



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/gmcl19>

Third Order Nonlinear Optical Properties of Polycrystalline Octithiophene Thin Films Studied by Electroabsorption Spectroscopy

Christine Videlot ^a, Abderahim Yassar ^a, Denis Fichou ^a, Takashi Isoshima ^b, Tatsuo Wada ^b & Hiroyuki Sasabe ^b

^a Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry-Dunant, 94320, Thiais, FRANCE

^b Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), and Core Research for Evolutional Science Technology (CREST), Japan Science and Technology Corporation (JST), 2-1 Hirosawa, Wako, Saitama, 351-0198, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: Christine Videlot, Abderahim Yassar, Denis Fichou, Takashi Isoshima, Tatsuo Wada & Hiroyuki Sasabe (1998): Third Order Nonlinear Optical Properties of Polycrystalline Octithiophene Thin Films Studied by Electroabsorption Spectroscopy, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 322:1, 29-34

To link to this article: <http://dx.doi.org/10.1080/10587259808030196>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Third Order Nonlinear Optical Properties of Polycrystalline Octithiophene Thin Films Studied by Electroabsorption Spectroscopy

CHRISTINE VIDELOT^a, ABDERAHIM YASSAR^a, DENIS FICHOUE^a,
TAKASHI ISOSHIMA^{b†}, TATSUO WADA^b, and HIROYUKI SASABE^b

^a Laboratoire des Matériaux Moléculaires, CNRS, 2 rue Henry-Dunant -
94320 Thiais, FRANCE;

^b Frontier Research Program, The Institute of Physical and Chemical
Research (RIKEN), and Core Research for Evolutional Science Technology
(CREST), Japan Science and Technology Corporation (JST), 2-1 Hirosawa,
Wako, Saitama 351-0198, JAPAN

Received 8 June 1998; accepted 14 June 1998

Electroabsorption (EA) studies at room temperature on polycrystalline thin films of α -octithiophene (8T), the longest non-substituted model oligomer of polythiophene, are reported. The EA spectra obtained on isotropic 8T films deposited on top of coplanar electrodes exhibit several intense and narrow peaks in the absorption region and on the absorption edge. They are compared with the derivatives of absorption spectrum, and it is shown that the excitation in the longer wavelength absorption presents a Frenkel exciton character. Third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$ is evaluated to be in the order of 10^{-10} esu at its maximum.

Keywords: electroabsorption spectroscopy; α -octithiophene, evaporated polycrystalline thin films, third-order nonlinear optical properties

INTRODUCTION

Oligothiophenes have recently emerged as efficient organic semiconductors with potential applications in electronic devices such as field-effect transistors (FETs) [1]. In addition to their excellent transport properties in vacuum-evaporated thin films, these π -conjugated compounds also possess large third-order nonlinear optical susceptibilities $\chi^{(3)}$ due to their highly delocalized π -electrons and fully planar geometry in the solid state. The influence of chain length, substitution by electro-active groups and molecular conformation have been studied by optical third harmonic generation (THG) in solution and in

[†] Address for correspondence. e-mail: isoshima@postman.riken.go.jp Fax: +81-48-462-4695

the condensed state [2-7], and it was revealed that the second-order molecular hyperpolarizability γ and third-order nonlinear optical susceptibility $\chi^{(3)}$ increase with chain length up to 8 or even 15 thiophene rings in the molecule.

Octithiophene (8T) shown in Figure 1 is the longest non-substituted oligomer of thiophene (length=32 Å) that can be synthesized and isolated as a pure crystalline compound [8]. Similar to its lower homologue sexithiophene (6T), it crystallizes in the monoclinic system ($P2_{1/a}$ space group) with four molecules in the unit cell [9]. The molecules are fully planar and parallel to each other in a herringbone fashion, resulting in a high carrier mobility up to three times higher ($\mu = 0.06\text{-}0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than that of 6T [10-12].

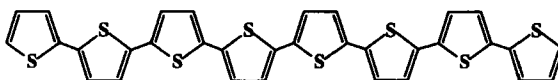


FIGURE 1 Structure of octithiophene.

Electroabsorption (EA) spectroscopy is a popular technique to investigate the nature of excitons, the polarizabilities of the Frenkel exciton states, and so on [13]. EA is also a powerful method to determine $\chi^{(3)}$ as a spectrum, although no measurements have been reported on thiophene oligomers. It is thus significant to investigate evaporated 8T thin films by this technique in order to investigate the influence of chain length and to evaluate its $\chi^{(3)}$.

In this paper, we report on EA measurements on evaporated 8T thin films to evaluate its susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$.

EXPERIMENTAL

The synthesis and purification of 8T have been described elsewhere [8]. High purity 8T films with the thickness of 100 nm were prepared by vacuum evaporation on substrates with electrodes at room temperature under a pressure of 10^{-5} torr and at a rate of 5-10 nm/minute. In these conditions, the 8T molecules are randomly oriented on the substrate resulting in isotropic polycrystalline films. Cr electrodes on the quartz substrates were patterned to have gaps of 10, 20 or 40 μm wide by photolithography using the lift-off technique. In this sample configuration, the external applied electric field is

parallel to the quartz substrate [14].

