Appl. Phys. B 70, 809–812 (2000) / Digital Object Identifier (DOI) 10.1007/s003400000209

Applied Physics B
Lasers
and Optics

Optical-limiting properties of neutral nickel dithiolenes

W.L. Tan[1], **W. Ji**[1], **J.L. Zuo**[2], **J.F. Bai**[2], **X.Z. You**[2], **J.H. Lim**[3], **S. Yang**[3], **D.J. Hagan**[3], **E.W. Van Stryland**[3]

[1] Department of Physics, National University of Singapore, Singapore 119260, Singapore
(Fax: +65-7776126, E-mail: phyjiwei@nus.edu.sg)
[2] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China
[3] School of Optics/CREOL, University of Central Florida, Orlando, FL 32816-2700, USA

Received: 3 August 1999/Revised version: 28 October 1999/Published online: 24 March 2000 – © Springer-Verlag 2000

Abstract. We report the observation of optical-limiting effects in benzene solutions of two neutral nickel complexes with multi-sulfur 1,2 dithiolene ligands, [Ni(medt)$_2$] **1** (medt = 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate) and [Ni(phdt)$_2$] **2** (phdt = 5,6-dihydro-5-phenyl-1,4-dithiin-2,3-dithiolate). The limiting effects were observed with nanosecond and picosecond laser pulses. The limiting thresholds of complexes **1** and **2** were $\approx 0.3\,\mathrm{J/cm^2}$, measured with the ps laser pulses at 532 nm. The linear absorption spectra of the two complexes indicated that their limiting response should cover the visible and near-infrared region (up to 900 nm). Both ps time-resolved pump-probe and *Z*-scan experiments revealed that the limiting effects should originate from excited-state absorption and refraction

PACS: 33.00; 42.65; 42.70

In recent years, there has been considerable interest in organic materials exhibiting strong nonlinear-optical behavior because of their applicability in a variety of optical devices [1]. In particular, optical limiters have received significant attention as a result of the growing needs for protection of human eyes and optical sensors from intense laser beams. An idea optical limiter should have the capability of being transparent under laser radiation of low energies and opaque at high energies. The most frequently reported materials are fullerenes (C_{60}) [1–6], and phthalocyanine complexes [7–10], which are generally regarded as the best candidates for optical-limiting applications. They are materials that exhibit strong reverse saturable absorption. In such a nonlinear process, electrons are excited from the ground state to excited states by linear absorption. Due to stronger absorption of the excited states, there is a decrease in the transmission, thus leading to the desired limiting effect.

We note that there exists another class of organic materials, nickel complexes of 1,2-dithiolene ligands. These dithiolenes have been used as Q-switch dyes for near-infrared lasers such as Nd:YAG lasers since the early seventies [11]. Recently, they have also been intensively investigated as optical-switching materials for optical communications [12–15], molecular magnets conductors, and superconductors [16–20]. To our best knowledge, no investigations have been carried out on the optical-limiting properties of dithiolene complexes. Here we report the observation of optical-limiting effects in two neutral nickel complexes with multi-sulfur dithiolene ligands, [Ni(medt)$_2$](medt = 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate) **1** and [Ni(phdt)$_2$] (phdt = 5,6-dihydro-5-phenyl-1,4-dithinn-2,3-dithiolate) **2**. The observation has been carried out by ns and ps laser pulses at a wavelength of 532 nm. The mechanisms leading to the observed limiting effects have also been investigated.

1 Experimental

The preparation of the two dithiolene complexes **1** and **2** was reported elsewhere [15]. The structures of the complexes were identified from IR spectra and elemental analysis [15]. Their chemical structures are shown schematically in Fig. 1. It can be seen that the four sulfur atoms surrounding the nickel atom yield a square planar coordination. The five-membered ring containing the nickel atom forms a de-localized π-electron system, making it favorable for nonlinear-optical properties.

