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Dyes and Pigments 74 (2007) 494–500
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Synthesis and third-order optical nonlinearities of anthracenedione derivatives

Zhibin Cai, Jianrong Gao*, Xiaonian Li

State Key Laboratory of Green Chemistry Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China

Received 1 July 2006; received in revised form 11 July 2006; accepted 11 July 2006
Available online 15 September 2006

Abstract

Six D–π–A–π–D anthracenedione derivatives were synthesized and characterized by UV, IR, ^{1}H NMR and elemental analysis. The third-order nonlinear optical properties of the compounds were measured using femtosecond degenerate four-wave mixing. The third-order nonlinear optical susceptibilities $\chi^{(3)}$ of the compounds were $2.64–3.83 \times 10^{-13}$ esu. The second-order hyperpolarizabilities γ of the molecules were $2.86–3.84 \times 10^{-31}$ esu. The response times were 86–108 fs.

Keywords: Nonlinear optics; DFWM technique; Anthracenedione derivatives; Synthesis

1. Introduction

Developments in optoelectronics have greatly increased the demand for new nonlinear optical (NLO) materials in recent years. In this regard, conjugated organic materials have drawn much attention because of their large third-order nonlinearities, fast response times, high damage thresholds and ease of processing [1–3]. Many organic materials such as stilbene, azobenzene, phthalocyanine and polyacetylene have been synthesized [4–12]. As an important class of dyes with large delocalized quasi three-dimensional π-electron system and exceptionally high thermal stability [13,14], anthracenedione derivatives have received researchers' interests in nonlinear optical applications [13,15].

In this work, we selected anthracenedione as the basic building block for the molecular design. The proposed anthracenedione derivatives have long π-conjugated chain, contain an electron-withdrawing central ring and some electron-donating groups at the ends in the form of donor–π–acceptor–π–donor (D–π–A–π–D). Six such compounds (Fig. 1) were synthesized and characterized by UV, IR, ^{1}H NMR and elemental analysis. The third-order NLO properties were measured using femtosecond degenerate four-wave mixing (DFWM) technique.

2. Experimental

2.1. Materials and instruments

1,5-Diamino anthraquinone and 2,6-diamino anthraquinone were technical products. Other chemical reagents were obtained commercially. All of them were used as received without further purification.

FT-IR spectra were recorded on a Vector 22 spectrometer using KBr pellets. ^{1}H NMR spectra were collected on a Varian 400 MHz apparatus, with TMS as internal standard and DMSO-d_6 as solvent. UV–vis spectra were recorded on a Shimadzu UV-2550 UV–vis spectrometer. Elemental analyses were conducted on a Thermo Finnigan Flash EA 1112 apparatus. Mass spectrum was taken on a Thermo Finnigan LCQ Advantage instrument. Melting points were measured on an X-4 micromelting point apparatus without correction.

* Corresponding author. Tel.: +86 571 88320428.
E-mail address: caizb-h@tom.com (J. Gao).

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doi:10.1016/j.dyepig.2006.07.020

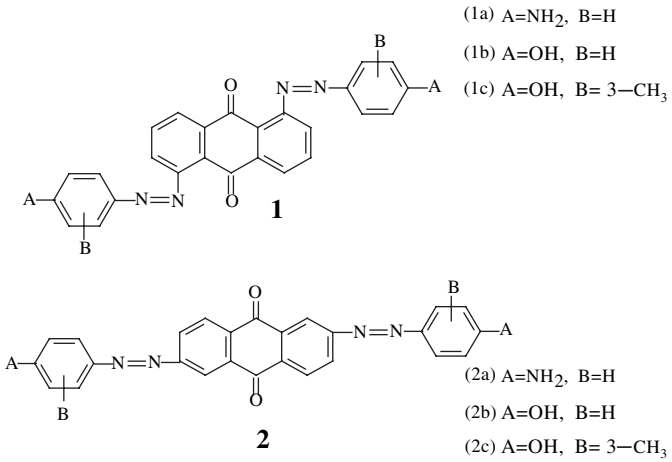


Fig. 1. Structures of the anthracenedione derivatives.