In the EA measurement setup, monochromated light was focused to $0.3 \text{ mm} \times 1 \text{ mm}$ spot on the sample, and the light transmitted through a gap between two electrodes went through a polarizer and detected by a photodiode. A sinusoidal ac-voltage at $f=140 \text{ Hz}$ in the range of 0-100 V, which corresponds to fields up to 10^5 V/cm , was applied to the sample without damaging the organic layer, and the absorption change at $2f$ was detected by the lock-in amplifier. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Figure 2 shows the UV-visible absorption spectrum and the EA spectrum of a polycrystalline 8T film. A broad absorption band extending over 300-600 nm with a peak around 400 nm was observed together with due to two vibronic side-bands at 550 and 500 nm. On the other hand, the EA response presented intense and narrow peaks at 570, 520 and 480 nm. These features are similar to those of 6T [13]. The EA signal was proportional to the square of the applied field F , as expected.

The absorption spectra of oligothiophenes is already elucidated by exciton interactions between nearest neighbor molecules in closed-packed organization: the coupling between the transition dipole of molecules at non-equivalent sites leads to Davydov splitting of the $1A_g \rightarrow 1B_u$ transition. The

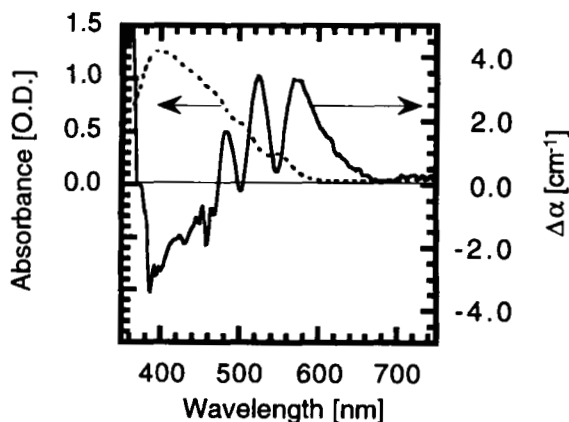


FIGURE 2 Absorption (dotted line) and electroabsorption (full line) spectra of a 100nm-thick polycrystalline 8T film at external field of $4.8 \times 10^4 \text{ V/cm}$.

transition between the ground state and the upper Davydov level is allowed and the transition between the ground state and the lower excited state becomes forbidden. The main peak observed at 400 nm is attributed to the allowed transition, and the small peak at 500 nm and its vibronic replica might be attributed to the forbidden transition allowed by disorder such as grain boundaries.

EA spectrum reflects the nature of the transitions involved: neutral transitions such as Frenkel excitons show EA spectra proportional to the first derivative of the absorption spectrum; highly polar transitions such as in charge-transfer (CT) excitons provide EA spectra proportional to the second derivative of it [13,15,16]. Figure 3 shows the EA spectrum together with the first and second derivatives of the absorption spectrum. It can be observed that the whole EA spectrum does not strictly follow neither the first nor the second derivative of the absorption spectrum. However, at the low energy side (500–650 nm) where the most intense EA peaks appear, the EA spectrum seems more similar to the 1st derivative than to the 2nd one, suggesting that the transitions in this region possess a Frenkel exciton character rather than a CT one.

The third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$ was evaluated as follows:

$$\chi^{(3)}(-\omega; \omega, 0, 0) = [(n\Delta n - k\Delta k) + i(n\Delta k + k\Delta n)] / 2\pi F^2 \quad (3)$$

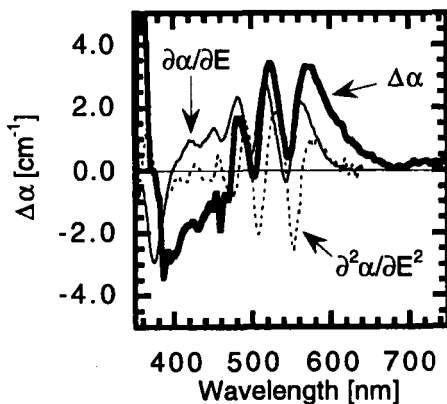


FIGURE 3 EA spectrum (thick full line), and first (thin full line) and second (thin dashed line) derivatives of the absorption spectrum of a 8T thin film sample.

