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Investigation of third-order nonlinear optical properties of two azo-nickel chelate compounds*

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This paper investigates the third-order nonlinear optical properties of two azo-nickel chelate compounds by the optical Kerr gate method at 830 nm wavelength with pulse duration of 120 fs. Both of the two compounds exhibited large third-order optical nonlinearity. The second-order hyperpolarizability, γ, of Compound 1 is of 1.0×10^{-31} esu. Due to the charge transfer, the γ of Compound 2 with electron donor and acceptor group is 4.9×10^{-31} esu, which is a four-time enhancement in comparison with Compound 1. The absorption spectra show that the electron push–pull effect, which induces intramolecular charge transfer, leads to the increased optical nonlinearity.

Keywords: nonlinear optics, ultrafast, azo chelate
PACC: 4265, 4280, 3300

1. Introduction

Besides an important class of dyes for textile industry, azo dyes attract interest in the fields of optical storage[1−5] and nonlinear optics.[6−8] Previous reports[9,10] showed that the third-order optical nonlinearity were significantly enhanced by the formation of organic–metal complexes.[11,12] Charge-transfer between metal and organic ligand leads to the intramolecular electron delocalization, which is generally considered to be responsible for the enhancement. Therefore, electron donor and acceptor groups were connected as azo-metal compounds. On the other hand, different from those main group metals, the transition metal atoms have unoccupied *d*-orbits. The *d*-orbit overlapping with π-orbits is more efficient in nonlinear optical effects than main group elements.[13] Based on these ideas, the transition metal-azo chelates have been synthesized for nonlinear optical materials.[14−16] These experiments show that they have large third-order optical nonlinearity in comparison with the monomers. In addition, their second-order hyperpolarizability, γ, varied according to laser wavelengths. For example, at 830 nm, the γ was about 10^{-32} esu,[16] while it is 10^{-29} esu at 647 nm.[14] The thin film was also tested with $\chi^{(3)}$ 10^{-8} esu at 532 nm.[15] The high nonlinear optical response at 647 nm and 532 nm were attributed to resonant enhancement, since these wavelengths were within the absorption bands.

2. Sample and experimental setup

In this paper, we report our investigation on the third-order optical nonlinearity of two azo-nickel chelate compounds, compound 1 (C1) and compound 2 (C2), as shown in Fig.1.

The two compounds are similar in structure. The primary difference is that the former one has no electron donor group and acceptor group attached to the azo ligands while the later one has. The synthesis followed the procedure reported previously.[17] For C2, 2-amino-6-carbomethoxybenzothiazole was diazotized with solid sodium nitrite in 85% phosphoric acid under 0–5°C in an ice-brine bath. Then the as-prepared

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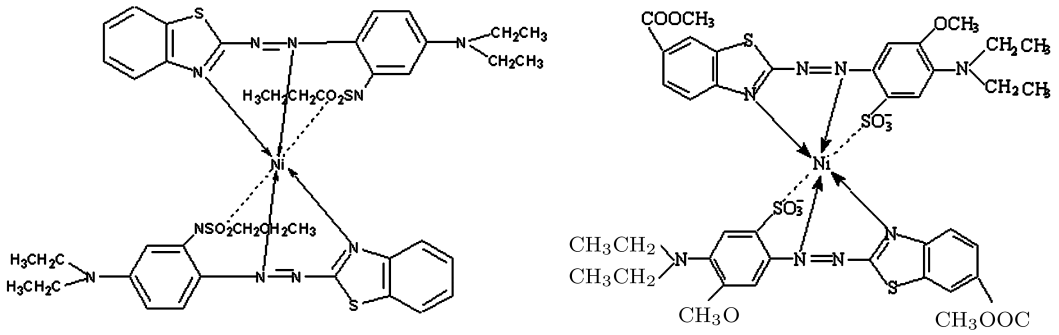


Fig.1. Molecular structures of C1 (left) and C2 (right).

diazonium solution was added portion-wise to the coupling component, *N*, *N*-diethyl-o-anisidine-4-sulphonic acid dissolved in a 2:1 mixture of water and acetic acid. The azo dye then formed. Subsequently, the azo dye was metallized with nickel acetate to produce chelate C2. By replacing the 2-amino-6-carbomethoxybenzothiazole with 2-aminobenzothiazole, and using a coupling component, 3-(*n*-propylsulfonylamnio)-*N*, *N*-diethylaniline dissolved in the 1:1 mixture of water and acetic acid, the chelate C1 was obtained. Analysis confirmed that both C1 and C2 are ML_2 type coordination configuration.

