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Journal of Photochemistry and Photobiology A: Chemistry 106 (1997) 85–90

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Chemical studies on the nonlinear optics of coordination compounds

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Abstract

There has been much progress in chemical studies on nonlinear optics organic, polymer, inorganic and organometallic solid materials, but less for coordination compounds. This paper presents some of our recent research with emphasis on the possibility of incorporation advantages of both organic (high nonlinear optical effect) and inorganic (stable large crystal) parts into the form of coordination compounds (include organic–inorganic salts) for nonlinear optical applications. © 1997 Elsevier Science S.A.

Keywords: Nonlinear optics; Coordination compounds; Chemical studies

1. Introduction

The interaction of light with some materials can give rise to a variety of nonlinear optical (NLO) effects. These materials have numerous uses in data storage, telecommunication and information processing. Theoretical scientists have designed many models to correlate NLO effect with some intrinsic molecular properties [1,2]. For instance, the sum-over-state (SOS) approach is most widely employed in practical calculations [3,4] of second-order molecular polarization using following formula [5]:

$$\beta = -\frac{e^3}{2\hbar^2}\left[\sum_{\substack{\mathrm{ee'}\neq \mathrm{g}\\ \mathrm{e}\neq \mathrm{e}}} \mu_{\mathrm{ge}}\mu_{\mathrm{ge'}}\mu_{\mathrm{ee'}}\frac{3\omega_{\mathrm{ge}}\omega_{\mathrm{ge'}}+\omega^2}{(\omega_{\mathrm{ge}}^2-\omega^2)(\omega_{\mathrm{ge'}}^2-\omega^2)} + \sum_{\mathrm{e}}\mu_{\mathrm{ge}}^2(\mu_{\mathrm{e}}-\mu_{\mathrm{g}})\frac{3\omega_{\mathrm{ge}}^2+\omega^2}{(\omega_{\mathrm{ge}}^2-\omega^2)^2}\right] \quad (1)$$

where ω is the angular frequency of the incident laser, μ_g and μ_e are the dipole moments of the ground state (GS) and the excited state (ES) respectively, μ_{ge} and μ_{ee}, are the dipole moments for the transition from GS to ES and between two ESs, and ω_{ge} and $\omega_{ge'}$ are the angular frequencies of the transition from the GS to a different ES. It should be noted that β is essentially a third-order tensor. The value calculated for β without any subscript from Eq. (1) is usually interpreted as the vector component along the direction of dipole moment, which sometimes is written as β_{vec}.

In order to obtain the high NLO properties for molecular-based materials, the problem can be separated into two interdependent parts. First, we must synthesize noncentrosymmetric molecules with high hyperpolarizability β, i.e. the so-called molecular design. Second, we must fabricate bulk materials by crystal growth, Langmuir–Blodget film deposition or other techniques to assemble molecules having the required orientation or degree of order, so as to maximize the desired NLO coefficients $\chi^{(2)}$, i.e. the so-called crystal engineering [6,7].

Most NLO materials with practical application are typical inorganic crystals consisting of atoms (or ions) in lattice sites, such as lithium niobate ($LiNbO_3$), potassium dihydrogen phosphate (KDP), β-barium borate (BBO) and gallium arsenide (GaAs). On account of the large flexibility for molecular design and the higher NLO coefficient, there has been much progress in basic research on organic, polymer and organometallic solid materials [8–10]. Molecules with donor–acceptor interaction, resulting from charge transfer between electron donating and withdrawing groups, are good candidates owing to their large changes in dipole moment and in transition dipole moment [11–16]. However, these materials are often mechanically and thermally unstable as well as having intense color. It is well known that the Langmuir–Blodgett [5,6] and chemical self-assembly [17–22] film depositions are the alternative techniques for the formation of ordered thin films to produce NLO effects, especially in geometries suitable to waveguide devices. Nevertheless, the defects of scattering microdomains, structural instability and structural irregularity [23,24] pose problems in applications.

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1010-6030/97/$17.00
PII S1010-6030(97)00043-9

In the last decade less progress has been achieved in the field of nonlinear optics of coordination compounds. The main aim of our recent research is to show the possibility of incorporating advantages of both organic and inorganic parts into the form of coordination compounds and to keep the synergistic behavior of nonlinear optics. The synthesis of designed compounds which form an organizing functionalized system by the process of supramolecular interaction is emphasized [25].

