_{00} mode at a 10-Hz repetition rate. The linearly polarized pulses were divided by a beam-splitter into two parts: the reflected one used as a reference to represent the incident light power; and the transmitted one was focused through the sample. Both the beams were recorded by two power probes simultaneously, and measured by a dual channel power meter which transferred the digitized signals to a computer. The sample was mounted on a computer-controlled translation stage that moved the sample along the *z*-axis with respect to the focus of the lens.

The experiments were performed at room temperature on spectroscopic-grade DMF solutions contained in a 1-mm thick quartz cell. As a reference, we performed a Z-scan on a sample of CS_2, and obtained n_2, which are in good agreement with the published results [19].

3. Results and discussion

3.1. Synthesis and characterization of chromophores

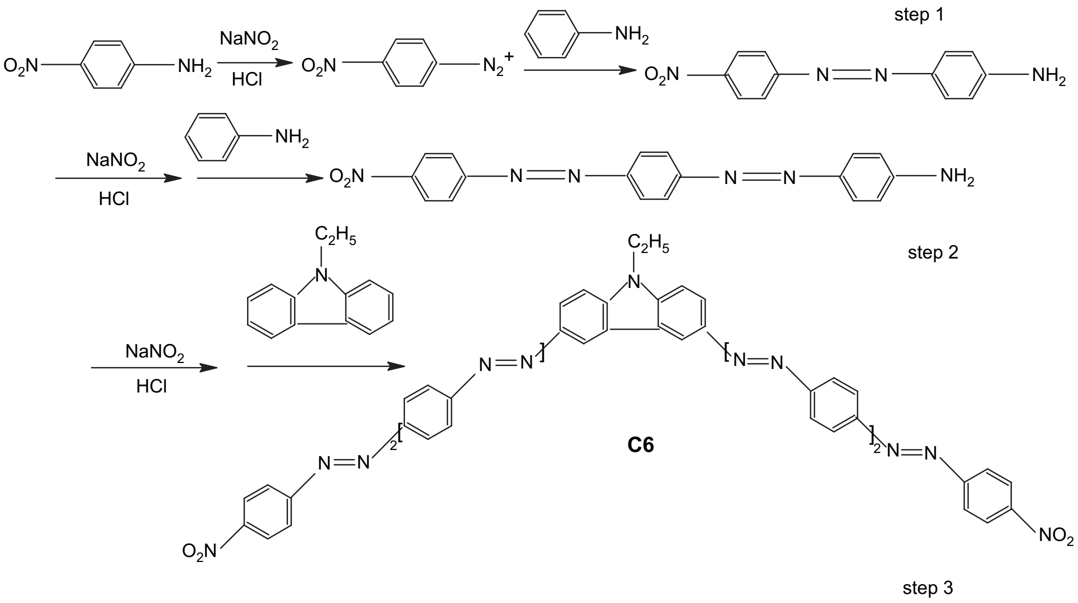
Six new carbazole-based azo chromophores were prepared by azo-coupling reaction. These NLO chromophores both with A-π-D-π-A structure consist of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing aryl units. For example, the synthetic procedure of chromophore **C6** is shown in Scheme 1. The reaction was performed in a three-step azo-coupling process under mild circumstances. We developed a useful synthetic method for long conjugated chain formation in which the core is generated from carbazole by a mild reaction.

The representative ^{1}H NMR spectrum of the chromophores and assignment are shown in Fig. 2. The resonance corresponding to carbazole moieties can be observed nearly at the same points. The FT-IR spectrum of **C1** is shown in Fig. 3. The clear appearance of $\sim 1594\ \mathrm{cm}^{-1}$ bands characteristic of N=N stretching, the $\sim 3060\ \mathrm{cm}^{-1}$, $1473\ \mathrm{cm}^{-1}$, and $748\ \mathrm{cm}^{-1}$ bands, characteristic of benzothiazole ring, indicated the chemical structure of **C1**. The characteristic absorption of the −C−S− stretching in the ring was observed at $621\ \mathrm{cm}^{-1}$. The characteristic absorption peaks at $\sim 1513\ \mathrm{cm}^{-1}$ and $1334\ \mathrm{cm}^{-1}$ bands indicated the existence of the nitro group.