2.2. Synthesis

2.2.1. 1,5-Bis[(p-amino phenyl) azo]-9,10-anthracenedione (**1a**)

1,5-Diamino anthraquinone (1.91 g, 8 mmol) was dissolved in concentrated sulphuric acid (20 mL). To this solution, at a temperature of 0–5 °C, a solution of sodium nitrite (1.45 g, 21 mmol) in concentrated sulphuric acid (18 mL) was slowly added. The reaction mixture resulted was further stirred for 3 h at 0–5 °C and then poured over ice. The precipitated 1,5-anthraquinonylene bisdiazonium sulphate was filtered and then dissolved in water (100 mL). To the solution of bisdiazonium sulphate, aniline (1.49 g, 16 mmol) was added dropwise at 0–5 °C. After stirring the reaction mixture for further 4 h, the mixture was neutralized with sodium hydroxide to pH 8–9. The precipitate was filtered, dried and recrystallized from DMF twice to give orange powder crystals with 16.8% yield (0.6 g). $T_m = 254–256$ °C. MS *m/z* 446 (M^+). Elem. Anal. Calcd for $C_{26}H_{18}N_6O_2$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.58; H, 4.08; N, 18.93. FT-IR (KBr), ν (cm^{-1}): 3451 (–NH), 3176 (–NH), 1674 (–C=O), 1589 (–N=N), 1286 (=C–N).

2.2.2. 1,5-Bis[(p-hydroxy phenyl) azo]-9,10-anthracenedione (**1b**)

This was synthesized as above by the reaction of 1,5-anthraquinonylene bisdiazonium sulphate and phenol. The product was red-brown powder crystal. Yield: 41.9% (1.5 g). $T_m > 300$ °C. Elem. Anal. Calcd for $C_{26}H_{16}N_4O_4$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.61; H, 3.61; N, 12.46. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 10.45 (s, 2H, OH), 8.19 (d, 2H, anthracenedione–H), 7.96 (t, 2H, anthracenedione–H), 7.88 (d, 4H, $J = 6.9$ Hz, benzene–H), 7.50 (d, 2H, anthracenedione–H), 7.02 (d, 4H, $J = 6.9$ Hz, benzene–H). FT-IR (KBr), ν (cm^{-1}): 3407 (–OH), 1666 (–C=O), 1580 (–N=N), 1264 (=C–N).

2.2.3. 1,5-Bis[(4-hydroxy-3-methyl phenyl) azo]-9,10-anthracenedione (**1c**)

This was synthesized as above by the reaction of 1, 5-anthraquinonylene bisdiazonium sulphate and 2-methyl phenol. The product was dark-purple powder crystal. Yield: 36.7% (1.4 g). $T_m > 300$ °C. Elem. Anal. Calcd for $C_{28}H_{20}N_4O_4$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.27; H, 4.50; N, 11.82. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 10.40 (s, 2H, OH), 8.19 (d, 2H, anthracenedione–H), 7.96 (t, 2H, anthracenedione–H), 7.76 (s, 2H, benzene–H), 7.73 (d, 2H, $J = 8.6$ Hz, benzene–H), 7.47 (d, 2H, anthracenedione–H), 7.03 (d, 2H, $J = 8.6$ Hz, benzene–H), 2.26 (s, 6H, CH_3). FT-IR (KBr), ν (cm^{-1}): 3413 (–OH), 2900 (–CH_3), 1666 (–C=O), 1582 (–N=N), 1264 (=C–N).

2.2.4. 2,6-Bis[(p-amino phenyl) azo]-9,10-anthracenedione (**2a**)

This was synthesized as above by the reaction of 2,6-anthraquinonylene bisdiazonium sulphate and aniline. The product was red powder crystal. Yield: 14.0% (0.5 g). $T_m = 278–279$ °C. Elem. Anal. Calcd for $C_{26}H_{18}N_6O_2$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.62; H, 3.93; N, 18.75. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 13.06 (s, 4H, NH), 8.00–8.21 (m, 6H, anthracenedione–H), 7.37–7.60 (m, 8H, benzene–H). FT-IR (KBr), ν (cm^{-1}): 3446 (–NH), 3210 (–NH), 1660 (–C=O), 1574 (–N=N), 1307 (=C–N).

