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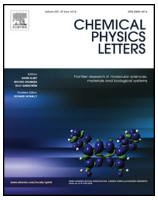

Synthesis, characterization and third-order nonlinear optical properties of symmetrical ferrocenyl Schiff base materials

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ABSTRACT

Six symmetrical ferrocenyl Schiff base materials were synthesized and characterized by UV, ^1H NMR, mass spectrometry (MS) and elemental analysis. Their off-resonant third-order nonlinear optical properties were measured using femtosecond laser and degenerate four-wave mixing (DFWM) technique. The third-order nonlinear optical susceptibilities $\chi^{(3)}$ were 1.961–6.363 × 10^{-13} esu. The nonlinear refractive indexes n_2 were 3.609–11.716 × 10^{-12} esu. The second-order hyperpolarizabilities γ of these molecules were 1.967–6.388 × 10^{-31} esu. The response time were 45.759–73.079 fs. The results indicate that these materials have potential nonlinear optical applications.

1. Introduction

There is a flurry of interest in the research and development with large third-order nonlinear optical (NLO) materials due to their potential applications prospects [1–4]. Metal organic NLO materials are of typical ones amongst them. A great deal of metal organic nonlinear optical materials have been investigated in the past decades and well known for their third-order nonlinear properties, *i.e.* metal-substituted phthalocyanines and poly(metal-ynes) [5–9]. These materials have been investigated as alternatives to inorganic species due to their low cost, fast and large nonlinear response over broad frequency range, inherent synthetic flexibility, high optical-damage threshold, and intrinsic tailorability [10–12]. As one type of metal organic materials, ferrocene metal organic compounds have unique electrochemical and optical properties, and thus showing great potential applications in optical [13–17] and other high-tech fields. NLO properties are key indexes in studying organic NLO materials. The third-order nonlinear properties of materials have attracted extensive interest [18–22].

Ferrocene derivative NLO materials are generally formed by the connection of the electron donating and withdrawing groups through the π-electron bridge, and this unique structural feature helps them obtain a higher nonlinear optical response [23,24]. For this reason, researchers have focused on synthesizing various compounds containing π-electron bridge which includes carbon–carbon double bonds (—C=C—) and carbon-nitrogen double bonds (—C=N—). The electron donating units in the push–pull system are usually aromatic rings, heteroaromatics and other chromophores. However, few studies have been carried out on the synthesis and optical nonlinearities of symmetrical ferrocene derivatives, which could become a good optical application. Therefore, it is essential for this research to be thoroughly explored. Our interest is particularly focused on investigating whether introducing various aryl symmetrical Schiff base groups into ferrocene molecule will have huge impact on the nonlinear optical response. Herein, We report the design and synthesis of a series of six symmetrical ferrocenyl Schiff base compounds **1**–**6** (Figure 1) which possess the bridge of carbon–nitrogen double bonds (—C=N—), being expected to greatly enhance their third-order optical nonlinearities. Our six representative compounds contain not only phenyl, substituted phenyl with electron-donating and electron-withdrawing groups, but also heterocycles. These compounds were characterized by UV, ^1H NMR, MS and elemental analysis. Their third-order NLO properties were measured using DFMW technique (Figure 2). The results indicate that these ferrocenyl derivatives possess large and ultrafast third-order NLO responses, showing great potential applications in photonics.

2. Experimental

2.1. Preparation and structural characterization

2.1.1. Synthesis of ferrocene-1,1′-dicarbaldehyde

The synthetic method was based on the literature reports [25]. ^1H NMR (500 MHz, $CDCl_3$) δ 9.950 (s, 1H, –CHO), 4.887 (s, 2H, Cp-H), 4.676 (s, 2H, Cp-H).