3.2. Linear optical properties

The UV−visible spectrum of the chromophores in DMF solution is shown in Fig. 4. The typical characteristic absorption behavior of the NLO carbazole azo chromophores was observed in the spectrum. This result suggests that the chromophores were affected by the different acceptors and conjugation lengths. The UV−visible spectrum of the chromophores shows the absorption bands at 225−350 nm attributed to the carbazole moiety and at 350−700 nm attributed to the $\pi-\pi^*$ transition of the azo conjugated unit. It can be seen that the increase in the degree of π delocalization results in a redshift of the absorption peak wavelength. The absorption spectrum of a conjugated NLO chromophore largely depends on the degree of electron conjugation within the π-orbitals. In particular, $\lambda_{\max} \propto L$, where L is the conjugation length. The absorption attributed to the conjugated units proportionally intensifies with the growth of the azo generation number, even though the absorption attributed to the carbazole core unit does not change. This delocalization is caused by the coplanarity of the aromatic systems.

Fig. 5 shows these solvatochromic phenomena in different solvents, which is the solvent dependence of the UV−visible absorption spectrum of molecules. In particular, the effect of solvent on position, shape, or intensity of the absorption bands of a molecule can be



Scheme 1. Synthesis of chromophore **C6**.

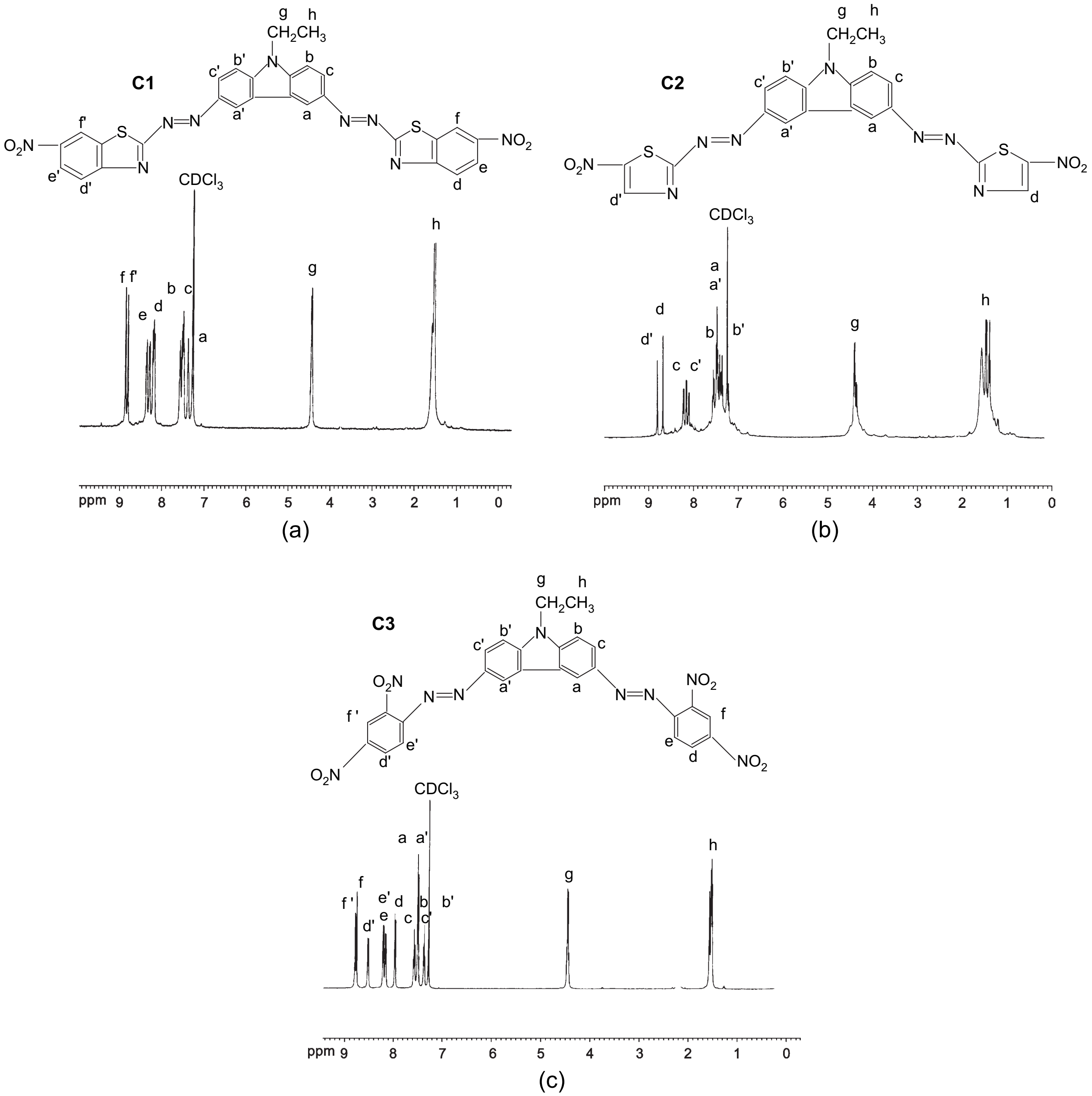


Fig. 2. ^1H NMR spectra of **C1** (a), **C2** (b), and **C3** (c) in $CDCl_3$.

determined from the UV–visible spectrum. This result suggests that the absorption changes with the polarity of different solvents.

3.3. The third-order NLO properties