2.2.5. 2,6-Bis[(p-hydroxy phenyl) azo]-9,10-anthracenedione (**2b**)

This was synthesized as above by the reaction of 2,6-anthraquinonylene bisdiazonium sulphate and phenol. The product was red needle crystal. Yield: 33.5% (1.2 g). $T_m > 300$ °C. Elem. Anal. Calcd for $C_{26}H_{16}N_4O_4$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.26; H, 3.62; N, 12.38. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 10.60 (s, 2H, OH), 8.49 (s, 2H, anthracenedione–H), 8.41 (d, 2H, $J = 8.4$ Hz, anthracenedione–H), 8.28 (d, 2H, $J = 8.4$ Hz, anthracenedione–H), 7.93 (d, 4H, $J = 8.8$ Hz, benzene–H), 7.00 (d, 4H, $J = 8.8$ Hz, benzene–H). FT-IR (KBr), ν (cm^{-1}): 3395 (–OH), 1659 (–C=O), 1581 (–N=N), 1292 (=C–N).

2.2.6. 2,6-Bis[(4-hydroxy-3-methyl phenyl) azo]-9,10-anthracenedione (**2c**)

This was synthesized as above by the reaction of 2,6-anthraquinonylene bisdiazonium sulphate and 2-methyl phenol. The product was red flake crystal. Yield: 55.1% (2.1 g). $T_m > 300$ °C. Elem. Anal. Calcd for $C_{28}H_{20}N_4O_4$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.80; H, 4.26; N, 11.72. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 10.55 (s, 2H, OH), 8.38 (s, 2H, anthracenedione–H), 8.34 (d, 2H, $J = 8.2$ Hz, anthracenedione–H), 8.20 (d, 2H, $J = 8.2$ Hz, anthracenedione–H), 7.75 (s, 2H, benzene–H), 7.74 (d, 2H, $J = 8.2$ Hz, benzene–H), 6.98 (d, 2H, $J = 8.2$ Hz, benzene–H), 2.20 (s, 6H, CH_3). FT-IR (KBr), ν (cm^{-1}): 3422 (–OH), 2962 (–CH_3), 1659 (–C=O), 1581 (–N=N), 1297 (=C–N).

2.3. Nonlinear optical measurements

The DFWM technique was used to measure third-order optical nonlinearities of the anthracenedione derivatives. The experimental setup is shown in Fig. 2(a). The pump source was