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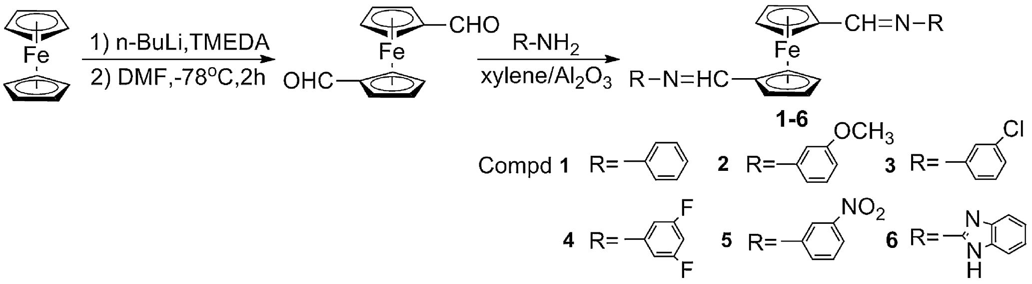

Figure 1. The synthetic routes of ferrocenyl Schiff base derivatives.

*2.1.2. Procedure for synthesis of Compounds **1–6***

Ferrocene-1,1′-dicarbaldehyde (0.22 g, 0.90 mmol), aromatic amine(2.14 mmol), and 75 mL xylene were sequentially added to a 150 mL three-neck round bottom flask. When the ferrocene-1,1′-dicarbaldehyde was completely dissolved with stirring vigorously, 0.2 g basic Al_2O_3 (1.96 mmol) was added. The reaction mixture was heated to reflux for 8 h and then filtered. Solvent was evaporated and the product was washed with solvent, affording a correspond-ing product in a certain yield.

Compound **1** was synthesized according to the general procedure above. After the reaction was completed, the reaction mixture was concentrated to give red oil product which was washed with petroleum ether and dichloromethane, giving a red needle crystalline solid in 89.9% yield. m.p. 92–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.325 (s, 2H, —CH=N—), 7.333 (t, J = 8 Hz, 4H, Ar-H), 7.204 (t, J = 7.5 Hz,2H, Ar-H), 7.132 (t, J = 7.5 Hz, 4H, Ar-H), 4.890 (t, J = 2 Hz, 4H, Cp-H), 4.556 (t, J = 4 Hz, 2H, Cp-H). MS (ESI): m/z = 393.1 $(M+H)^+$. Elem. Anal. Calcd for $C_{24}H_{20}N_2Fe$: C, 73.48; H, 5.14; N, 7.14. Found: C, 73.29; H, 5.26; N, 7.09.

Compound **2** was washed with petroleum ether to give reddish brown oil product in 24.3% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.326 (s, 2H, —CH=N—), 7.230 (t, J = 8 Hz, 2H, Ar-H), 6.802 (d, J = 10 Hz, 2H, Ar-H), 6.761 (d, J = 8 Hz, 2H, Ar-H), 6.710 (d, J = 9.5 Hz, 2H, Ar-H), 4.879 (s, 4H, Cp-H), 4.558 (s, 4H,Cp-H), 3.809 (s,6H, –OCH_3). MS (ESI): m/z = 463.09 $(M+H)^+$. Elem. Anal. Calcd for $C_{26}H_{24}N_2O_2Fe$: C, 69.04; H, 5.35; N, 6.19. Found: C, 68.95; H, 5.41; N, 6.13.

Compound **3** was washed with petroleum ether and ethyl acetate to afford a red solid product in 89.9% yield. m.p. 90–91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.282 (s, 2H, —CH=N—), 7.236 (t, J = 8 Hz, 2H, Ar-H), 7.163 (d, J = 8 Hz, 2H, Ar-H), 7.101 (d, J = 1.5 Hz, 2H, Ar-H), 6.975 (d, J = 8 Hz, 2H, Ar-H), 4.887 (s, 4H, Cp-H), 4.574 (s, 4H, Cp-H). MS (ESI): m/z = 461.04$(M+H)^+$. Elem. Anal. Calcd for $C_{24}H_{18}N_2Cl_2Fe$: C, 62.51; H, 3.93; N, 6.07. Found: C, 62.41; H, 3.89; N, 6.14.