The nonlinearities of the samples were tested by the time-resolved optical Kerr gate (OKG) technique.[18] The laser source is a Ti:sapphire laser system (Mira 900 F, Coherent, USA) pumped by a solid state green pump laser (Verdi-10, Coherent, USA). The system delivers laser pulse of 120 fs, at 830 nm, 76 MHz. The laser beam was split into two portions with intensity ratio of 12:1. The stronger one acted as pump beam while the weaker one was probe beam. The polarizations between the two linear polarized beams were adjusted to 45°. The two beams propagated parallel before being focused by a single convex lens. The pump beam and the probe beam overlapped in the 1 mm-thick sample cell, which was placed at focus. After the sample cell, the pump beam was blocked; the probe beam was collimated and then went through a polarization analyser, whose transmitting axis is perpendicular to the original polarization of the probe beam. The analyser picked out the generated Kerr signal. Finally, it was collected by a photodiode connected to a lock-in amplifier (Stanford, SR830). For time-resolved measurement, the pump beam propagated through an optical delay line driven by a step motor to provide relative temporal delay to the probe beam. To improve the signal to noise ratio, dual-beam chopping with different frequency was applied.

3. Results and discussion

Both of the compounds were dissolved in 2,2,3,3-tetrafluoro-1-propanol at concentrations of about 10^{-4} mol/l. The optical Kerr (OKE) response of the solvent was small and neglectable. The OKE response of C1 was shown in Fig.2. It is a symmetric curve with its full width at half maximum similar to the laser pulse width of 120 fs. It proved that the signals came from the electronic instantaneous response.

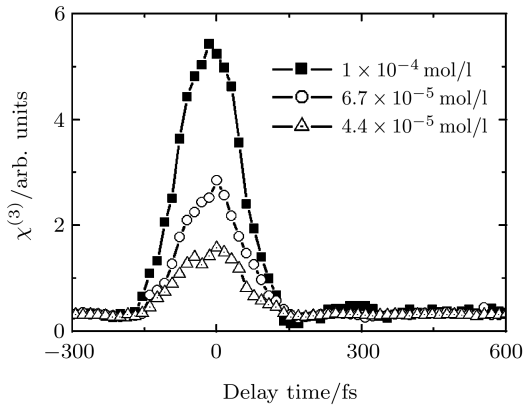


Fig.2. OKE signal of C1 at concentrations of 1×10^{-4} mol/l, 6.7×10^{-5} mol/l and 4.4×10^{-5} mol/l.

The third-order optical susceptibility of the sample was calculated by comparison with the reference sample, CS_2, which was tested under the same condition. As the $\chi^{(3)}$ of CS_2 was accredited as 1×10^{-13} esu,[19] $\chi^{(3)}$ of the sample solutions can be

calculated with the following equation:

$$\chi_{\mathrm{S}}^{(3)} = \chi_{\mathrm{R}}^{(3)} \left(\frac{I_{\mathrm{S}}}{I_{\mathrm{R}}}\right)^{\frac{1}{2}} \left(\frac{n_{\mathrm{S}}}{n_{\mathrm{R}}}\right)^{2} \frac{\alpha l}{\mathrm{e}^{-\alpha l/2}(1-\mathrm{e}^{-\alpha l})}, \quad (1)$$