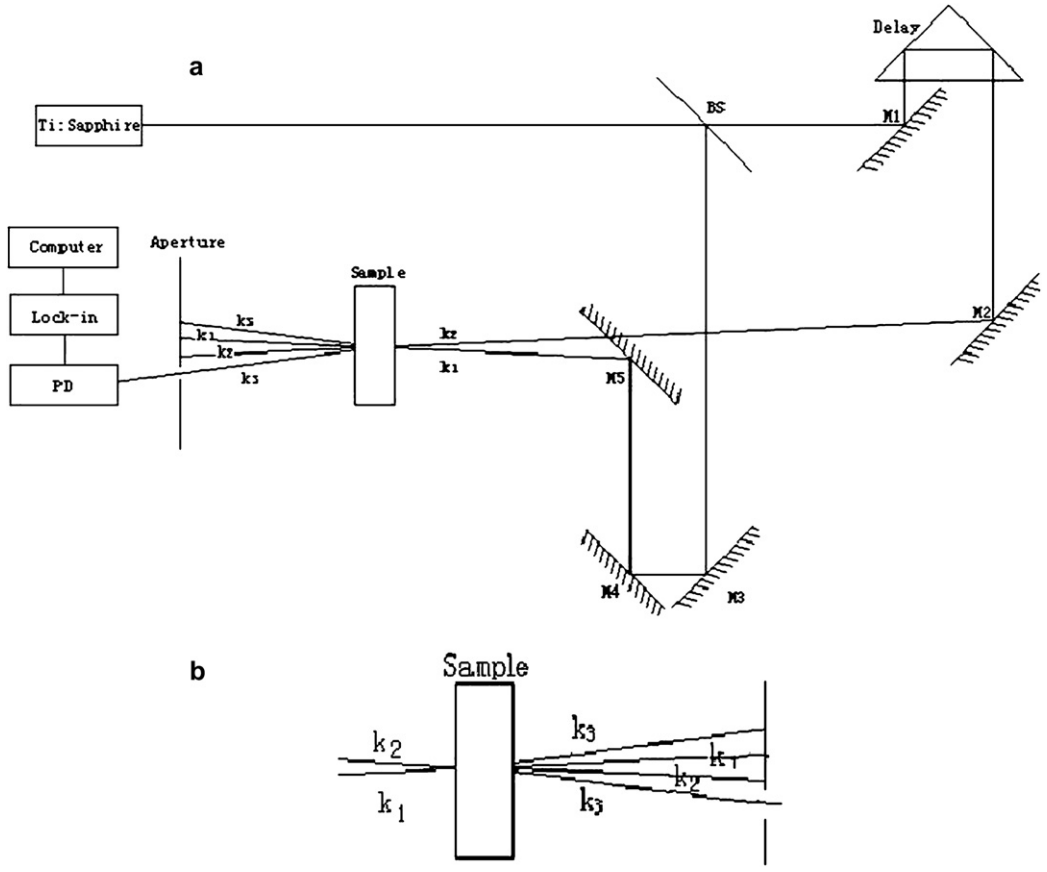


Fig. 2. (a) Experimental setup of DFWM; and (b) wave vector diagram of two beam DFWM.

a Ti:Sapphire laser (Spectra-physics Spitfire Amplifier) with 80 fs pulse width, 800 nm wavelength, and 1 KHz pulse repetition rate. The input beam was split into two beams k_1 and k_2 with nearly equal energy by use of a beam splitter (BS), then focused on a plot of the sample. The wave vector diagram of two beam DFWM is shown in Fig. 2(b), where k_3 was signal beam generated by input beams through the sample. The angle between the beams k_1 and k_2 was about 5°. The k_2 could be controlled by a stepping motor so that the arrival time at the sample could be varied. When k_1 and k_2 were overlapped spatially in the sample, the generated signal beam k_3 passed through an aperture, recorded by a photodiode and then analyzed by a Lock-in amplifier and computer.

The experiments were performed at 22 °C on DMF solutions contained in a 1 mm thick quartz cell. As a reference, the optical nonlinearity of the standard sample CS_2 was also observed.

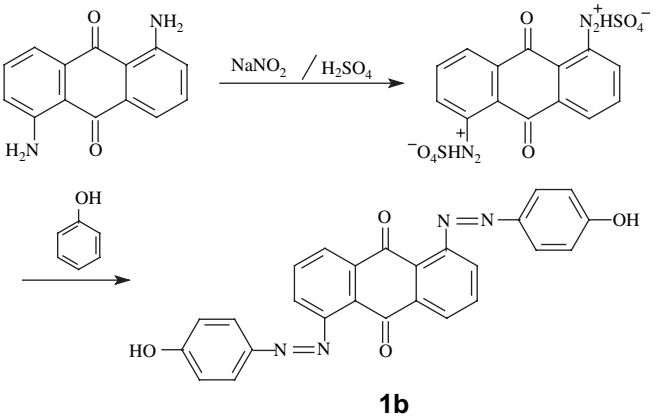
3. Results and discussion

3.1. Synthesis and characterization

Among six anthracenedione derivatives, **1c**, **2a**, **2b** and **2c** are new compounds; and **1a** and **1b** were reported without specific preparation process [16–18]. These compounds were prepared by diazotisation-coupling reaction. For example, the synthetic route of **1b** is shown in Scheme 1.

The representative ^{1}H NMR spectra of the compounds and assignment are shown in Fig. 3.

The FT-IR spectrum of **2b** is shown in Fig. 4. The characteristic absorption peaks of the hydroxy group and carbonyl group were observed at 3395 cm^{-1} and 1659 cm^{-1}, respectively. The characteristic absorption peaks at 1581 cm^{-1} and 1292 cm^{-1} indicated the existence of N═N and ═C–N, respectively.



Scheme 1. Synthesis of **1b**.

3.2. The third-order NLO properties

The linear UV–vis absorption spectra of six anthracenedione derivatives in DMF solutions are shown in Fig. 5. These compounds exhibited absorption peaks between 340 and 660 nm. The laser wavelength (800 nm) used in the experiment of DFWM is far from their resonant bands. Thus the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of the compounds are off-resonant nonlinear responses.