The third-order nonlinear optical susceptibility $\chi^{(3)}$ was determined with the Z-scan technique in a single-beam configuration. The laser beam is focused onto the sample and the total power of the transmitted beam, as well as the power in its central part, is recorded in the far field as a function of the sample position along the beam axis z. This technique allows the simultaneous measurement of nonlinear refractive index n_2. The index of refraction n is expressed in terms of nonlinear indexes n_2 or γ through [19–21]:

$$n = n_0 + \frac{n_2}{2}|E|^2 = n_0 + \gamma I \tag{1}$$

$$\Delta n_0 = n - n_0 = \gamma I \tag{2}$$

Usually, Z-scans for a thin refractive sample with weak absorption are measured in the circumstances of a Gaussian beam propagating throughout a diaphragm behind a sample with the Gaussian profile of the resultant

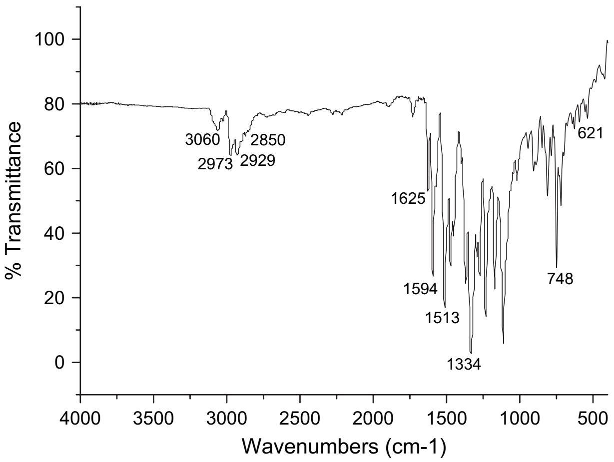


Fig. 3. FT-IR spectrum of **C1**.

radial phase shift. In such conditions, only two terms of a Taylor series expansion of the resultant electric field at the diaphragm are taken. Thus, a final formula, giving a bridge between the normalized transmittance difference from peak to valley, ΔT_{p-v}, and the on-axis refractive index change Δn_0 in the beam waist, takes the form:

$$\Delta n_0 = \frac{\Delta T_{p-v}}{0.406(1-s)^{0.25} k L_{\mathrm{eff}}} \tag{3}$$

$$n_2 = \frac{c n_0}{40\pi} \frac{\Delta n_0}{I_0} \tag{4}$$

where $S = 1 - \exp[(-2r_a/\omega_a)^2]$ is the diaphragm linear transmittance, r_a is the beam radius at the diaphragm and ω_a is its radius, $k = 2\pi/\lambda$, λ is the wavelength, and L_{eff} is the sample effective thickness, which is expressed as:

$$L_{\mathrm{eff}} = \frac{1-\exp(-\alpha L)}{\alpha} \tag{5}$$

where, in turn, α is the absorption coefficient and L is the sample's physical thickness. Eqs. (3) and (4) are applied for the calculation of the refractive index change and nonlinear index of an optically nonlinear medium using the Z-scan data.