Compound **4** was washed with petroleum ether to give a red solid product in 49.9% yield. m.p. 114–115 °C.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.249 (s, 2H, —CH=N—), 6.620 (d, J = 1.5 Hz, 4H, Ar-H), 6.605 (s, 2H,A-rH), 4.892 (s, 4H, Cp-H), 4.591 (s, 4H,Cp-H). MS (ESI): m/z = 465.2 $(M+H)^+$. Elem. Anal. Calcd for $C_{24}H_{16}N_2F_4Fe$: C, 62.09; H, 3.47; N, 6.03. Found: C, 62.18; H, 3.58; N, 6.01.

Compound **5** was washed with petroleum ether and ethyl acetate to afford a red solid product in 45.2% yield. m.p. 188–189 °C. ^{1}H NMR (500 MHz, $CDCl_3$):δ 8.341 (s, 2H, —CH=N—), 7.977 (d, J = 8 Hz, 2H, Ar-H), 7.833 (d, J = 1.5 Hz, 2H, Ar-H), 7.410 (t, J = 8 Hz, 2H, Ar-H), 7.365 (d, J = 8 Hz,1H, Ar-H),4.963(d, J = 1.5 Hz, 4H, Cp-H), 4.631 (t, J = 1.5 Hz, 4H,Cp-H). MS (ESI): m/z = 482.98$(M+H)^+$. Elem. Anal. Calcd for $C_{24}H_{18}N_4O_4Fe$: C, 59.77; H, 3.76; N, 11.62. Found: C, 59.64; H, 3.79; N, 11.55.

Compound **6** was synthesized following the general procedure described above. After the reaction was completed, the reaction mixture was concentrated under vacuum to afford red oil crude, the crude product was washed with petroleum ether and ethanol to give a black powder-like solid product in 20.5% yield. m.p.

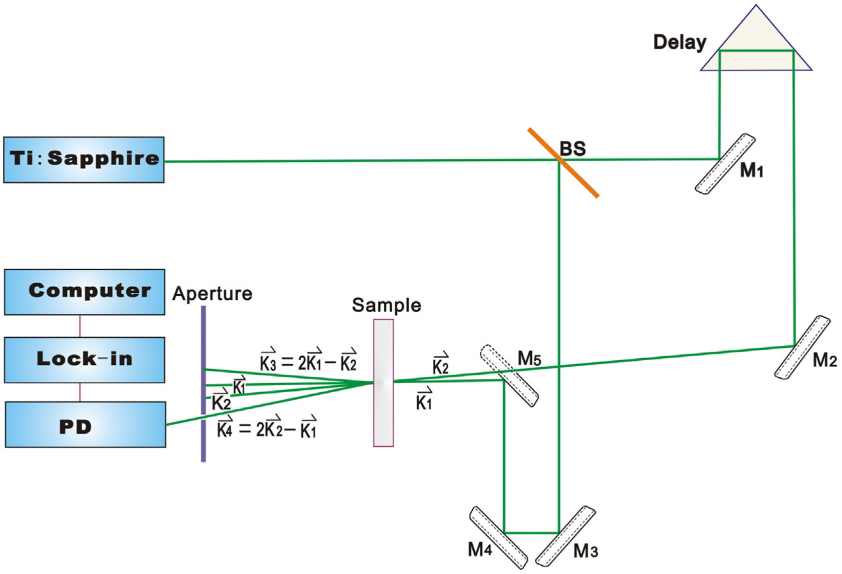

Figure 2. Experimental setup of DFWM.

91–93 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 9.955 (s, 2H, —CH=N—), 7.775–6.962 (m, 8H,Ar-H), 6.605 (s, 2H, Ar-H), 4.896 (s, 2H, Cp-H), 4.642 (s,2H,Cp-H). MS (ESI):cacld for (M+H)$^+$:473.1169 found m/z = 473.1174. Elem. Anal. Calcd for $C_{26}H_{18}N_6Fe$: C, 66.40; H, 3.86; N, 17.87. Found: C, 66.29; H, 3.82; N, 17.92.