The two dithiolene complexes were dissolved in benzene (C_6H_6) and contained in 1-mm-thick quartz cells for optical measurements. Their electronic spectra were recorded with a spectrophotometer (Hitachi U-3410). Their nonlinear-optical responses were measured with frequency-doubled, pulsed Nd:YAG lasers, which produced laser pulses of 7 ns (FWHM) and ps duration at 532 nm. The lasers were operated at a repetition rate of 10 Hz. The spatial profiles of the pulses were nearly Gaussian after passing through a spatial filter. Three types of experimental setup used for the nonlinear-optical measurements are described as follow:

(a) The optical-limiting behavior was observed by measuring the nonlinear (energy-dependent) transmission of the two solutions. The laser pulses were split into two parts: the reflected was used as a reference, and the transmitted was focused onto the sample. The transmitted pulses were focused onto the sample by a focusing lens. The sample was placed at the focus where the spot radii of the pulses were $30 \pm 5\,\mu\mathrm{m}$ and $24 \pm 5\,\mu\mathrm{m}$ (HWe^{-2}M) for the 7-ns

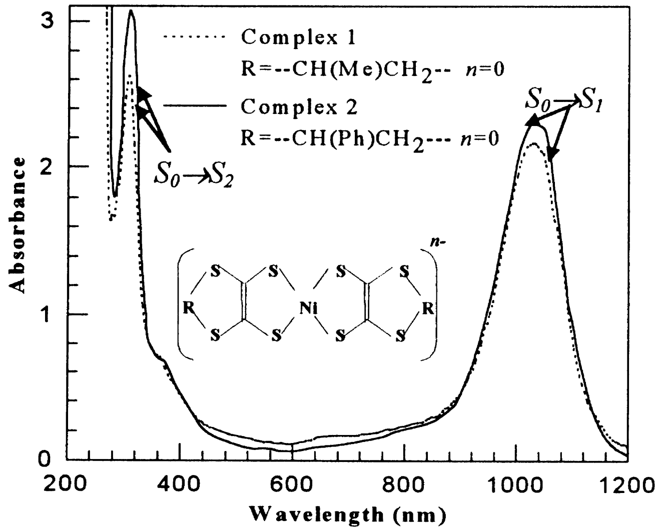

Fig. 1. Absorption spectra of complexes **1** (– – –) and **2** (—) in benzene solution with 1-mm optical path and concentration of 1.9×10^{-4} M for complex **1** and 6.1×10^{-4} M for complex **2**. *Inset* shows the structures of the two complexes. S_1 and S_2 correspond to the excited singlet states

and 35-ps pulses, respectively. It should be noted that the uncertainty in the measurements of the spot size is the main source for our experimental error (up to 55%) in the determination of the laser pulse fluence. An aperture with a transmittance of 40% was placed in front of the transmission detector when the measurements were performed. Both the incident and transmitted pulse energies were monitored simultaneously by using two energy detectors (Rjp-735 energy probes, Laser Precision), which were connected to a computer by an IEEE interface.

(b) The *Z*-scan setup [21, 22] was similar to that used for the above measurements except that the sample was moved along the propagation direction (*Z* axis) of the transmitted beam with respect to the focal plane. By keeping the incident pulse energy constant, the pulse energy transmission through the sample was measured with respect to the sample *Z*-position. The aperture was placed in front of the transmission detector in the closed-aperture *Z*-scans and removed in the open-aperture *Z*-scans.

(c) The setup of the ps time-resolved pump-probe was a standard arrangement, where the peak irradiance of the probe pulse was approximately 1% of the pump pulse. The probe pulse was focused to a spot size approximately one fourth as large as the pump pulse so as to reduce the spatial averaging effects while sampling the largest nonlinearity. The spot size of the pump pulse was 100 μm and the pulse duration was 28 ps (FWHM). The pump and probe pulses were incident on the sample at an angle of 3° with respect to each other.

2 Results and discussion

The absorption spectra of complexes **1** and **2** in benzene solution are depicted in Fig. 1. It is noticed that there is a relatively low absorption in the visible and near-IR region (400–900 nm) for the complexes. The spectra are dominated by two intense absorption bands, one band is centered at around 1000 nm ($\pi - \pi^*$ transition) and the other at around 300 nm (ascribed to S → M charge transfer band) [15]. These indicate that they have generally a broader transparent window than phthalocyanines (500–700 nm) [7]. Since a broad transparent range is an important criterion in the assessment of optical-limiting materials, the spectra of these nickel dithiolene complexes have shown that their limiting response should cover a wider range, thus they are superior to phthalocyanines complexes.