The third-order nonlinear optical susceptibility $\chi^{(3)}$ is calculated by comparing the measured signal for the sample with that for CS_2 as reference under the same experimental condition according to the following formula [19]:

$$\chi_s^{(3)} = \left(\frac{I_s}{I_r}\right)^{1/2} \frac{L_r}{L_s} \left(\frac{n_s}{n_r}\right)^2 \frac{\alpha L \exp(\alpha L/2)}{1-\exp(-\alpha L)} \chi_r^{(3)}$$

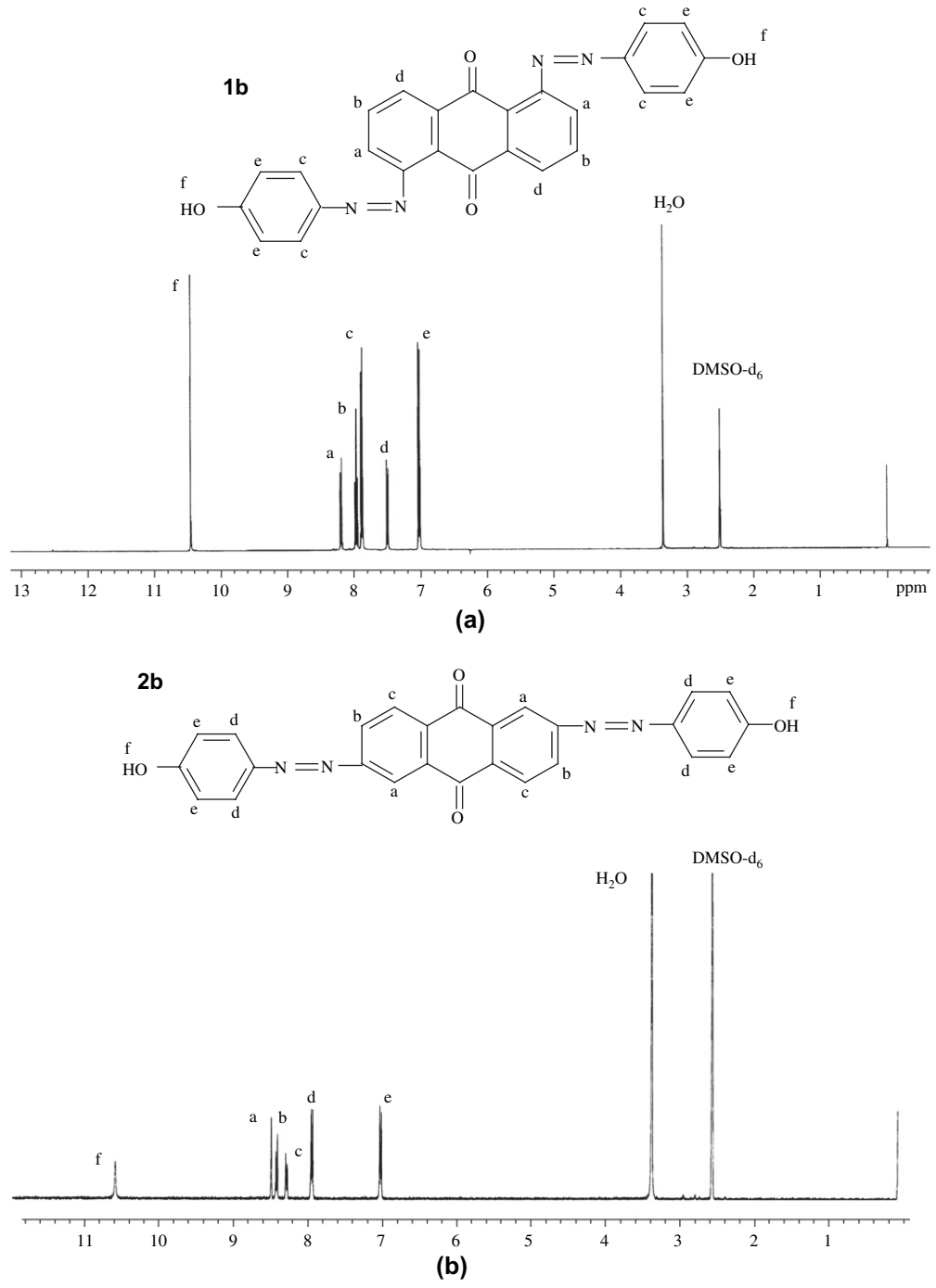


Fig. 3. ^{1}H NMR spectra of **1b** (a) and **2b** (b) in DMSO-d_6.