The subscripts, S and R, refer to sample and reference; I, n, α and l are the optical Kerr signal intensity, the refractive index, the absorption coefficient, and the effective length of the sample respectively. $\chi^{(3)}$ of C1 solution at of 1×10^{-4} mol/l was calculated as 0.37×10^{-13} esu. The concentration dependence were also verified under the same condition. This means that the nonlinearites observed is from isolated single molecule instead of any aggregation effect. The third-order optical nonlinearity of the single molecule, i.e., the second-order hyperpolarizability, γ, was calculated as:

$$\gamma = \chi^{(3)}/(NL), \quad (2)$$

where N is the concentration of the molecule, L is the local field correction factor, which is defined as $L = [(n^2+2)/3]^4$. The γ of C1 was then obtained as 1.0×10^{-31} esu. Same procedure was applied to C2. Its γ was 4.9×10^{-31} esu. Comparing with other organic compounds, we find that the two samples have relatively large third-order optical nonlinearities at this non-resonant condition.

Heflin*et al*[20] pointed out that the non-resonant second-order hyperpolarizability mainly came from virtual transitions between states that produce large charge separation. This charge separation can be improved by introducing conjugation into the system. Generally, there are two ways to produce charge-transfer states: the first is to connect electron donor groups and acceptor groups with molecular conjugation systems, the other is to introduce metal atom into conjugation systems to form a coordinate compound. In the later case, the transfer of electron density between the metal atom and the conjugated ligands leads to large molecular hyperpolarizability. Tailoring these materials with various central metal atoms, we find that their oxidation states, sizes and so on can optimize the nonlinear optical properties of the system.

For our samples, the large third-order optical nonlinearities came from intramolecular charge transfer, which are shown in the absorption spectra. In azo system, there are three absorption bands in UV–visible region.[21] The band at 200–300 nm is the $\phi - \phi^*$ transition localized in aromatic system, which is not sensitive to the environment. The band at 300–400 nm is $\pi - \pi^*$ transition, which is very sensitive to substituent effect. The 400–500 nm band comes from $n - \pi^*$ transition. This transition is partially forbidden. When the respective components in the azo system are substituted by electron donating groups, or, metal atoms, $\pi - \pi^*$ band will undergo a large bathochromic shift and may overlap with $n - \pi^*$ band, as shown in Fig.3 for 450–800 nm.

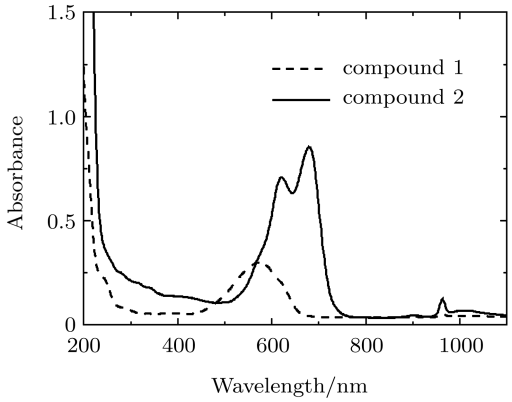


Fig.3. Absorption spectra of C1 and C2.

In C2, even the $\pi - \pi^*$ transition shifts to the right of the $n - \pi^*$ transitions. In C1, this band is mainly contributed from $\pi - \pi^*$ transition, while the $n - \pi^*$ transition appears as shoulder on red side. It can be seen that the $\pi - \pi^*$ transition undergoes a large bathochromic shift due to the intra-molecular electron transfer. Large molecular hyperpolarizabilities are then expected. The bathochromic shift in C2 is much larger than that of C1. We refer this difference to the electron push–pull effect formed by the $COOCH_3$ and OCH_3 groups attached to the azo component. This effect enhances the charge transfer in this compound. Greater third-order optical nonlinearity for C2 was observed.

According to the three-level model,[22,23] the mechanism for the third-order optical nonlinearity can be expressed by three terms: the one-photon resonance term, the two-photon resonance term and the dipole moment difference term. At wavelength of 830 nm, the absorption of the two compounds is nearly zero. One-photon resonance is minimized. At two-photon resonant wavelength, 415 nm, their absorption is very small, the two-photon absorption can be neglected also. Then the third-order optical nonlinearity of the two compounds came from the dipole moment difference between ground state and excited state. That means the nonlinearity came from the charge separation in laser excitation field.