2. Experimental section

2.1. Measurements of NLO properties

2.1.1. Second-order NLO property measurement

According to the principles proposed by Kurts and Perry [26] the strength of second harmonic generation (SHG) efficiency of the compounds is estimated by measuring powder of 76–154 μm diameter and 0.8 mm thickness in the form of pellet. The pressure in compacting the pellet is 300 MPa. The experimental arrangement includes a high power mode-locked Nd:YAG laser with 200 ps pulse at a repetition rate of 5 Hz at a selected wavelength of 1064 nm. The laser beam is split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference of urea or KDP pellet.

2.1.2. Third-order NLO property measurement

The NLO susceptibility $\chi^{(3)}$ for the complexes is measured by the techniques of degenerate four-wave mixing (DFWM) [27] or z-scan [28] in solution of DMF or CH_3CN. In DFWM, amplified mode-locked nanosecond pulses at 450 mm are obtained from 10 Hz amplification and 20 ns mode-locked pulses are obtained from a synchronously pumped dye laser pumped by a quasi-molecular laser. The average energy of the pulses is 25 mJ. The vertical polarized output at 450 nm is split into three beams. The intensity of the phase conjugate beam, proportional to the square of $\chi^{(3)}$ is measured. The z-scan technique is based on the transformation of phase distortion to amplitude distortion during beam propagation. Using a Gaussian laser beam in a tight-focus limiting geometry, the transmittance of a nonlinear medium through a finite aperture placed in the far field as a function of the sample position (z) is measured with respect to the focal plane.

2.2. Synthesis of coordination compounds

All organic solvents used for the synthesis and physical measurements are of reagent grade and used without further purification.

2.2.1. Preparation of zinc thiosemicarbazones

Ethanol solutions of the Schiff base of $[(CH_3OC_6H_5)\text{-}(HNNHCSNH_2)]$ (0.43 g) and zinc chloride (0.69 g) were mixed. The colorless crystalline solid formed after refluxing for 4 h was isolated, washed with ethanol and dried in vacuo over P_2O_5. Pure crystal was obtained by slow evaporating dichloromethane solution in air.

2.2.2. Preparation of palladium(II) and platinum(II) dithiocarbamato complexes

Potassium chlorometallite $K_2M(II)Cl_4$ ($M=Pd$, Pt) was dissolved in water and treated with a 1:2 molar ratio of the appropriate ammonium dithiocarbamate dissolved in the same solvent. Orange precipitates of the bis[*N*-(4-aminophenyl)dithiocarbamato] palladium(II) and platinum(II) complexes were formed, which were filtered off, washed several times with water and dried in vacuo over P_2O_5.

The di(tetrakis-*n*-butylammonium)bis[*N*-(4-aminophenyl)dithiocarbamato] palladium(II) and platinum(II) complexes were prepared according to the following synthetic route: 1 mmol of the appropriate $[M(S_2CNH\text{-}C_6H_4NH_2)_2]$ ($M=Pd$, Pt) complex was treated with an aqueous solution containing an excess of NaOH and the mixture was left at room temperature under continuous magnetic stirring. A clear solution was obtained, and 2 mmol of Bu^n_4NBr dissolved in ethanol was added. A yellow–green precipitate appeared which was filtered off, washed with water and dried in vacuo over P_2O_5.

2.2.3. Preparation of salts based on polyoxometalates with organic donors

We take $[NMPH]_5BW_{12}O_{40}$ (NMPH = *N*-methylprolinedone) as an example. To 20 ml of a 50 mM aqueous solution of $H_5BW_{12}O_{40}$ was added 1 ml of NMPH with stirring. An immediate precipitate resulted. The resulting precipitate was collected and then sucked as dry as possible on a fritted-glass funnel. The precipitate was recrystallized from a solvent mixture of acetonitrile and water to obtain crystals.

2.3. Nonlinear optics of coordination compounds

By the SOS formulation of Eq. (1), we have some intuitive understanding of the advantage of NLO properties of coordination compounds. There is a small energy gap between ground and excited states, and more optical absorption transitions, such as ligand-to-metal and metal-to-ligand charge-transfer bands in the UV–visible region. The intensities of these bands are associated with their transition dipole moments. The metal centers with a variety oxidation states can act as acceptors or donors. Another character of coordination compounds is that they can coordinate and stabilize the organic ligands and also can be used to tune the electronic properties of organic fragments [29].

