

R&D630T-PH-01

PROJECT

"SYNTHESIS AND APPLICATION
OF LARGE HETEROMETALLIC CLUSTER SYSTEMS"

S **DTIC**
ELECTE
FEB 06 1995 **D**
G

CONTRACT NO: DA3A45 - 90 - C - 0034

Tenth and Final Interim Report

15th February 1994

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	<i>per form 50</i>
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and/or Special
<i>A-1</i>	

DTIC QUALITY INSPECTED 3

19950130 003

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

1. EXECUTIVE SUMMARY

This three year project was concerned with the chemical synthesis of nanometric particles, related structures, and their application in nonlinear optics.

Significant progress was made in all areas, i.e.

1.1 Chemical Synthesis

- (i) Routes were developed to novel heterometallic assemblies. For details see 6th Interim Report (March 1993).
- (ii) Synthesis of polymers with nonlinear properties enhanced by incorporating metal units. For details see 5th Interim Report (August 1992) and earlier reports.
- (iii) Fullerenes were synthesised by recessive heating of graphite, and the apparatus and techniques modified to optimise yields and separation. See 3rd Interim Report (August 1991).
- (iv) Metallo Fullerene species have been synthesised, characterised (see attached publication in press) and their nonlinear properties measured; see 9th Interim Report (January 1994).
- (v) Well defined nanometric gold clusters (in the range 50-400Å) were prepared and characterised using the citrate/PVP technique. For details see 7th Interim Report (October 1993).

1.2 Nonlinear Optical Measurements

- (i) Ultrashort pulse techniques were developed to study the optical nonlinearity of metal particles down to the femtosecond time domain. In the course of the work the following general observations were made.
 - The nonlinearity is indeed faster than any pulse applicable, i.e. rises and relaxes below 20fs.
 - Contrary to previous theories by Flytzanis et al., the nonlinearity is not size dependent, but scales with the square of the absorption coefficient in agreement with a hot electron origin of the effect.
 - The size of the nonlinearity per particle is of order $10^{-15} \text{ m}^2/\text{V}^2$ (10^{-8} esu), and hence substantial, the imaginary part of the nonlinearity is dominant and positive, whereas the real part is negative. (see 7th interim report - October 1993)

- (ii) The incorporation of metal centres into the backbone of rigid rod conjugated polymers affords materials with reproducible ultrafast nonlinearity. In the near infrared, enhancement factor up to two orders of magnitude could be observed, with the first row transition elements showing the greatest enhancement. (see 2nd Interim Report - March 1991), and attached reprints.
- (iii) Our group was amongst the first to observe optical nonlinearity in Fullerenes, both off-resonant at 1064nm and resonant optical in the visible (see 5th Interim Report - August 1992). A review of the area by the principal investigators is attached. In addition, basic spectroscopic characterisation of carbon nanotubes was reported, and other optoelectronic effects in fullerenes were studied (see 8th Report - November 1993).

2. Staffing

During the course of the project, nine graduate students and one post doc were associated. Of these, five have already been awarded PhD's, two obtained MSc, and two others are in the final stages of preparing doctoral theses. Two of these, Dr Andrew Davey and Dr Declan Weldon are now employed as postdoctoral research fellows. The initial Chemistry postdoc on the project, Dr Sylvia Draper, has proceeded to a permanent lectureship of inorganic chemistry in Trinity College Dublin. Finally, since the finish of the project, Professor David J Cardin has been appointed to the chair of inorganic chemistry in Reading University, UK.

3. Conferences and Reports

The principal investigators and their associates have reported results obtained on the project on numerous occasions at conferences, laboratory visits and seminars. This includes several invited talks.

Locations include: Oxford, UK (2), Manchester, UK, Cambridge (2-3), London, UK (3), Athens, G, Essex, UK, Barcelona, E, Warwick, UK, Sussex, UK, Southampton, UK, Austin, USA, U. Davis, Ca, USA, Yale, CT, USA

Santiago - Chile, Punta Arenas - Chile, Dayton - OH, Pulman - WA, Honolulu - HI, Senday - JAP, Jakarta - Indones, Dayton - NT, AUS, Sydney - AUS, Allied Syn - NJ, Moscow - RUS, San Diego - CA, Chicago - IL, Vienna - A, Kirchberg - A, Paris - F, Brussels - B, Oxford (2) - UK, Cambridge (1) - UK, London (2) - UK, Edinburgh Glasgow, Turbingen, Regensburg, Essen, Gieben, Berlin, Jena, Potsdam, Bielefeld, Hamburg, Mainz, Stuttgart

4. Financial

All financial statements have been submitted independently by the Finance Office at Trinity College Dublin.

Third Order Optical Non-linearity in Porous Silicon using Z- Scan

Fryad. Z. Henari, Kai Morgenstern, Vladimir A. Karavanskii,*
Vladimir. S. Dneprovskii* and Werner. J. Blau

Physics Department, Trinity College, University of Dublin,
Dublin 2, Ireland

*Semiconductor Physics Department, Moscow State University,
119899 Moscow, Russia.