The real part of third-order nonlinear susceptibility $\chi^{(3)}$ is converted from [22]:

$$\mathrm{Re}[\chi^{(3)}] = \frac{n_0^2 n_2}{12\pi^2} \tag{6}$$

In addition, the third-order susceptibility $\chi^{(3)}$ can be related to the second-order molecular hyperpolarizability γ by [20,22]:

$$\mathrm{Re}[\gamma] = \frac{\mathrm{Re}\left[\chi^{(3)}\right]}{N f^4} \tag{7}$$

where N is the number of molecules per unit volume, and f is the local field correction factor according to Lorentz expression $f = \left(n_0^2 + 2\right)/3$. Hence, the molecular hyperpolarizability is calculated with Eq. (7).

The Z-scan measurements performed on DMF solutions of six samples are reported in Fig. 6 and show that nonlinear refractive index is positive giving rise to a valley–peak Z-scan curve. The second-order molecular hyperpolarizability γ values for six samples are also shown in Table 1.

The curves fit to

$$\frac{T}{P_5} = 1 - 2P_3 \frac{P_1(P_4x - P_2)^2 - 2(P_4x - P_2) + 3P_1}{\left[(P_4x - P_2)^2 + 1\right]\left[P_4(x - P_2)^2 + 9\right]}$$

where P_1–P_5 are correlated coefficient, T is the transmittance of Z-scan, x is the sample position along the z-axis with respect to the focus of the lens.

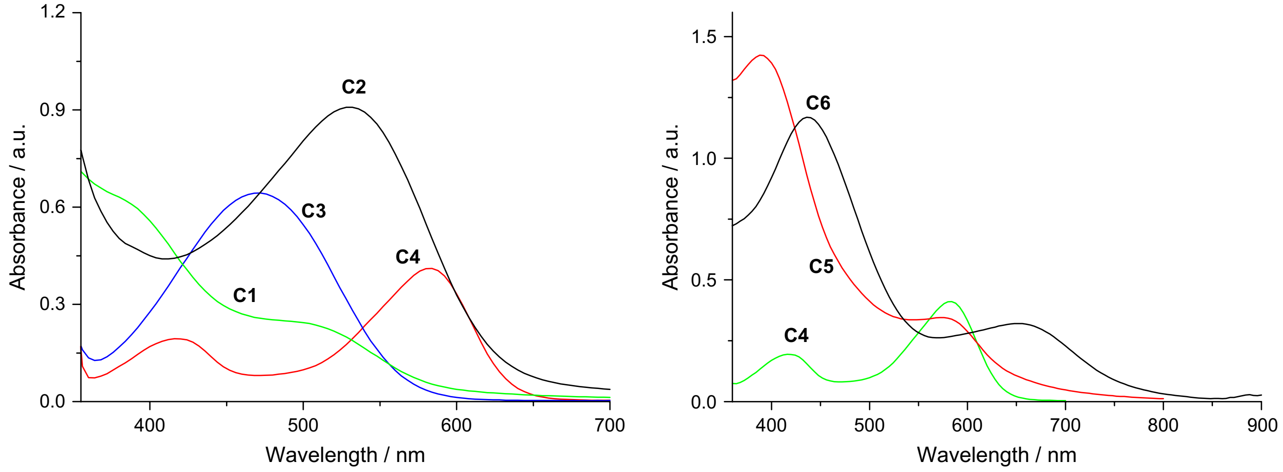


Fig. 4. UV–visible spectra of chromophores **C1–C6** in DMF.