Until now there have been few researches on the NLO of classical coordination compounds. Most interest has focused on square-planar metal aromatic complexes $MX[P(Et)_3]_2$ ($M=Ni$, Pd, and Pt; $X=I$, Br and Cl) with X as donor [30]. Recently, research on transition metal coordination complexes has been conducted [31–33], but reports of main group metal complexes with slight color are quite few. The

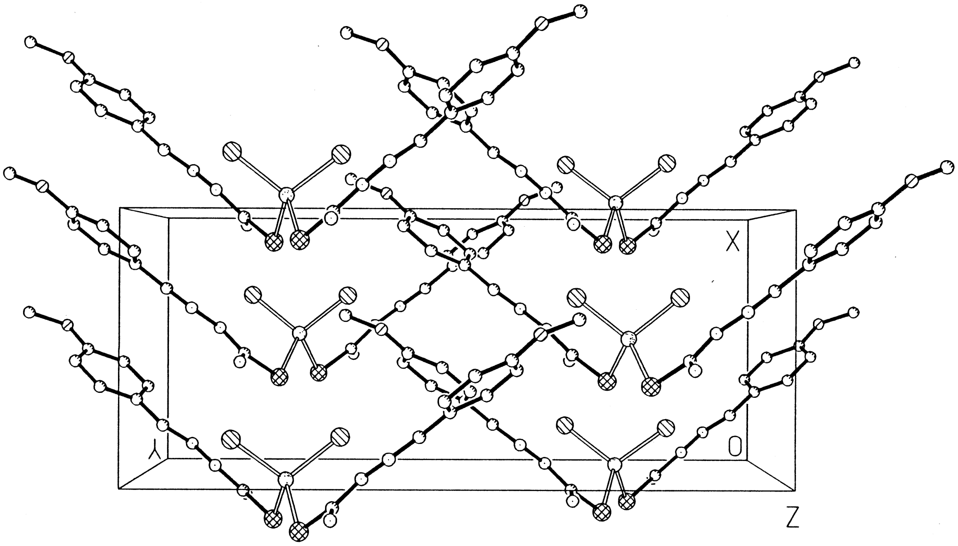

Fig. 1. The packing diagram of the unit cell for the complex $[CH_3OC_6H_4CH{=}NNHCSNH_2]_2ZnCl_2$ showing the assembly of molecules.

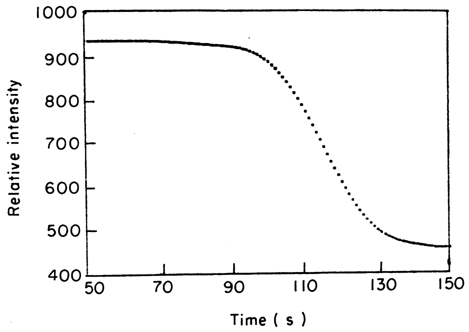

Fig. 2. DFWM response of the complex of $[PdL_2]$ showing rapid decay response.

distorted octahedral complex has been presented on the basis of the relationship between the microscopic structure and the macroscopic SHG effect. Some thiourea (TU) cadmium chloride and thiosemicarbazide (TSC) cadmium chloride derivatives have been explored as new frequency doubling crystals [34], such as $Cd(TU)_2Cl_2$ ($I^{2\omega}/I^{2\omega}SiO_2 = 700$) and $Cd(TSC)Cl_2$ ($I^{2\omega}/I^{2\omega}{}_{KDP} = 13.98$).

Our new complex of zinc thiosemicarbazones ($C_{18}H_{22}N_6S_2Cl_2O_2Zn$) crystallizes in the monoclinic space group Cc with the cell parameters $a = 9.083(1)$ Å, $b = 22.142(1)$ Å, $c = 11.789(1)$ Å, $\beta = 90.05(1)°$, $Z = 4$ (Fig. 1). The distorted tetrahedral configuration of zinc complex in crystal makes the compound crystallized in noncentrosymmetry space group. The complex shows an SHG seven times greater than that of urea, and much better than the previous complexes of thiosemicarbazide. The importance of molecular assembly in complex can be emphasized by the fact that the ligand of the Schiff base $[CH_3OC_6H_4CH{=}NNHCSNH_2]$ crystallizes in the space group of $P2_1/c$ with centrosymmetry, and does not show any SHG effect.