The third order optical nonlinearities $\chi^{(3)}$ of porous silicon (PS) was measured using Z-scan technique. The intensity dependent absorption was observed and attributed to a two photon absorption process. The enhancement of $\chi^{(3)}$ over crystalline silicon reported. The real and imaginary parts of $\chi^{(3)}$ have been measured at 665 nm and found to be $2.5 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$ and $-8.8 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ respectively.

Porous silicon (PS) has generated enormous interest in the view of the possible applications in optoelectronics. The most interesting feature of this material is the strong visible luminescence[1,2]. Several authors attribute the enhanced luminescence of PS compared with the bulk Si to a radiative recombination of carriers spatially confined within nanostructures (quantum wires and quantum dots) [1,3-5]

PS is a promising material for optical switching. It has a nonlinearity characterised by a relatively high and fast third order nonlinearity $\chi^{(3)}$ [6,7,8]. It has been shown in [9] that in semiconductor crystallites of nanometers size a limited number of processes lead to a strong nonlinearity compared with two and three dimensional semiconductors. We suggest that the mechanism involved here, near the lowest resonance of the quantum dots and wires, are state filling and multiphoton absorption. Both mechanism have been already observed in PS [6,8,10].

In this paper we report to the best of our knowledge the first direct measurements of the sign and magnitude of both the real and imaginary parts of the third order nonlinearity $\chi^{(3)}$ of porous silicon. Experiments were performed at a wavelength of 665 nm with 500 ps laser pulses using the Z-scan technique.

The sample used in this experiment was a n-type silicon (111) wafer with resistivity 0.01 Ω . cm. It was anodised in a solution of HF(49%): ethanol solution. The thickness of the sample was measured using an electron microscope and found to be 36 μ m. The UV- excited photoluminescence (PL) of the PS sample was recorded by a 355 nm Argon ion laser at room temperature. The PL intensity was so high that it could be seen with the naked eye. Such high intensities can be utilised for the fabrication of LED's. The PL spectrum is shown in Fig.(1), where

the broadband PL centred at 660 nm with FWHM of 160 nm. i.e excitation via 355 nm (3.5 eV) band contributed to the luminescence around 660 nm (1.78 eV).

The Z-scan technique [11] was used to measure the nonlinear susceptibility of porous silicon (PS). The technique relies on the fact that the intensity of a focused laser beam varies along the axis of a convex lens and is a maximum at the focus. By moving the film through the focus, the intensity dependent absorption can be measured as a change of the transmission through the sample (open aperture). The nonlinear refraction is determined by the spot size variation at the plane of a finite aperture and detector combination (closed aperture). The sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

The laser used in this experiment was a PRA N₂ pumped dye laser operating at a wavelength of 665 nm, with pulse width of 500 ps. The laser output was adjusted to give 12 μ J. The laser beam was focused to a waist of 25 μ m with a lens of focal length 60 mm giving a typical power density of 4.0×10^9 W/cm². Each data point plotted corresponds to an average of 10 independent measurements.

The transmission with and without the aperture was measured in the far-field as the sample was moved through the focal point; this enables the separation the nonlinear refractive index from nonlinear absorption. Fig(2) shows the normalised transmission without an aperture as a function of the distance along the lens axis. The transmission is symmetric with respect to the focus ($z=0$ mm) where there is a minimum. Thus an intensity dependent absorption effect is observed. The intensity dependent absorption effect in this case can be considered to be a two photo absorption (TPA) effect. In a three level system, TPA can be described by[12]

$$\beta \propto \frac{1}{(E_{gn} - \hbar\omega)(E_{gm} - 2\hbar\omega - i\Gamma)}, \quad (1)$$

where Γ is the state width, g and n are the lower and upper fundamental levels respectively, m is the intermediate level. The single photon incident energy $\hbar\omega$ approaches the energy difference E_{gn} between the lower and upper level as demonstrated by a strong absorption of the UV radiation at 355 nm. The two photon absorption proceeds through the intermediate state m as confirmed by a PL peak at 660 nm. The middle level probably arises from exciton localisation and exciton-exciton interaction due to quantum confinement.

The normalised transmittance for the open aperture condition is given by [11]

$$T(z) = 1 - \frac{q_o}{2\sqrt{2}} \quad \text{for } |q_o| < 1, \quad (2)$$

where

$$q_o = \frac{\beta I_o (1 - e^{-\alpha L})}{(1 + z^2 / z_o^2) \alpha}$$

Here, α is the absorption coefficient, L is the thickness of the sample, I_o is the intensity of the laser beam at the focus ($z=0$), and z is the Rayleigh range of the beam. A fit of Eq.2 to the experimental data is depicted in Fig.2 and yields a value of $\beta = 8.7$ m/GW. This value should be compared to the value of 0.37 m/GW for crystalline silicon[13]. The former is an order of magnitude higher which is consistent with a quantum confined material such as PS.