2.2. Nonlinear optical properties measurement

DFWM technique is a conventional method for measuring both electronic and dynamic nonlinearities. The theories and working procedures for DFWM have been shown and discussed in many literature reports [26–32]. In our letter, the third-order NLO properties were measured using femtosecond DFWM technique, with a Ti: Sapphire laser. The laser power of our measurements was 0.8 mj, and the pulse width was determined to be 40 fs on a SSA25 autocorrelator. The operating wavelength was centered at 800 nm, and the repetition rate of the pulses was 1 kHz. Figure 2 shows the experimental setup. In this setup, 'BS' stands for beam splitter, M_1–M_5 represent specific mirrors in the experiments. There are also four beams in this setup, and the wave-vectors k_1, k_2, k_3, k_4 represent the two split beams and the other two generated beams, respectively. It is essential that the ω_i of these four beams are approximately the same (ω_i indicates the frequency of a beam), that is $\omega_1 = \omega_2 = \omega_3 = \omega_4$. k_3 and k_4 were generated from the two split beams (k_1,k_2) being overlapped and mixed spatially in the samples. And the relations of these four wave-vectors were as follows: $k_3 = 2k_1 - k_2$, $k_4 = 2k_2 - k_1$ ($2k_1$, $2k_2$ represent the second-harmonic generation of k_1, k_2). The intensity of k_3 or k_4 indicates the third-order nonlinear optical properties of the corresponding material.

During the measurement, the laser was set to be stable. The input beam was split into two beams k_1 and k_2 with nearly equal energy by use of a beam splitter, then focused on a plot of the sample. The beam k_2 passed through a delay line driven by a stepping motor so that the optical path length difference between k_2 and k_1 beams could be adjusted during the measurement. The angle between beams k_1 and k_2 was around or less 5°. Beams k_3 and k_4 were generated when k_1 and k_2 were overlapped spatially in the sample. k_4 passed through an aperture, recorded by a photodiode and subsequently analyzed by a Lock-in amplifier and computer.

In our experiments, the third-order nonlinear optical susceptibility $\chi^{(3)}$ was measured *via* a comparison with that of a reference sample CS_2. This value was calculated from the DFWM signal (I), which originated from the beams k_4 processed by Lock-in amplifier and computer. During experiments, we found that the signal intensities values were quite different for various samples, however it did litter impacts on the calculations and final results. For these six compounds, the measuring intensities ranged from 20 a.u. to 50 a.u. in our work. The DFWM signal curve for CS_2 and signal for solution (dichloromethane) are available in Support Information.

3. Results and discussion

Figure 3 displays the UV–visible absorption spectra for six compounds dissolved in dichloromethane. The laser wavelength (800 nm) used in the experiment of DFWM was out of the absorption region. In order for the off-resonant third-order optical nonlinearities of the compounds to be measured. The solvent dichloromethane has no nonlinear signal under the light intensity used, so the third-order optical nonlinearities measured come from those six compounds only.

The third-order nonlinear optical susceptibility $\chi^{(3)}$ is measured *via* a comparison with that of a reference sample CS_2. This value was calculated from the DFWM signal (I), the linear refractive index (n), the sample thickness (L) and absorption correction factor using the following equation [33]