In comparison with our recent research results on bis(2-chlorobenzaldehyde thiosemicarbazone) cadmium with halide $[CdL_2X_2]$ [$L = ClC_6H_4CH{=}NNHCSNH_2$, X = Br, I], the present results also show the importance of the molecular assembly and conjugate properties. The CdL_2Br_2 with space group Cc shows a larger SHG efficiency than that of urea [35]. However, the related complex of cadmium iodide $[CdL_2I_2]$ with the same ligand crystallizes in the triclinic space group P1. The centrosymmetric structure again means the complex shows no SHG efficiency.

Based on an MNDO Hamiltonian [36] and PM3 parametrization [37] with the MOPAC program package, the molecular hyperpolarizability β_μ, the vector component along the dipole moment direction of the organic ligand and its zinc complexes are calculated to be -2.6×10^{-30} esu, and -4.6×10^{-30} esu respectively, which are comparable with that of *p*-nitroaniline (PNA, 6.3×10^{-30} esu) and much greater than that of urea (0.14×10^{-30} esu); they are consistent qualitatively with the above SHG experiments. The negative sign of β_μ can be explained by the fact that the smaller dipole moment of the lowest excited state than that of ground state. The β value of the zinc complex is larger by a factor of 2 than that of the ligand.

The factors that govern third-order NLO polarization are not well understood. Most researches have been on highly polarizable molecules and materials with conjugate systems [8]. Metal complexes with sulfur-rich dithiolene ligands are very interesting from the viewpoint of their conductive behavior owing to their intermolecular S···S interaction of the ligand [38]. A series of metal dithiolenes have featured in third-order NLO studies and χ^3 values are found in range from 7.16×10^{-14} to 1.4×10^{-11} esu [39,40].

Third-order NLO responses for our new dithio-complexes were measured using the DFWM technique with the $\chi^{(3)}$ values shown in the Table 1, which are one order larger than the value of $\chi^{(3)}$ of CS_2 [45]. The crystal structure of bis[*N*-(4-aminophenyl)dithiocarbamato] palladium(II) complex, $(Bu^n_4N)_2[Pd(S_2C{=}NC_6H_4NH_2)_2]$ has been determined to be a square-planar configuration with a space group of $P2_1/c$. Fig. 2 gives the nanosecond resolved DFWM response of the sample $[PdL_2]$, which shows rapid decay response. The

$\chi^{(3)}$ values for $(\mathrm{Bu^n_4N})_2[\mathrm{Pd(S_2C{=}NC_6H_4NH_2)_2}]$ and $(\mathrm{Bu^n_4N})_2[\mathrm{Pt(S_2C{=}NC_6H_4NH_2)_2}]$ are larger than those of $[\mathrm{Pd(S_2CNHC_6H_4NH_2)_2}]$ and $[\mathrm{Pt(S_2CNHC_6H_4NH_2)_2}]$. This may be because the former complexes, in deprotonated form, have a higher degree of delocalization than their neutral parent complexes.

2.4. *Nonlinear optics of organic–inorganic salts*

Recently there have been a number of reports in the literature addressing charge-transfer complexes [41–43], which may constitute a range of molecular solids with novel structural, magnetic and transport properties, arising from organic donor and large quasi-spherical inorganic acceptors, e.g. $\mathrm{(TTF)_3Mo_6O_{19}}$. Polyoxoanions interact with organic molecules essentially by virtue of their acid–base properties, high electron-acceptor ability [44] and induce the coexistence of mixed valence states in both organic and inorganic systems. There are many papers which discuss the photochemical and the photochromism processes of polyoxometalates [45,46], but to our knowledge there is no paper about the NLO properties of these kinds of compounds. The polyoxometalate has the capacity to reduce and form crystals. On the other hand, some organic dyes have large dipole moments with unusually high basicity [47]. Principally, we know that the molecule probably has a second-order NLO effect, if the conjugated molecule contains both a donor and an acceptor which are favorable for charge transfer.

A solvated complex of α-$\mathrm{H_4SiW_{12}O_{40}\cdot 4HMPA\cdot 2H_2O}$ has been synthesized [48]. The reflectance electronic spectra and IR spectrum of solid indicate that there is interaction between the α-$\mathrm{H_4SiW_{12}O_{40}}$ and the organic substrate. The compound with space group $P2_1$ shows the second-order and third-order NLO response of $I^{2W}=0.71\ I^{2W}{}_{\mathrm{KDP}}$ and $\chi^{(3)}=2.63\times 10^{-11}$ esu. The photosensitive charge-transfer salt of $\mathrm{[HTEA]_3[PMo_{12}O_{40}]\cdot 1.5H_2O}$ complex also shows certain NLO properties [43]. Its $\chi^{(3)}$ is 1.06×10^{-14} esu, which indicates that the photochromic complex can produce hyperpolarizabilty under photoexcitation.