The photo-dynamics in these dithiolene complexes can be described by a five-level energy structure in Fig. 2, which shows the possibility of both singlet and triplet excited state absorption. The absorption corresponding to excitation from the ground state to the S_1 band is peaked at wavelengths around 1000 nm and covers the visible region in the spectrum. Because of this initial absorption at 532 nm electrons are excited from the ground state into the S_1 vibrational manifold. Then they relax quickly (on fs time scales) to the bottom of the S_1 band and make excited-state absorption ($S_1 \to S_2$) possible for ps laser pulses. If the laser pulses are longer than a few ns, inter-system crossing transfers some electrons from the S_1 band to the T_1 band, leading to triplet excited-state absorption ($T_1 \to T_2$). If the excited-state absorption ($S_1 \to S_2$ or/and $T_1 \to T_2$) is greater than the initial ground-state absorption, reverse saturable absorption occurs. It is shown below that this happens to the nonlinear absorption in the dithiolene complexes.

Figure 3 shows the normalized transmittance of complexes **1** and **2** in benzene solution measured with the ns and ps pulses. The linear transmittance of the two solutions was about 83% at 532 nm. When the aperture was used, the linear transmittance of both the solutions was about 33%. At very low input fluences, the transmissions of the two solutions behave linearly. The transmittance begins to decrease rapidly as the incident fluence reaches about 0.1 J/cm^2 for both complexes **1** and **2**. The limiting threshold is defined here as the incident fluence at which the transmittance falls to 50% of the linear transmittance. From Fig. 3, the lim-

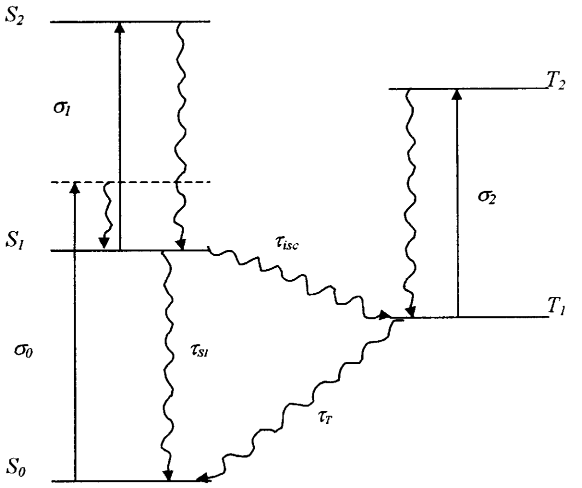

Fig. 2. Generic five-level structure for nonlinear-optical behavior of complexes **1** and **2**. S_0, S_1, and S_2 are singlet states and T_1 and T_2 are triplet states. The σ's are the absorption cross-sections and the τ's are the lifetimes. The *wavy* lines correspond to spontaneous decay processes. Note that the total decay time for the S_1 band is $\tau_{S_1}\tau_{\text{isc}}/(\tau_{\text{isc}} + \tau_{S_1})$

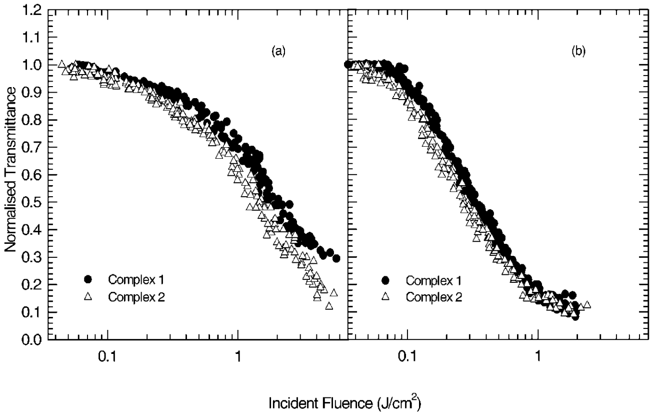

Fig. 3a,b. Fluence-dependent transmittance of the complexes measured at 532 nm. **a** The *filled circles* (•) and the *open triangles* (△) were the data measured with 7-ns laser pulses for complexes **1** (1.9×10^{-4} M) and **2** (6.1×10^{-4} M), respectively. **b** The *filled circles* (•) and the *open triangles* (△) were the data measured with 35-ps laser pulses for complexes **1** (1.9×10^{-4} M) and **2** (6.1×10^{-4} M), respectively

iting thresholds of complexes **1** and **2** are determined to be $\approx 0.3\,\mathrm{J/cm^2}$ for the ps measurements and $\approx 2.0\,\mathrm{J/cm^2}$ for the ns case. It should be pointed out that the optical-limiting responses were measured with the aperture placed in front of the transmission detector. The limiting effects were observed to deteriorate without the aperture, indicating that a self-lensing effect had enhanced the limiting effect in Fig. 3.