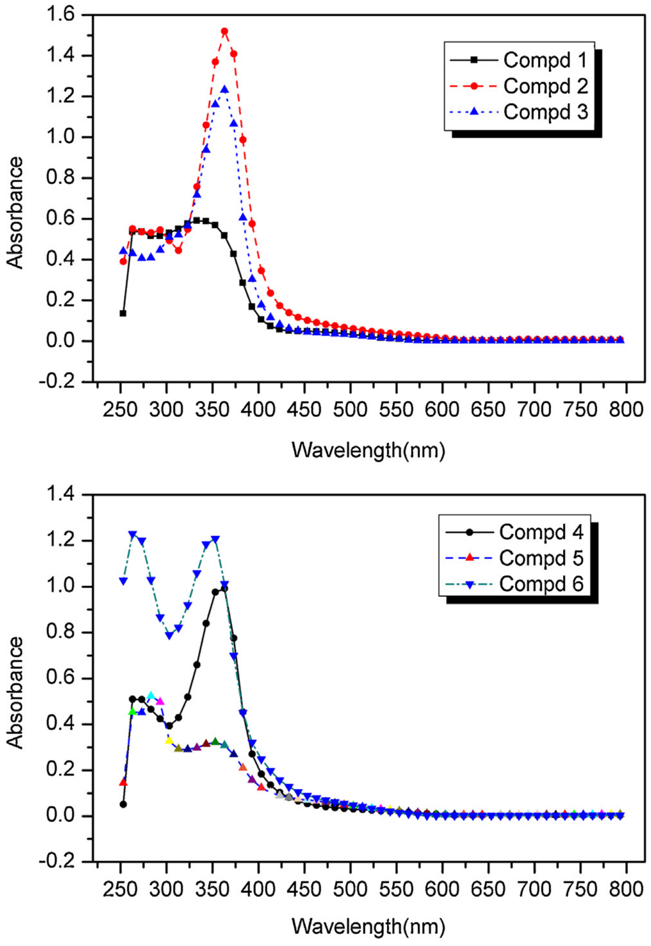

Figure 3. The UV–vis absorption spectra of Compounds **1–6**.

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

where the subscripts 's' and 'r' represent the parameters for the sample and CS_2. And α is for the linear absorption coefficient. The fraction ($\alpha L\exp(\alpha L/2)/1 - \exp(-\alpha L)$) comes from the sample absorption and is equal to 1 approximately while the sample has little absorption around the used laser wavelength. Therefore, the above equation can be simplified as the following,

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

The values of $\chi_r^{(3)}$ and n_r for CS_2 are 6.8×10^{-13} esu and 1.632, respectively [34]. The nonlinear refractive index n_2 in isotropic media is estimated through the equation [35] $n_2(\text{esu}) = 12\pi\chi^{(3)}/n_s^2$, where n_s is the linear refractive index of the measured samples solution, measured by 2WAJ Abbe refractometer.

The second-order hyperpolarizability γ of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by [36]: $\gamma = \chi^{(3)}/(Nf^4)$, $f = (n_s^2 + 2)/3$ where N is the number density of the solute per milliliter, and f^4 is the local field correction factor (n_s is the linear refractive index of the measured samples solution as above).

The temporal response of the phase conjugate signal as a function of the delay time of the input beam is shown in Figure 4. The curves are obtained *via* fitting the time convolution between autocorrelation function of pulse and single exponent decline function $\exp[t/(-T_2)]$. The response time (τ) of the samples is corresponded