For our new salts based on polyoxometalates with organic donors, the intensity of the SHG for these compounds compared with that of KDP are listed in Table 2.

The results indicate that the second-order NLO property is influenced by the anion. The SHG signals of polyoxotungstate are obviously stronger than those of polyoxomolybdate with the same organic donors. The central atom of the anion also influences the NLO property in the order B > Si > Ge > P. The signal of the compound with the anion center atom B is the strongest among the compounds (larger than that of KDP).

Table 2
The second order nonlinear optic data of the NMPH polyoxometalates

Compounds	Results (ref. to KDP) [a]
$\mathrm{[NMPH]_3PW_{12}O_{40}}$	M
$\mathrm{[NMPH]_3GeW_{12}O_{40}}$	0.71
$\mathrm{[NMPH]_5BW_{12}O_{40}}$	0.85
$\mathrm{[NMPH]_5BW_{12}O_{40}}$	1.1
$\mathrm{[NMPH]_3PMo_{12}O_{40}}$	W
$\mathrm{[NMPH]_4GeW_{12}O_{40}}$	W

[a] M, medium; W, weak.

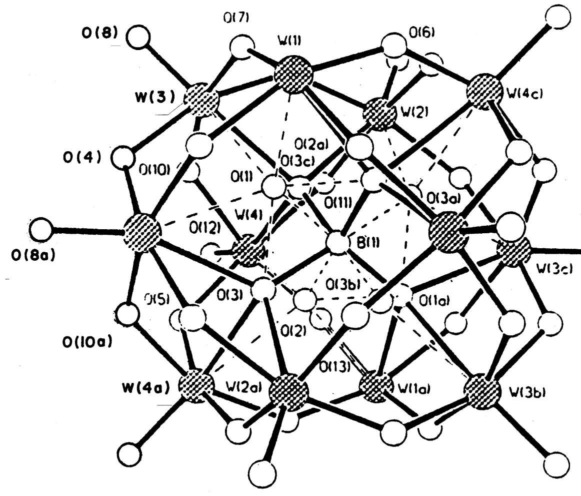

Fig. 3. The anion structure of $\mathrm{[NMPH]_5BW_{12}O_{40}\cdot 2H_2O}$.

One of the typical solvated complex of $\mathrm{[NMPH]_5}$-$\mathrm{BW_{12}O_{40}\cdot 2H_2O}$ is composed of the heteropolytungstate $\mathrm{H_5BW_{12}O_{40}}$ and the organic substrate *N*-methylpyrolindone (NMP). The complex is photosensitive under irradiation of sunlight, resulting in a charge transfer by oxidation of the NMP and reduction of the polyoxometalate. The colorless compound crystallizes in the monoclinic, space group C2/m. The unit cell has $a=17.834(5)$ Å, $b=20.027(4)$ Å, $c=13.292(3)$ Å, $\beta=129.010(0)°$, $V=3689$ Å^3 and $Z=2$ (Fig. 3) [49]. The compound shows a certain third-order and second-order NLO response of $\chi^{(3)}=2.11\times 10^{-11}$ esu and $I^{2w}=1.1I^{2w}{}_{\mathrm{KDP}}$ due to the disorder.

The third-order property of some these compounds in aqueous solution at 10^{-3} M was also determined. The third-order susceptibilities of the four compounds $\mathrm{[HMPAH]_4SiW_{12}O_{40}}$ (I), $\mathrm{[HMPAH]_3GeW_{12}O_{40}}$ (II), $\mathrm{[NMPH]_4\,SiW_{12}O_{40}}$ (III), and $\mathrm{[NMPH]_5BW_{12}O_{40}}$ (IV) were calculated to be $3.16\times 10^{-11,}$ 7.03×10^{-12}, 2.46×10^{-11} and 2.11×10^{-11} esu respectively. The third-order NLO properties of the compounds are dominated by nonlinear refraction. One of the typical third-order NLO properties of compound IV is shown in Fig. 4.

Those polyoxometalates having characters of electro-optic, photoconduction and charge transport may potentially be a new kind of photorefractive material, which is another major field of NLO effects [50].