To gain insight into the mechanisms for the limiting effects, we performed the ps time-resolved pump-probe experiments and Z-scan measurements. The pump-probe experiments were conducted at the pump fluence of $0.06\,\mathrm{J/cm^2}$. The pump-probe results for complexes **1** and **2** are displayed in Fig. 4. The linear transmittance for complexes **1** and **2** was 67% and 85%, respectively. The ground-state absorption cross-sections, σ_0, were measured to be $9.3 \times 10^{-18}\,\mathrm{cm^2}$ for **1** and $2.8 \times 10^{-18}\,\mathrm{cm^2}$ for **2** at 532 nm. The data in Fig. 4 are a typical behavior resulting from excited-state absorption. Based on the five-level model [23], we fit the data with (1),

$$T(t) = T(0)^{b\exp(-t/\tau_T)+(1-b)\exp(-t/\tau_S)}, \tag{1}$$

where $T(t)$ is the normalized nonlinear transmittance; τ_T is the time for the $T_1 \rightarrow S_0$ relaxation; τ_S is the total decay time of the S_1 state and b is given by

$$b = \frac{\sigma_2^\alpha - \sigma_0}{\sigma_1^\alpha - \sigma_0}\phi, \tag{2}$$

where σ_1^α and σ_2^α are the cross sections of the excited singlet and triplet state, respectively; and ϕ is the percentage of the total excited-state population that ends up in the triplet state and is given by $\tau_S/\tau_{\mathrm{isc}}$, τ_{isc} is the inter-system crossing time. By the best fits, we determined that $\tau_T \geq 0.1\,\mu\mathrm{s}$ and $\tau_S = 0.8$ ns for **1**; and $\tau_T \geq 0.1\,\mu\mathrm{s}$ and $\tau_S = 1.5$ ns for **2**. We also found that $b = 0.23$ and 0.45 for complexes **1** and **2**, respectively.

To obtain the nonlinear cross-sections for these complexes, we conducted the Z-scan measurements. The Z-scan results for complexes **1** and **2** are shown in Fig. 5, and

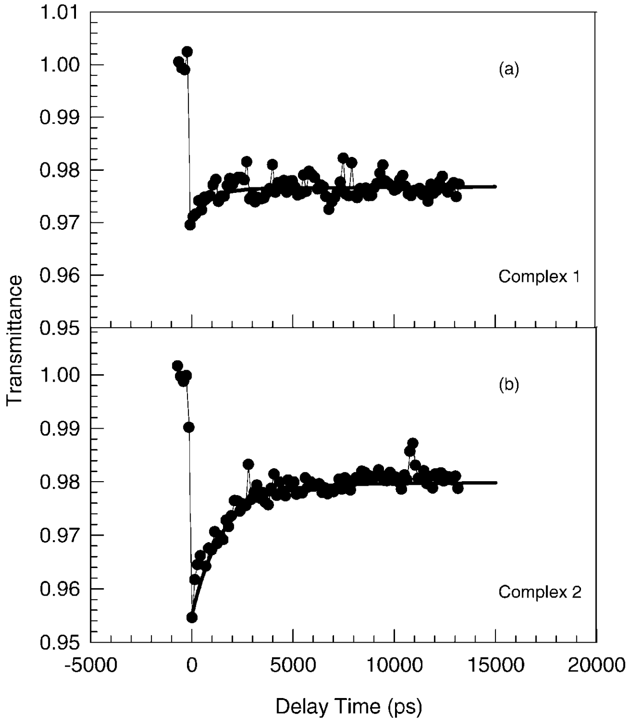

Fig. 4a,b. Probe transmittance as a function of time delay for **a** complex **1** (1.4×10^{-3} M) and **b** complex **2** (6.2×10^{-4} M). The pump fluence was $0.06\,\mathrm{J/cm^2}$. The *filled circles* (•) are the experimental data and the *thick curves* (—) are the theoretical fits