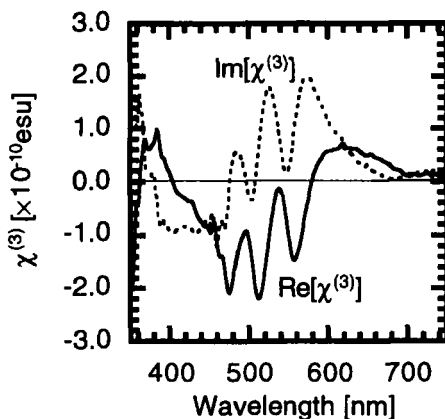


FIGURE 4 Spectrum of the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$ of a 8T film.

where Δn and Δk are the change of refractive index n and extinction coefficient k due to applied electric field F . Δn and Δk was obtained from $\Delta\alpha$ through the Kramers-Krönig transformation, and dispersion of n and k of the 8T films were measured by ellipsometry. The refractive index at 633 nm was about $n=2.1$ in good agreement with previous report [17]. In the absorption region, n increases up to $n=2.3$ and shows anomalous dispersion at short wavelength region. Figure 4 shows the spectral dependence of the real and imaginary parts of $\chi^{(3)}(-\omega; \omega, 0, 0)$ of a 8T thin film. The magnitude of $\chi^{(3)}(-\omega; \omega, 0, 0)$ was up to 2×10^{-10} esu. Although it is difficult to directly compare this value to $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ of 6T (2×10^{-12} esu [3]) and polythiophene (10^{-11} - 10^{-12} esu [18]) thin films measured by THG, this high value might be ascribed to the high degree of conjugation in the 8T molecule together with the high structural order of the 8T polycrystalline films.

CONCLUSION

Electroabsorption measurements on polycrystalline non-oriented octithiophene thin films at room temperature has been reported for the first time. These preliminary results suggest that the transitions at 500-600 nm presents a Frenkel exciton character rather than a CT exciton one. The nonlinear susceptibility $\chi^{(3)}(-\omega; \omega, 0, 0)$ was evaluated as high as 2×10^{-10} esu. Further EA measurements are in progress on oriented thin films and single

crystals of 8T in order to examine the influence of structural order on the third-order optical nonlinearity.

ACKNOWLEDGEMENT

This work is partly supported by a *Programme International de Coopération Scientifique* (PICS N°509) granted by CNRS.

REFERENCES

- [1] For a recent review, see *Handbook of Oligo- and Polythiophenes*, edited by D. Fichou (WILEY-VCH, Weinheim, 1998).
- [2] M.T. Zhao, B.P. Singh, and P.N. Prasad, *J. Chem. Phys.* **89**, 5535 (1988).
- [3] D. Fichou, F. Garnier, F. Charra, F. Kajzar, and J. Messier, *J. Organic Materials for Nonlinear Optics*, edited by R. Hahn and D. Bloor, Royal Soc. Chem., London, (1989), p.176.
- [4] H. Thienpont, G.L.J.A. Rikken, E.W. Meijer, W. ten Hoeven, and H. Wynberg, *Phys. Rev. Lett.*, **65**, 2141 (1990).
- [5] L.T. Cheng, J.M. Tour, R. Wu and P.V. Bedworth, *Nonlinear Optics* **6**, 87 (1993).
- [6] F. Kajzar, *Nonlinear Optics* **5**, 329 (1993).
- [7] T. Wada, L. Wang, D. Fichou, H. Higuchi, J. Ojima and H. Sasabe, *Mol. Cryst. Liq. Cryst.*, **255**, 149 (1994).
- [8] D. Fichou, M-P. Teulade-Fichou, G. Horowitz, and F. Demanze, *Adv. Mater.*, **9**, 75 (1997).
- [9] D. Fichou, B. Bachet, F. Demanze, I. Billy, G. Horowitz and F. Garnier, *Adv. Mater.* **8**, 500 (1996).
- [10] R. Hajlaoui, D. Fichou, G. Horowitz, B. Nessakh, M. Constant and F. Garnier, *Adv. Mater.* **9**, 557 (1997).
- [11] G. Horowitz, R. Hajlaoui, D. Fichou and A. El Kassmi, submitted to *J. Appl. Phys.*
- [12] D. Fichou, S. Delysse and J-M. Nunzi, *Adv. Mater.*, **9**, 1178 (1997).
- [13] L.M. Blinov, S.P. Palto, G. Ruani, C. Taliani, A.A. Tevosov, S.G. Yudin and R. Zamboni, *Chem. Phys. Lett.*, **232**, 401 (1995)
- [14] J. W. Wu, T. Wada, and H. Sasabe, *Phys. Rev. A* **50**, 3541 (1994)
- [15] S. J. Martin, H. Mellor, D. D. C. Bradley, and P. L. Burn, *Opt. Materials*, **9**, 88 (1998)
- [16] L. Sebastian and G. Weiser, *Chem. Phys.*, **61**, 125 (1981)
- [17] H. Knobloch, D. Fichou, W. Knoll, and H. Sasabe, *Adv. Mater.* **5**, 570 (1993).
- [18] H. Okawa, T. Hattori, A. Yanase, Y. Kobayashi, A. Carter, M. Sekiya, A. Kaneko, T. Wada, A. Yamada and H. Sasabe, *Mol. Cryst. Liq. Cryst.* **3**, 169 (1992).