3. Conclusion

From the typical coordination compounds with NLO properties reported here, it is evident that the assembly of these asymmetrical molecules in the crystal according to their NLO

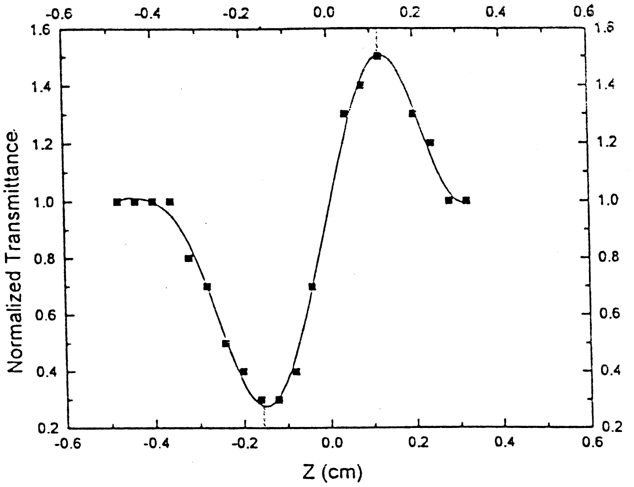

Fig. 4. The *z*-scan data of 4.7×10^{-3} M of complex IV at 532 nm with $I_0=3.26$ GW cm^{-2}.

properties is important from the views of molecular design and crystal engineering. In particular, associated with the considerable difficulties in growth of large and high quality crystals of these materials, which is a major obstacle to the full exploitation of their excellent properties [51], new technologies must be developed for producing the precursor and packing them as useful materials [52].

The potential application of the new functionalized coordination compounds, especially in the areas of optoelectronic materials, is undertaken in our laboratory.

Acknowledgements

Supported by the State Science and Technology Commission and the National Nature Science Foundation of China.