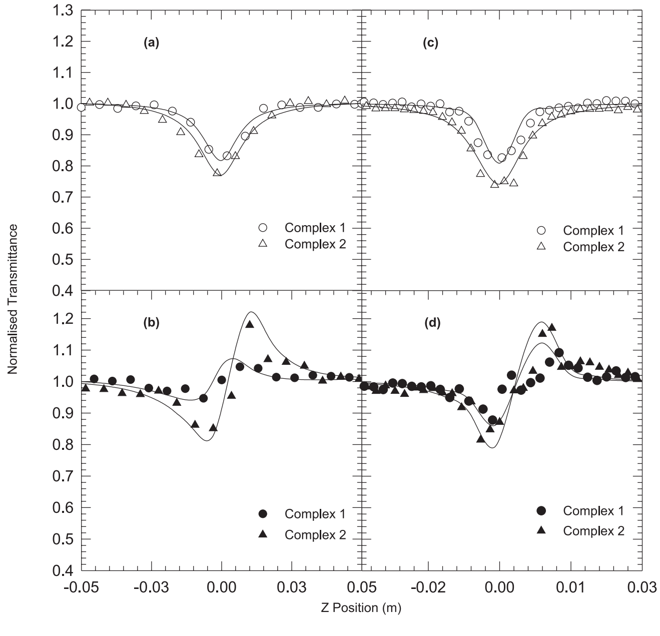

Fig. 5a–d. Z-scan results for complexes **1** (1.9×10^{-4} M) and **2** (6.1×10^{-4} M). The data in **a** and **b** were obtained with the 7-ns pulses. The results in **c** and **d** were recorded with the 35-ps pulses. The input energies for the ns and ps measurements were 25 μJ and 5 μJ, respectively. The *open circles* (○) and *open triangles* (△) were the Z-scan data measured without the aperture and the *filled circles* (•) and *filled triangle* (▲) were those obtained from dividing the closed-aperture Z-scans by the open-aperture ones

Table 1. Q-band electronic absorption of nickel dithiolenes, phthalocyanines, and naphthalocyanines, and their excited-state properties

Sample	Q-band/ nm	Pulse width/ FWHM	$\tau_T/$[c] µs	$\tau_{\mathrm{isc}}/$[d] ns	$\tau_{S1}/$[e] ns	$\sigma_1^\alpha/$[f] 10^{-17} cm^2	$\sigma_2^\alpha/$[g] 10^{-17} cm^2	$\sigma_1^{\mathrm{r}}/$[h] 10^{-17} cm^2	$\sigma_2^{\mathrm{r}}/$[i] 10^{-17} cm^2
CAP[a]	670	29 ps and 61 ps	N.A[b]	18	7	2.3	N.A[b]	1.8	N.A[b]
SiNc[a]	774	29 ps and 61 ps	N.A[b]	16	3.15	3.9	N.A[b]	0.47	N.A[b]
Complex **1**	1000	7 ns and 35 ps	≥ 0.1	13	0.85	5.0	2.2	2.0	1.8
Complex **2**	1000	7 ns and 35 ps	≥ 0.1	6	2	2.5	1.0	3.2	1.8

[a] [7]
[b] Results not available
[c] Triplet state lifetime
[d] Inter-system crossing time
[e] Singlet state lifetime
[f] Singlet excited-state absorption cross-section
[g] Triplet excited-state absorption cross-section
[h] Singlet excited-state refraction cross-section
[i] Triplet excited-state refraction cross-section

show a positive sign for the nonlinear refraction in complexes **1** and **2**. This indicates that the laser beam propagating in both the complexes should undergo a self-focusing process. This self-focusing process can enhance limiting effectiveness as shown in our nonlinear transmission measurements. The positive sign of the refractive nonlinearities in the two complexes is similar to that found in metallophthalocyanines; and such nonlinearities are attributed to excited-state refraction [7]. The best fitting results by using the five-level model [23] are shown in Fig. 5. In the fittings, all the lifetimes used are those determined from the pump-probe data. Because the ps pulses are much shorter than the inter-system crossing time required to populate the triplet state, the five-level model is simplified to the three-level model. Therefore, the ps Z-scans measured with and without the aperture enabled us to unambiguously extract the absorptive cross-section, and refractive cross-section, (σ_1^{r}) for the excited singlet state [7]. With the knowledge of the values of σ_1^α and σ_1^{r}, there are two unknown parameters in the five-level model for the ns Z-scans and they are the absorptive cross-section and refractive cross-section, (σ_2^{r}) for the excited triplet state. By fitting the ns Z-scans obtained with and without aperture, these two parameters can be unambiguously determined. These cross sections are listed in Table 1. By considering a 15% fitting error and a maximum of 55% experimental error for our experiment, the uncertainty is about 70% for these cross sections. Table 1 shows that the nonlinear optical properties of the dithiolene complexes compare favorably with those of silicon naphthalocyanines (SiNc) and chloro-aluminium phthalocyanines (CAP) [7].