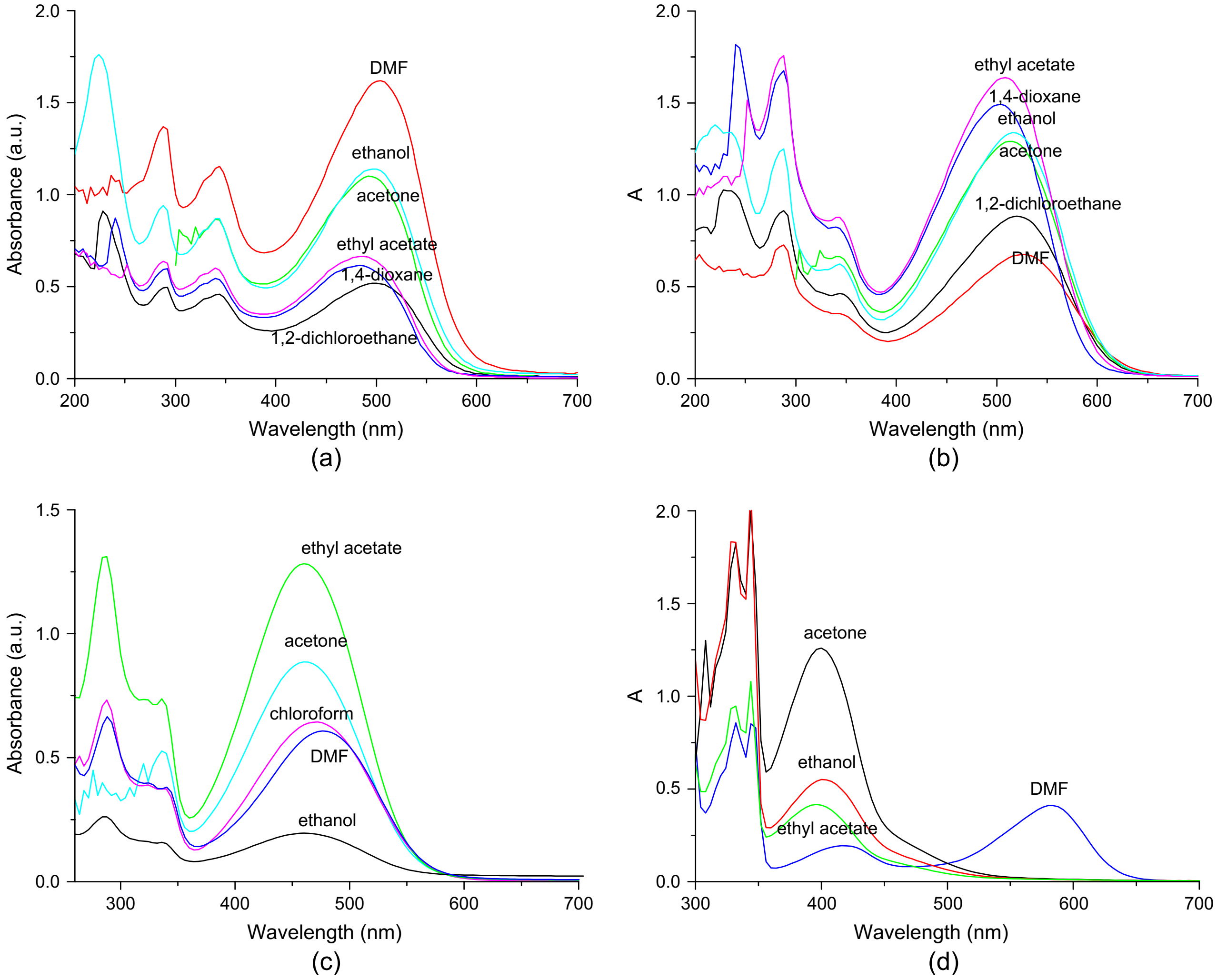


Fig. 5. UV–visible spectra of chromophores **C1** (a), **C2** (b), **C3** (c), and **C4** (d) in different solvents.