References

[1] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.
[2] B.F. Levine, C.G. Bethea, J. Chem. Phys. 63 (1975) 2666.
[3] J. Ward, Rev. Mod. Phys. 37 (1965) 1.
[4] H.A. Kurtz, J.J.P. Stewart, K.M. Dieter, J. Compt. Chem. 11 (1990) 82.
[5] I.R. Girling, N.A. Cade, P.V. Kolinsky, J.D. Earls, G.H. Cross, I.R. Peterson, Thin Solid Films 132 (1985) 101.
[6] J.F. Nicoud, R.J. Twieg, in: D.S. Chemla and J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 1, Academic Press, Orlando, FL, 1987, p. 242.
[7] F.S. Zyss, J.L. Oudar, Phys. Rev. A 26 (1982) 2028.
[8] S.R. Marder, J.E. Sohn, G.D. Stucky (Eds.), Materials for Nonlinear Optics: Chemical Perspectives, ACS Symp. Ser 455 (1991).
[9] J. Zyss, Molecular Nonlinear Optics: Materials, Physics and Devices, Academic Press, New York, 1994.
[10] D.S. Chemla, J. Zyss, Nonlinear optical properties of organic molecules and crystal, Vol. 1, Academic Press, Orlando, FL, 1987.
[11] Sun Zhen-Fan, You Xiao-Zeng, Li Da-guang, Acta Chim. Sinica. 52 (1994) 762.
[12] L.T. Cheng, W. Tam, S.R. Marder, A.E. Stiegman, G. Rikken, C.W. Spangler, J. Phys. Chem. 95 (1994) 16643.
[13] Cun-Yuan Zhao, Yong Zhang, Wei-Hai Fang, Xiao-Zeng You, J. Mol. Struct. (Theochem), 73 (1996) 367.
[14] H.A. Kurtz, J.J.P. Stewart, K.M. Dieter, J. Comp. Chem. 11 (1990) 82.
[15] J.O. Morley, V.J. Docherty, D. Pugh, J. Chem. Soc. Perkin Trans. 2 (1987) 1352.
[16] Fang Qi, Yang Yao, Wang Hua-Qin, Sun Hong-Zhe, You Xiao-Zeng, Acta. Sinica 52 (1994) 138.
[17] J. Sagiv, J. Am. Chem. Soc. 102 (1980) 92.
[18] H. Keller, W. Schrepp, H. Fuchs, Thin Solid Film, 210–211 (1992) 815.
[19] S. Yitzchaik, S.B. Roscoe, A.K. Kakkar, D.S. Allan, T.J. Marks, Z. Xu, T.G. Zhang, W.P. Lin, G.K. Wong, J. Phys. Chem. 97 (1993) 6958.
[20] D.Q. Li, M.A. Ratner, T.J. Marks, J. Am. Chem. Soc. 12 (1990) 7389.
[21] X.Q. Zhang, W.Y. Wang, X.Z. You, Y. Wei, Appl. Surf. Sci. 4 (1995) 267.
[22] Xue-Qun Zhang, Xiao-Zeng You, Si-Hong Ma, Yu Wei, J. Mater. Chem. 5 (1995) 643.
[23] C. Ye, N. Minami, T.J. Marks, J. Yang, G.K. Wong, in: J. Messier, F. Kajar, P. Prasad, D. Ulrich (Eds.), Nonlinear Optical Effects in Organic Polymers, Kluwer, Dordrecht, 1989, p. 173.
[24] D. Lupo, W. Prass, U. Schunemann, A. Laschewsky, H. Ringsdort, I. Ledoux, J. Opt. Soc. Am. B 5 (1988) 300.
[25] F. Vogtle, Supramolecular Chemistry, Wiley, Chichester, 1991.
[26] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 36 (1968) 3798.
[27] R.A. Fisher (Ed.), Optical Phase Conjugation, Academic Press, New York, 1983.
[28] W.E. Williams, M.J. Soileau, E.W. Van Stryland, Opt. Commun. 50 (1984) 256.
[29] J.P. Collman, L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, 2nd ed., University Science Books, Mill Alley, 1987.
[30] W. Tam, J.C. Calabrese, Chem. Phys. Lett. 144 (1988) 79.
[31] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.
[32] W.M. Laidlaw, R.G. Denning, T. Verbiest, E. Chauchard, A. Persoons, Nature 363 (1993) 58.
[33] S.D. Bella, I. Fragala, I. Ledoux, T.J. Mark, J. Am. Chem. Soc. 17 (1995) 9481.
[34] Xu Dong, Jiang Min-Hua, Tao Xu-Tang, Shao Zong-Shu, J. Synth. Cryst. (China) 10 (1987) 1.
[35] Yu-Peng Tian, Chung-Ying Duan, Cun-Yuan Zhao, Zhong-Lin Lu, Xiao-Zeng You, T.C.W. Mak. Inorg. Chem., (1997) in press.
[36] M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc. 99 (1977) 4907.
[37] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.
[38] You Xiao-Zeng, Zhang Yong, in: Chi-Ming Chi (Ed.), Advances in Transition Metal Complexes, JAI, New York, 1996.
[39] Jing-Lin Zuo, Tian-Ming Yao, Fei You, Xiao-Zeng You, Hoong-Kun Fun, Boon-Chuan Yib, J. Mater. Chem., 6 (1996) 1633.
[40] C.S. Winter, C.A.S. Hill, A.E. Underhill, Appl. Phys. Lett. 58 (2) (1991) 107.
[41] D. Attanasio, M. Bonamico, V. Fares, P. Imperatonri, L. Suber, J. Chem. Soc., Dalton Trans. (1990) 3221.
[42] C.J. Gomez-Garcia, L. Quahab, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Delhaes, Angew. Chem. Int. Edn. Engl. 33 (1994) 223.
[43] Xue-Xiang Xu, Xiao-Zeng You, Polyhedron 14 (1995) 1815.
[44] G.M. Varga, E. Papaconstontinou, M.T. Pope, Inorg. Chem. 9 (1970) 662.
[45] E. Papaconstantinou, Chem. Soc. Rev. 18 (1989) 1.
[46] Han Shiying, Chen Jie, You Xiaozeng, J. Chem. Soc. Faraday Trans. 85 (1989) 829.
[47] G. Kraml, G. Gritzner, J. Chem. Soc., Faraday Trans. 81 (1985) 2875.
[48] J.Y. Niu, X.Z. You, C.Y. Duan, H.K. Fun, Z.Y. Zhou, Inorg. Chem. 35 (1996) 4211.
[49] Jing-Yang Niu, Jing-Ping Wang, Xiao-Zeng You, Zhong-Yuan Zhou, to be submitted for publication.

[50] Pochi Yeh, Introduction to Photorefractive Nonlinear Optics, Wiley–Interscience, New York, 1993.

[51] G.D. Stucky, Prog. Inorg. Chem. 40 (1992).

[52] G.J. Ashwell (Ed.), Molecular Electronics, Wiley, New York, 1992.