3 Conclusion

The optical-limiting and nonlinear-optical properties of two neutral nickel dithiolene complexes, [Ni(medt)$_2$] **1** and [Ni(phdt)$_2$] **2** have been observed with ns and ps laser pulses. The observed nonlinear effects in the two complexes can be explained by excited-state absorption and refraction. These two complexes are shown to be promising for limiting applications in the visible and near-infrared spectral region.

Acknowledgements. We gratefully acknowledge the financial support of the National University of Singapore and the National Nature Science of P.R. China.

References

1. R. Crane, K. Lewis, E.W. Van Stryland, M. Khoshnevisa: *Materials for Optical Limiting I* (Material Research Society, Pittsburgh 1994)
2. L.W. Tutt, A. Kost: Nature **356**, 225 (1992)
3. D.G. McLean, R.L. Sutherland, M.C. Brant, D.M. Brandelik, P.A. Fleitz, T. Pottenger: Opt. Lett. **18**, 858 (1993)
4. V.V. Golovlev, W.R. Garrett, C.H. Chen: J. Opt. Soc. Am. B **13**, 2801 (1996)
5. S.R. Mishra, H.S. Rawat, S.C. Mehendale: Appl. Phys. Lett. **71**, 46 (1997)
6. S. Guha, W.T. Roberts, B.H. Ahn: Appl. Phys. Lett. **68**, 3686 (1996)
7. T.H. Wei, D.J. Hagan, M.J. Sence, E.W. Van Stryland, J.W. Perry, D.R. Coulter: Appl. Phys. B **54**, 46 (1992)
8. J.W. Perry, K. Mansour, S.R. Marder, K.J. Perry, D. Alvarez Jr. I. Choong: Opt. Lett. **19**, 525 (1994)
9. J.S. Shirk, R.G.S. Pong, F.J. Bartoli, A.W. Snow: Appl. Phys. Lett. **63**, 1880 (1993)
10. J.W. Perry, K. Mansour, I.-Y.S. Lee, X.-L. Wu, P.V. Bedworth, C.T. Chen, D. Ng, S.R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe: Science **273**, 1533 (1996)
11. K.H. Drexhage, U.T. Müller-Westerhoff: IEEE J. Quantum Electron. **QE-8**, 759 (1972)
12. C.S. Winter, C.A.S. Hill, A.E. Underhill: Appl. Phys. Lett. **58**, 107 (1991)
13. C.S. Winter, S.N. Oliver, R.J. Manning, J.D. Rush, C.A.S. Hill, A.E. Underhill: J. Mater. Chem. **2**, 443 (1992)
14. C.S. Winter, R.J. Manning, S.N. Oliver, C.A.S. Hill: Opt. Commun. **90**, 139 (1992)
15. J.L. Zuo, T.M. Yao, F. You, X.Z. You, H.K. Fun, B.C. Yip: J. Mater. Chem. **6**, 1633 (1996)
16. P. Cassoux, L. Valade, H. Kobayashi, R.A. Clack, A.E. Underhill: Coord. Chem. Rev. **110**, 115 (1991)
17. C. Faulmann, A. Errami, B. Donnadieu, I. Malfunt, J.P. Legros, P. Cassoux, C. Rovira, E. Canadell: Inorg. Chem. **35**, 3856 (1996)
18. J.M. Williams, J.R. Ferraro, R.J. Thorn, K.D. Carlson, U. Geiser, H.H. Wang, A.M. Kini, M.H. Whangbo: *Organic Superconductors (including fullerenes)* (Prentice Hall, Englewood Cliffs, NJ 1992)
19. P. Cassoux, L. Valade: In *Inorganic Materials*, ed. by D.W. Bruce, D.O. Hare (Wiley, Chichester, England 1996)
20. J.S. Miller, A.J. Epstein: Angew. Chem. Int. Ed. Engl. **38**, 385 (1994)
21. M. Sheik-Bahae, A.A. Said, E.W. Van Stryland: Opt. Lett. **14**, 955 (1989)
22. M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland: IEEE J. Quantum Electron. **26**, 760 (1990)
23. D.J. Hagan, T. Xia, A.A. Said, T.H. Wei, E.W. Van Stryland: International Journal of Nonlinear Optical Physics **2**(4), 483 (1993)