The second hyperpolarizability is often expressed by the following three-level model as [23,24]:

$$\gamma(0;0,0,0) \propto \frac{\mu_{01}^2(\mu_0-\mu_1)^2}{\omega_1^3} - \frac{\mu_{01}^4}{\omega_1^3} + \sum_n \frac{\mu_{01}^2\mu_{1n}^2}{\omega_1^2\omega_n} \tag{8}$$

Here ω_n is the transition energy between the ground and nth excited states, μ_{01} and μ_{1n} are transition moments between the ground and lowest excited states and between the lowest and nth excited states, respectively, and $\mu_0 - \mu_1$ denotes the difference in the dipole moments of the two states. This expression can be considered as the approximated formula of the following more complicated equation by ignoring the frequency factor ($\omega \to 0$).

$$\gamma(-\omega;\omega,\omega,-\omega) \propto \underset{D_{\mathrm{i}}}{\frac{\mu_{01}^2(\mu_1-\mu_0)^2\omega_1}{(\omega_1^2-\omega^2)(\omega_1^2-4\omega^2)}} - \underset{N_{\mathrm{i}}}{\frac{\mu_{01}^4\omega_1\left(\omega_1^2+\omega^2/3\right)}{(\omega_1^2-\omega^2)^3}} + \sum_n \underset{\mathrm{TP_i}}{\frac{\mu_{01}^2\mu_{1n}^2\left[\omega_1^2\omega_n+\omega^2(4\omega_1+\omega_n)\right]}{(\omega_1^2-\omega^2)^2\left(\omega_n^2-4\omega^2\right)}} \tag{9}$$

In Eq. (9), sum consist of three different terms: the dipolar term D_{i}, the negative term N_{i}, and the two-photon term $\mathrm{TP_i}$. However, for the present carbazole chromophore which has a large dipole moment at the excited state and ground state and has no two-photon