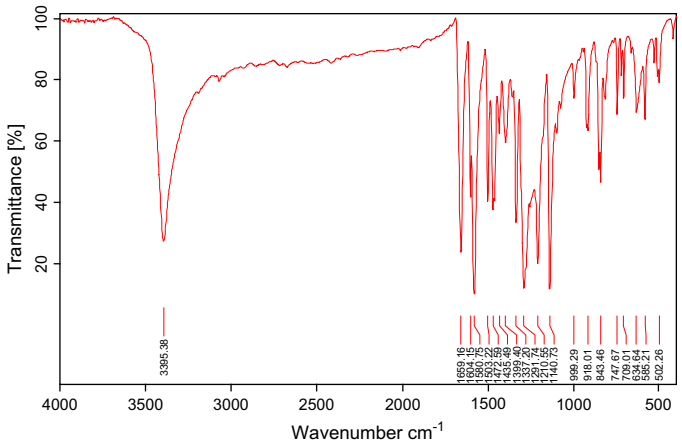
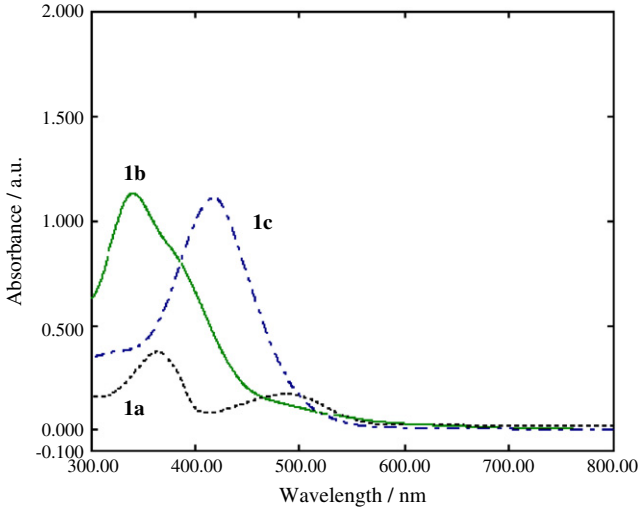


Fig. 4. FT-IR spectrum of **2b**.



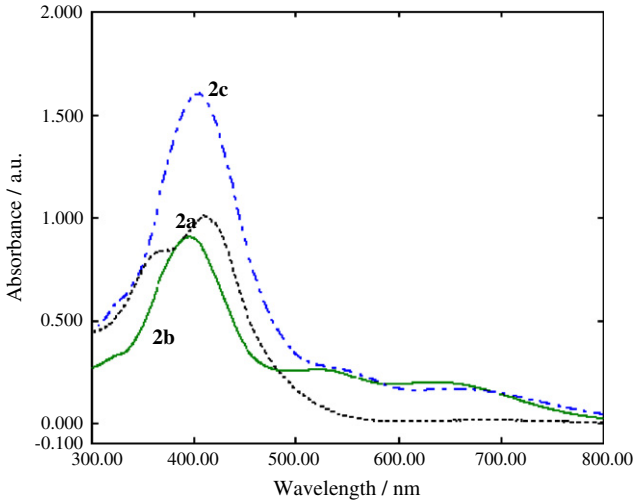


Fig. 5. UV–vis spectra of **1a**–**2c** in DMF.

where I is the intensity of the phase conjugated beam, L is the sample path length, n is the linear refractive index, and α is the linear absorption coefficient. The subscripts "s" and "r" refer to the sample and CS_2, respectively. The values of $\chi_r^{(3)}$ and n_r for CS_2 are 6.7×10^{-14} esu and 1.632, respectively [20].

The nonlinear refractive index n_2 in isotropic media is estimated through the equation [21]:

$$n_2(\text{esu}) = 12\pi\chi^{(3)}/n^2$$

where n is the linear refractive index of the solution.

The second hyperpolarizability γ of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by [22]:

$$\gamma = \frac{\chi^{(3)}}{Nf^4}$$

where N is the number density of the solute per milliliter, and f^4 is the local field correction factor which is $[(n^2+2)/3]^4$ (n is the linear refractive index of the solution).

The temporal response of the phase conjugate signal as a function of the delay time of the input beam is shown in Fig. 6. From Fig. 6, the response times of the samples could be obtained.

The values of $\chi^{(3)}$, n_2, γ and response times for the samples deduced and calculated from the experimental results are listed in Table 1.