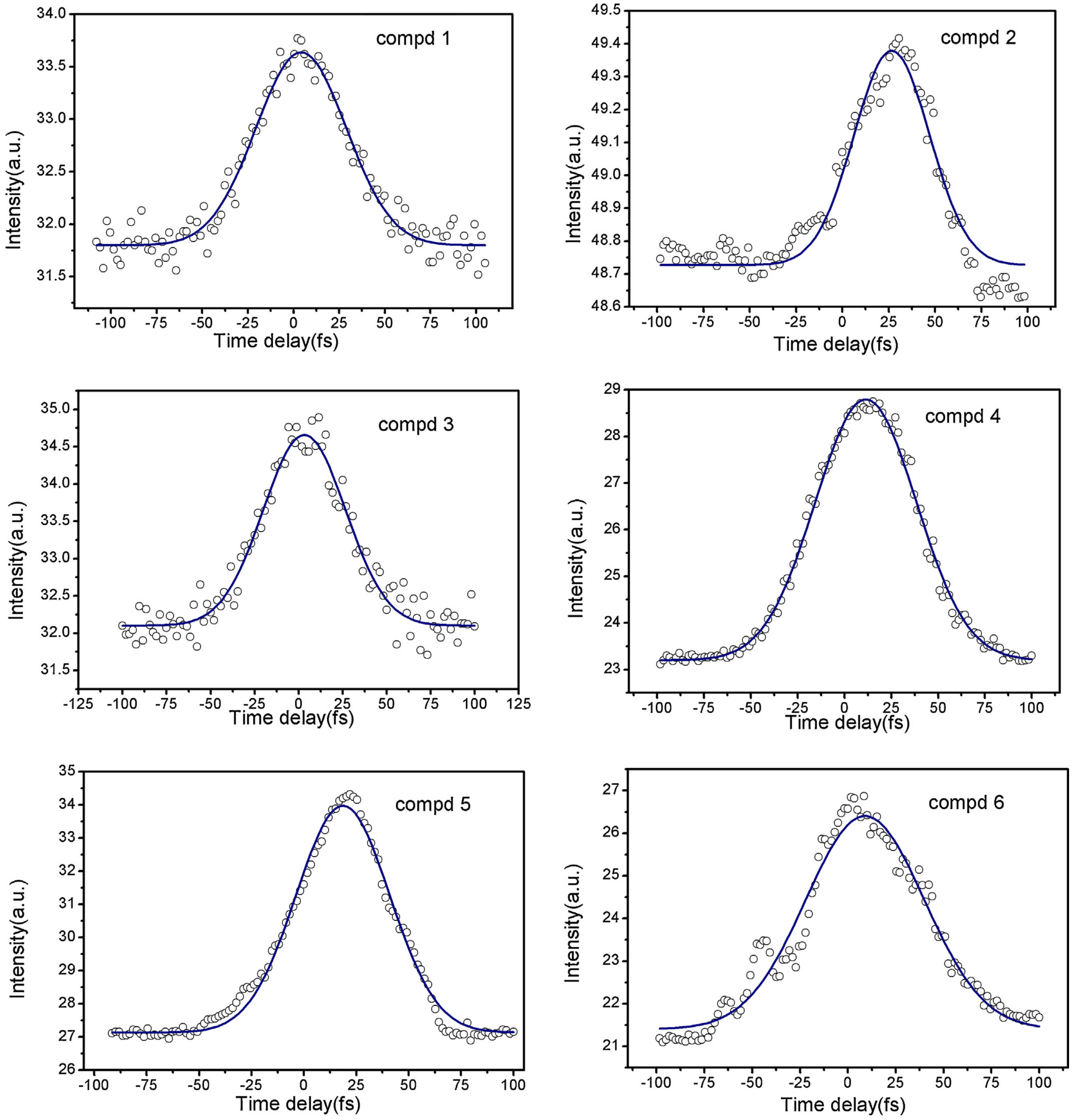

Figure 4. DFWM signal *versus* delay time for Compounds **1–6** in dichloromethane solution.

Table 1
The relevant parameters values for Compounds **1–6**.

Compound[a]	λ_{max} (nm)	ε_{max} ($L\,mol^{-1}\,cm^{-1}$)	n	$\chi^{(3)}$ (10^{-13} esu)	n_2 (10^{-12} esu)	γ (10^{-31} esu)	τ (fs)
1	335	4702	1.4306	3.307	6.088	3.319	49.842
2	365	4684	1.4308	1.961	3.609	1.967	49.705
3	363	4781	1.4309	3.935	7.242	3.946	45.759
4	368	4859	1.4306	5.713	10.518	5.733	60.836
5	285	4902	1.4305	6.363	11.716	6.388	51.342
6	265	4895	1.4309	5.470	10.067	5.483	73.079

[a] The experimental data except λ_{max} and ε_{max} were obtained in 5.0×10^{-4} mol/L solution.

to the half-peak width, and the intensity of the optical conjugate wave (I) is corresponded to the peak height. The values of $\chi^{(3)}$, n_2, γ and response time for the samples were deduced and calculated from the experimental results are listed in Table 1.