4. Conclusion

The third-order optical nonlinearities of the two Ni-azo compounds were measured by time-resolved OKE method. Both compounds exhibited large second-order hyperpolarizability. By analysing their absorption spectra, the third-order nonlinearities are figured out as off-resonance effect, coming mainly from the electron delocalization by charge-transfer. The electron push–pull effect formed by the donor and acceptor group in C2 enhanced the charge transfer of the system. Larger third-order optical nonlinearity than that of C1 was observed.

References

[1] Eich M, Wendor J H and Reck B 1987 *Makro Chem. Rapid Commun.* **8** 59

[2] Uematsu T and Imamura S (Mitsubishi Kagakukk) 1995 *Jpn. Kokai Tokkyo Koho* JP. 07254167

[3] Ochiai T, Kurose Y, Nagao T, Tsukaharo T and Inamura S (Mitsubishi Kasei Corp) 1993 *European Patent Application* EP 0572973

[4] Umehara H, Yanagimachi M, Taniguichi Y, Hirose S, Misawa T and Takuma H (Mitsui Toatsu Chemicals) 1996 *Jpn. Kokai Tokkyo Koho* JP. 08108623

[5] Chapman D D, Ramanuj G and Andras Kovacs C. (Eastman Kodak Co) 1994 *European Patent Application* EP 0649880

[6] Katz H E, Singer K D, Sohn J E, Dirk C W, King L A and Gordon H M 1987 *J. Am. Chem. Soc.* **109** 6561

[7] Clark R J H and Hester R E 1991 *Advances in Material Science Spectroscopy* (New York: Wiley)

[8] Yesodha S K, Pillai C K S and Tsutsumi N 2004 *Prog. Poly. Sci.* **29** 45

[9] Nicholas J L 1995 *Angew. Chem. Int. Ed. Engl.* **34** 21

[10] Whittall I R, McDonagh A M, Humphrey M G and Samoc M In Robert W and Anthony H (Eds.) 2000 *Advances in Organometallic Chemistry, Organometallic Complexes in Nonlinear Optics* II: *Third-Order Nonlinearities and Optical Limiting Studies* **43** (San Diego: Academic) pp349–405

[11] Huang W T, Li Y, Xiang H, Yang H and Gong Q H 2005 *Chin. Phys.* **14** 11

[12] Wang Z W, Wang X F, Liu C L, Zhao J X and Gu S X 2005 *Chin. Phys.* **14** 551

[13] Shirk J S, Lindle J R, Bartoli F J, Homan C A, Kafafi Z H and Snow A W 1989 *Appl. Phys. Lett.* **55** 1287

[14] Wu S J, Qian W, Xia Z J, Zou Y H, Wang S Q, Shen S Y and Xu H J 2000 *Chem. Phys. Lett.* **330** 535

[15] Gu Y Z, Gan F X, Wang S Q and Xu H J 2001 *Opt. Commun.* **197** 501

[16] Tian Z Y, Huang W T, Xiao D B, Wang S Q, Wu Y S, Gong Q H, Yang W S and Yao J N 2004 *Chem. Phys. Lett.* **391** 283

[17] Wang S Q, Shen S Y, Xu H J, Gu D H, Yin J L and Tang X D 1999 *Dyes and Pigments* **42** 173

[18] Gong Q H, Li J L, Zhang T Q and Yang Y 1998 *Chin. Phys. Lett.* **15** 30

[19] Minoshima K, Taiji M and Kobayashi T 1991 *Opt. Lett.* **16** 1683

[20] Heflin J R, Wong K Y, Zamani-Khamiri O and Garito A F 1988 *Phys. Rev.* B **38** 1573

[21] Griffiths J 1972 *Chem. Soc. Rev.* **1** 481

[22] Dirk C W 1995 *J. Am. Chem. Soc.* **117** 2214

[23] Kuzyk M G and Dirk C W 1990 *Phys. Rev.* A **41** 5098