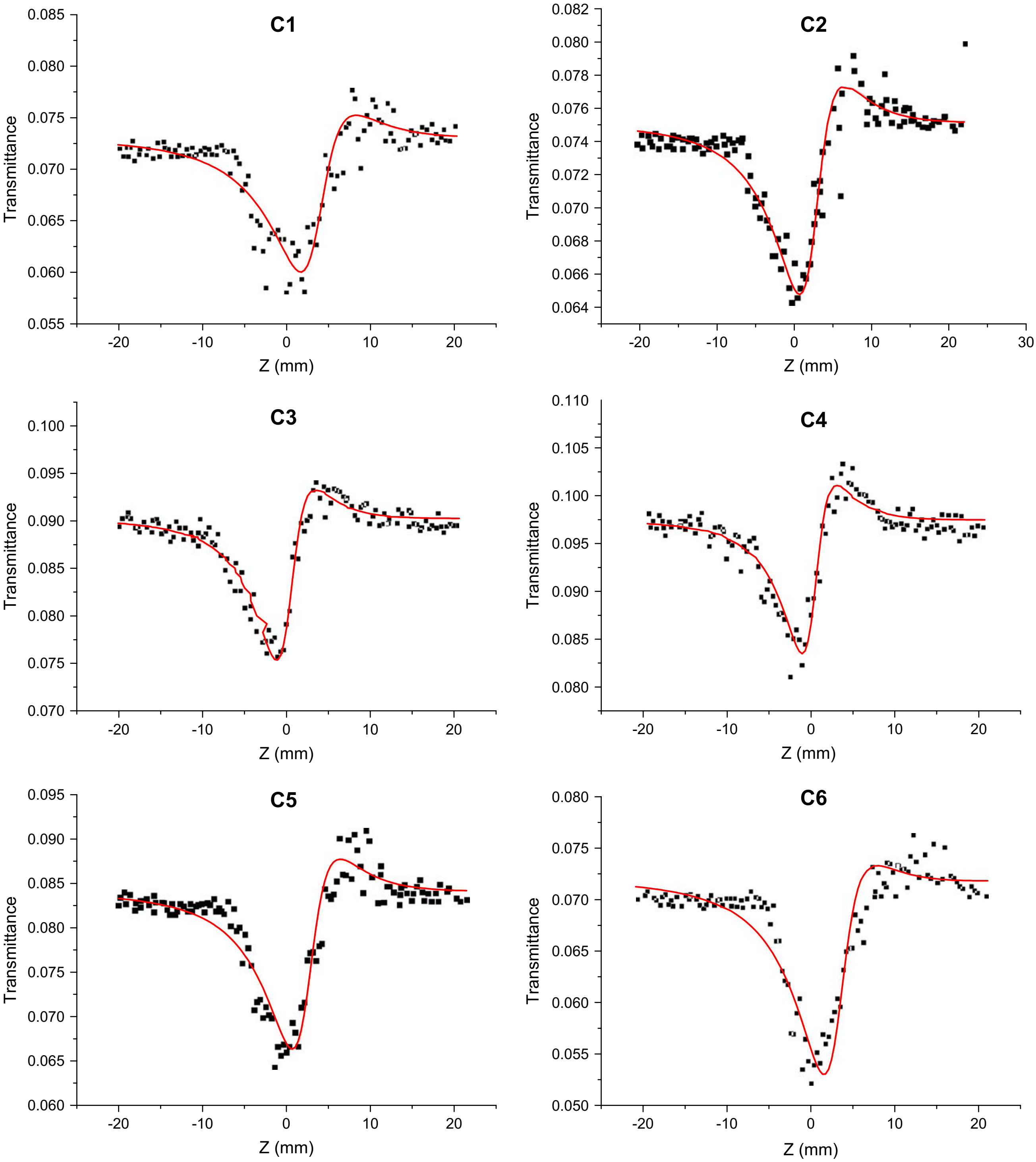


Fig. 6. Measured Z-scan of NLO chromophores **C1–C6** in a 1-mm thick quartz cell.

absorption (TPA), only the first term is expected to be dominant and can be employed for the analysis. It is clear that γ increases as a function of the difference in excited state and ground state dipole moments ($\mu_1 - \mu_0$). A chemical transformation which increased ($\mu_1 - \mu_0$) and enhanced charge transfer faster than the other parameters in Eq. (1) would therefore lead to an increase in γ.

These chromophores **C1–C6** both with A-π-D-π-A structure consist of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing aryl units, and is considered to have intramolecular charge transfer (CT) both in the ground and excited states. As shown in Table 1, the second-order hyperpolarizabilities γ of **C1–C6** increase with increasing lengths of conjugation

Table 1
Second-order molecular hyperpolarizability γ for six samples

Sample	λ_{max} (nm) in DMF	γ ($\times 10^{-36}$ esu)
C1	499	2265
C2	530.5	1479
C3	472	1824
C4	582	1652
C5	574.5	2523
C6	653	2867

and increasing strengths of electron donor–acceptor. From **C4** to **C6**, it has been shown that the extended conjugation length (*n* from 1 to 3) increases the second-order hyperpolarizability γ, accompanied by a redshift of the absorption spectrum. Thiazole and benzothiazole rings are employed as the conjugating moieties between donor and acceptor substituents in chromophores **C1** and **C2**. Since heteroaromatic rings such as thiazole and benzothiazole have a lower delocalization energy than that of benzene, its substituents in donor–acceptor chromophores should be expected to result in an enhanced NLO response.

Our results indicate that larger second-order hyperpolarizabilities can be readily obtained in such carbazole chromophores because of increasing molecular conjugation length with two aromatic bridges in the two-dimensional conjugated system. Therefore, it is very probable that the increase in the obtained γ values considerably arises from the conjugation path of the delocalized electrons for large third-order nonlinear optical effects.

4. Conclusions

We have described the synthesis and the third-order optical nonlinearities in the picosecond range of novel two-dimensionally carbazole chromophores possessing the same donor groups and π-connecting system with various strength withdrawing groups and conjugation length. The results show that the γ increases as the strength of withdrawing group and conjugation length increases. Further enhancement of the γ has been achieved via replacement of phenyl rings in the conjugated backbone by heteroaromatic spacers such as benzothiazole and thiazole rings. It is concluded that the dipolar contribution of two-dimensionally chromophores is important for optimizing the γ values. It is an eminent guideline on the way to materials with sufficiently large nonlinearities for practical applications.

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