These anthracenedione derivatives **1a**–**2c** possess highly delocalized π-conjugated electron system. Owing to the increase of the conjugation length, the values of γ are higher than those of the raw materials 1,5-diamino anthraquinone and 2,6-diamino anthraquinone, which are only 1.91×10^{-31} esu and 2.02×10^{-31} esu, respectively [23]. These derivatives contain electron-withdrawing carbonyl groups and electron-donating hydroxy, amino and methyl groups in the form of D–π–A–π–D, which makes the molecules have stronger intramolecular charge transfer. The strength of electron donor is 3-methyl-4-hydroxy > 4-amino > 4-hydroxy, so the values of γ are **c** > **a** > **b**. When 1,5-anthracenedione derivatives are compared to 2,6-anthracenedione derivatives, the γ values of the latter are larger than those of the former, which are attributed to the longer distance between electron donor and electron acceptor in the latter.

The results indicate that larger second-order hyperpolarizabilities and ultrafast response times can be obtained in these anthracenedione derivatives because of increasing conjugation length and D–π–A–π–D structure.

4. Conclusions

In conclusion, six anthracenedione derivatives possessing D–π–A–π–D structure were synthesized and characterized. The third-order nonlinear optical properties in the femtosecond range were investigated using DFWM technique at 800 nm. The results show that the γ increases as the strength of electron-donating groups, the distance between electron donor and electron acceptor and conjugation length increase. Moreover, the results reveal that these compounds possess ultrafast response times which are no more than 110 fs.