Saswati Ghosal et al. [18] used the femtosecond laser (the light source is Nd:YAG laser, wavelength 602 nm, pulse width 400 fs) and the optical path of the DFWM experiment for the measurement, and obtained γ (ferrocene) was $1.61 \pm 0.18 \times 10^{-35}$ esu. Other than that, the representative γ values for 1-styrylferrocene ($FcCH=CH\text{-}C_6H_5$) and 1,1′-distyrylferrocene ($Fc(CH=CHC_6H_5)_2$) which possessed carbon–carbon double bond as the bridge group were $8.55 \pm 1.98 \times 10^{-35}$ esu, $2.70 \pm 0.26 \times 10^{-34}$ esu, respectively. Moreover, the γ values for some similar materials (single-substituted ferrocenyl Schiff bases) reported in the same experimental conditions ranged from 2.10×10^{-31} to 3.15×10^{-31} esu [37]. However, our results showed that the γ values of our six compounds were in the range of $1.967–6.388 \times 10^{-31}$ esu. Obviously, the second-order hyperpolarizabilities of our molecules (except **2**) are several orders or much higher than those results by researchers listed above. The enhancement of the NLO properties for our materials by comparison with most reported compounds is believed to the increasing of the conjugation length and nitrogen atoms within the molecules possessing lone pair electrons.

In addition to these ferrocene derivatives **1**–**6** containing a conventional electron-donating centered ferrocene ring, the symmetrical bis-imino (conjugate π system)groups introduced into ferrocene display a structure feature of π–donor–π (π–D–π), which leads to a higher degree conjugation, thus providing a better chance for charge transfer. As a result, the designed compounds gave better optical properties than the starting material ferrocene as well as those reported single substituted ferrocene derivatives. On the other hand, those with 3-chrolobenzene or 3,5-difluorobenzene moieties which contain electron-withdrawing functionalities, together with carbon–nitrogen double bonds (—C=N—) can, in theory, significantly interact with the electron-rich ferrocenyl at the center of the molecules, thus forming a structure feature of acceptor–π–donor–π–acceptor (A–π–D–π–A),which significantly increases the probability of charge transfer. In principle, the better the electron acceptor is, the higher degree for the hyperpolarizability of the molecule will be. Due to the halogen's dual electronic nature of electron-withdrawing *via* induction and electron-donating *via* conjugation within the molecules, the decreasing order of electron acceptor is as the following 3,5-difluro > 3-Cl, which is consistent with the order of **4** > **3**. Since nitro group is a strong electron-withdrawing group, Compound **5** gave high γ value without surprise. Compared with the structure of Compound **1** (π–D–π), Compounds **3**–**5** gave higher γ values as expected. Whereas compound **2** with an electron-donating methoxyl group and double aryl imino groups with ferrocene is believed to adopt a structure feature of donor–π–donor–π–donor (D–π–D–π–D). By comparison of D–π–D–π–D with A–π–D–π–A structure unit, the latter is obviously more conducive to the flow of the intramolecular electrons. Therefore, the γ values of compounds **3**–**5** are all higher than that of compound **2** as expected. Moreover, D–π–D–π–D structure is theoretically more disadvantageous with regard to the flow of intramolecular electrons than π–D–π system, which is verified by the experimental results, and the γ value of Compound **2** is even lower than that of Compound **1**. Because of the fused heterocyclic structure unit, compound **6** has higher degree of electron delocalization with lower delocalization energy than the benzene ring. As a result, intramolecular charge transfer with Compound **6** is more prone to occur under the action of external electric field. Therefore, compound **6** shows comparatively high γ value. Consequently, the decreasing order of γ values in principle for these material molecules is as follows: **5**, **4** > **3** > **1** > **2**; **6** > **1**, thus being fully consistent with the experimental results listed in Table 1.

In summary, these six compounds exhibit good third-order nonlinear optical properties with different $\chi^{(3)}$, γ, n_2 values and response time due to their individual structure features.

4. Conclusions

Six organometallic third-order nonlinear optical materials of the symmetrical ferrocenyl Schiff base were synthesized and characterized. Their off-resonant third-order NLO were investigated by the DFWM technique. Their large and ultrafast nonlinearities are believed to originate from the large increase for the degree of the conjugation system, extensive electronic delocalization and polarization. The factors such as long conjugation system, formation of π–D–π structure, strong electron-donating abilities of substituents, and symmetry of the molecule all contribute to the high third-order optical nonlinearity.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:10.1016/j.cplett.2015.01.057.

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