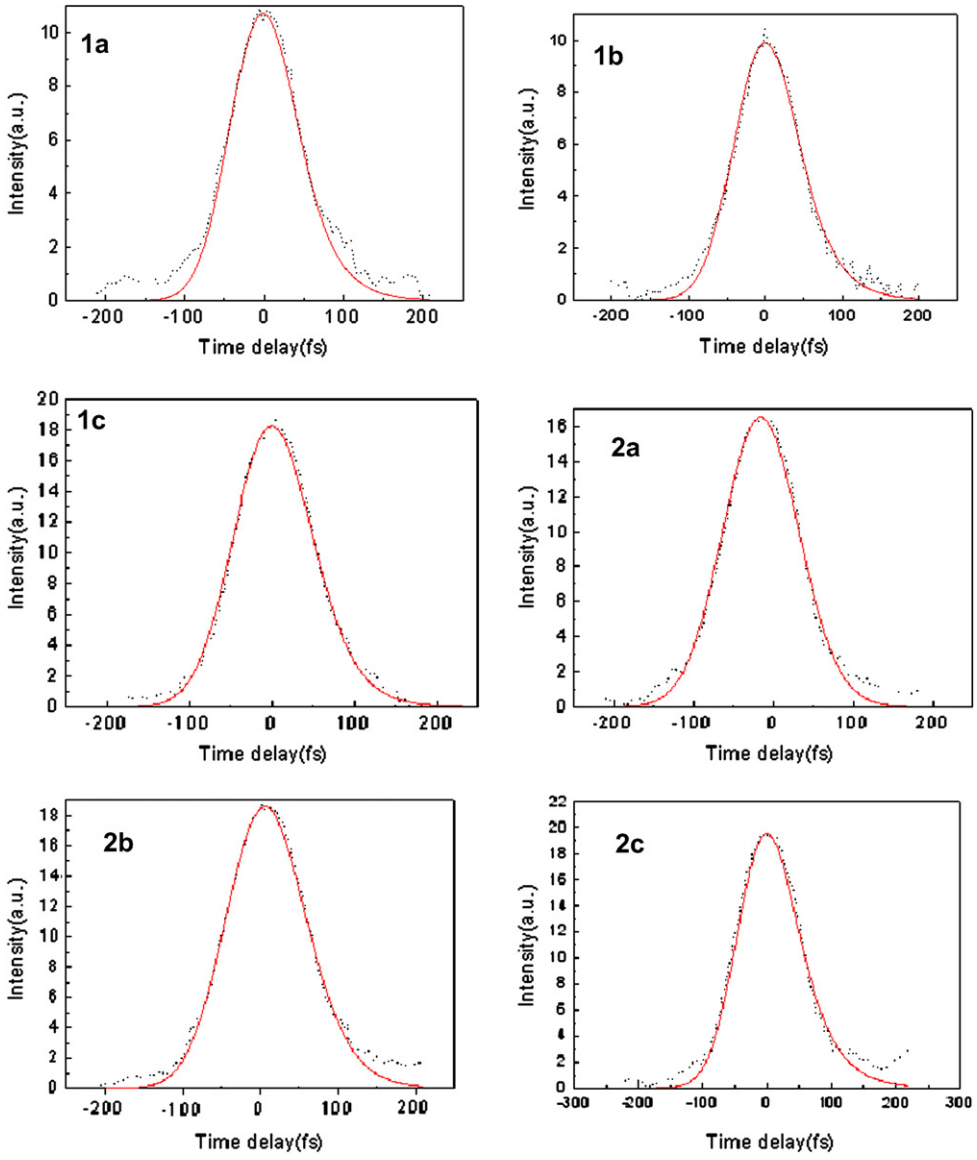


Fig. 6. DFWM signal versus delay time for **1a**–**2c** in DMF solution.

Acknowledgements

We are very grateful to Dr. Li Deng and Professor Zhenrong Sun, Key Laboratory of Optical and Magnetic Resonance Spectroscopy, East China Normal University, for the DFWM experiment and helpful discussion. This research was financially supported by the National Natural Science Fund of China (Grant no. 20376076).

Table 1
The values of $\chi^{(3)}$, n_2, γ and response times for **1a**–**2c**

Sample	c (10^{-4} mol/L)	n	$\chi^{(3)}$ (10^{-13} esu)	n_2 (10^{-12} esu)	γ (10^{-31} esu)	Response time (fs)
1a	4.70	1.4313	2.76	5.08	2.94	86
1b	4.60	1.4320	2.64	4.85	2.86	86
1c	5.46	1.4320	3.55	6.52	3.25	101
2a	4.60	1.4310	3.40	6.25	3.70	108
2b	5.10	1.4316	3.75	6.90	3.68	108
2c	5.00	1.4310	3.83	7.06	3.84	94

References

[1] Gao JR, Wang Q, Cheng LB. Mater Lett 2002;57:761.
[2] Sun WF, Bader MM, Carvalho T. Opt Commun 2003;215:185.
[3] Gang F, Takefumi Y, Kazuo K, Hiroakio O, Shunsuke T. Synth Met 2005;155:68.
[4] Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. John Wiley; 1991.
[5] Marder SR, Kippelen B, Jen AK-Y, Peyghambarian N. Nature 1997;388:845.
[6] Kanis DR, Ratner MA, Marks TJ. Chem Rev 1994;94:195.
[7] Linsday GA, Singer KD. Polymers for second-order nonlinear optics. Washington: ACS; 1995.
[8] Iraqi A, Wataru I. Chem Mater 2004;16(3):442.
[9] Kimoto A, Cho J, Higuchi M, Yamaoto K. Chem Lett 2003;32(8):674.

[10] Zhang Y, Wang L, Wada T, Sasabe H. Macromolecules 1996;29:1569.
[11] Hameurlaine A, Dehaen W. Tetrahedron Lett 2003;44:957.
[12] Grigalevicius S, Blazys G, Ostrauskaite J, Grazulevicius JV, Gaidelis V, Jankauskas V, et al. J Photochem Photobiol A: Chem 2003;154:161.
[13] Zhang X, Muenster R, Jarasch M. Mol Cryst Liq Cryst Sci Technol 1998;Sect A(321):609.
[14] Matsui M, Sedyohutomo A, Satoh M, et al. Dyes Pigments 1998;40:21.
[15] Yang S, Yang M. Chin J Struct Chem 2000;19(4):301.
[16] Reichel I, Schmidt W. Rev Chim Acad Rep Populaire Roumaine 1960;5(1):107.
[17] Toshio M. J Soc Chem Ind Jpn 1931;34:51.
[18] Gatterman L, Rolfe H. Ann 1921;425:135.
[19] Yang Y, Samoc M, Prasad PN. J Chem Phys 1991;94:5282.
[20] Orczyk ME, Samoc M, Swiatkiewicz J, Prasad PN. J Chem Phys 1993;98:2524.
[21] Jenekhe SA, Lo SK, Flom SR. Appl Phys Lett 1989;54(25):2524.
[22] Mandal BK, Bihari B, Sinha AK, Kamath M, Chen L. Appl Phys Lett 1995;66:932.
[23] Gao JR, Chen X, Cheng LB, Zheng YD, Wu JZ. Acta Opt Sin 1998;18(5):533.