The normalised transmission for the closed aperture Z-scan is given by [11]

$$\Delta T(z, \Delta\phi) = \frac{4\Delta\phi x}{(x^2 + 9)(x^2 + 1)}, \quad (3)$$

where $x = z/z_0$ and $\Delta\phi$ is a phase change. The solid line in Fig.3 is obtained from fitting the above equation using $\Delta\phi = 0.92$. The value of $\Delta\phi$ can also be calculated from the peak-valley transmission difference using equation $\Delta T_{p-v} = 0.406 \cdot (1 - S)^{0.25} |\Delta\phi|$ where S is the normalised aperture size ($S=0.08$).

The nonlinear index γ is given by [11]

$$\gamma = \frac{\Delta\phi\lambda\alpha}{2\pi I_0(1 - e^{-\alpha L})} \quad (4)$$

The real part of the third-order nonlinear susceptibility $\chi^{(3)}$ is related to γ through

$$\text{Re}\chi^{(3)} = 2n^2\varepsilon_0c\lambda, \quad (5)$$

and the imaginary part is related to the TPA coefficient β by

$$\text{Im}\chi^{(3)} = \frac{n^2\varepsilon_0c\lambda\beta}{2\pi}, \quad (6)$$

where n is the linear refractive index, ε_0 is the permittivity of free space and c is the velocity of light. The experimentally determined values of $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ at the wavelength 665 nm are $+ 2.5 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$ and $-8.8 \times 10^{-18} \text{ m}^2 \text{ V}^{-2}$ respectively. By comparing the value of $\text{Im}\chi^{(3)}$ and $\text{Re}\chi^{(3)}$ one can conclude that the $\text{Re}\chi^{(3)} > 3 \text{Im}\chi^{(3)}$ i.e. the $\text{Re}\chi^{(3)}$, which gives rise to refractive index changes, is dominant. The value of $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ nonlinearities of PS reported here are of the same order of the nonlinearities of artificial materials such as microcrystalline glasses[14], ($10^{-17} - 10^{-18} \text{ m}^2 \text{ V}^{-2}$). The absolute value

of $\chi^{(3)}$ was calculated from $\{ (\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2 \}^{1/2}$, and gives $+2.7 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$.

In conclusion, the sign and the magnitude of both real and imaginary parts of $\chi^{(3)}$ have been directly determined in PS, using the Z-scan technique. The enhanced $\chi^{(3)}$ over the crystalline silicon is reported, which is probably due to quantum confinement. This large $\chi^{(3)}$ effect will renew interest in the use of this material in nonlinear optical devices such as optical limiters and switching.

The authors acknowledge the help of the members of Professor J. Hegarty's group in particular Jiang Xing for using the PL set-up.

Figure Caption

Fig 1 : PL spectrum of PS excited by UV radiation.

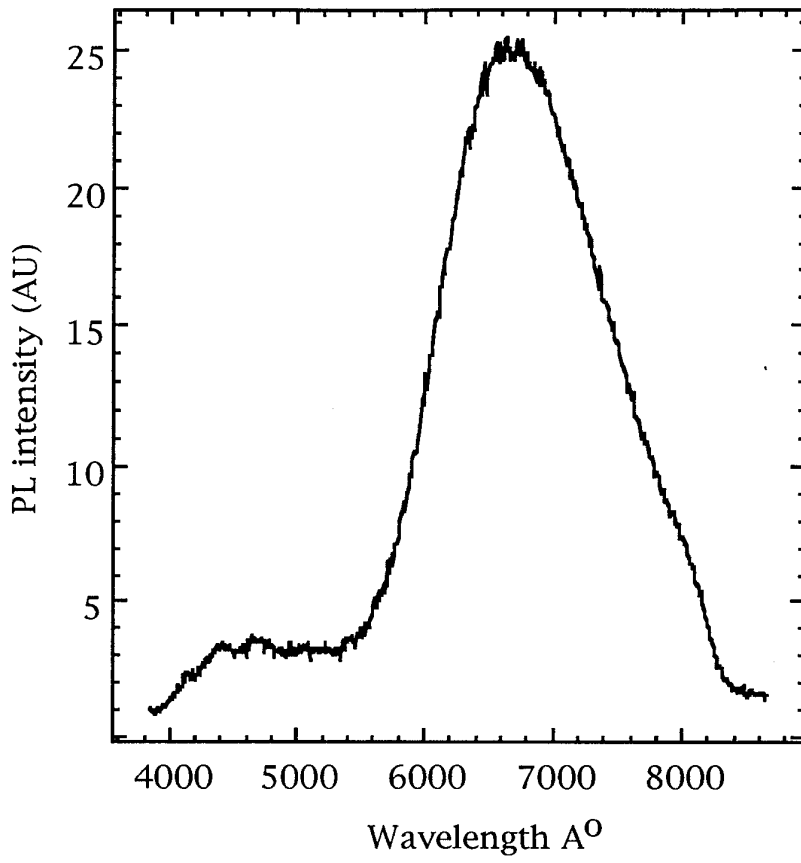
Fig 2.: Normalised transmittance (open aperture) at 665 nm of PS

The solid line is a fit data of Equation 2 with $\beta = 8.7 \text{ m/MW}$

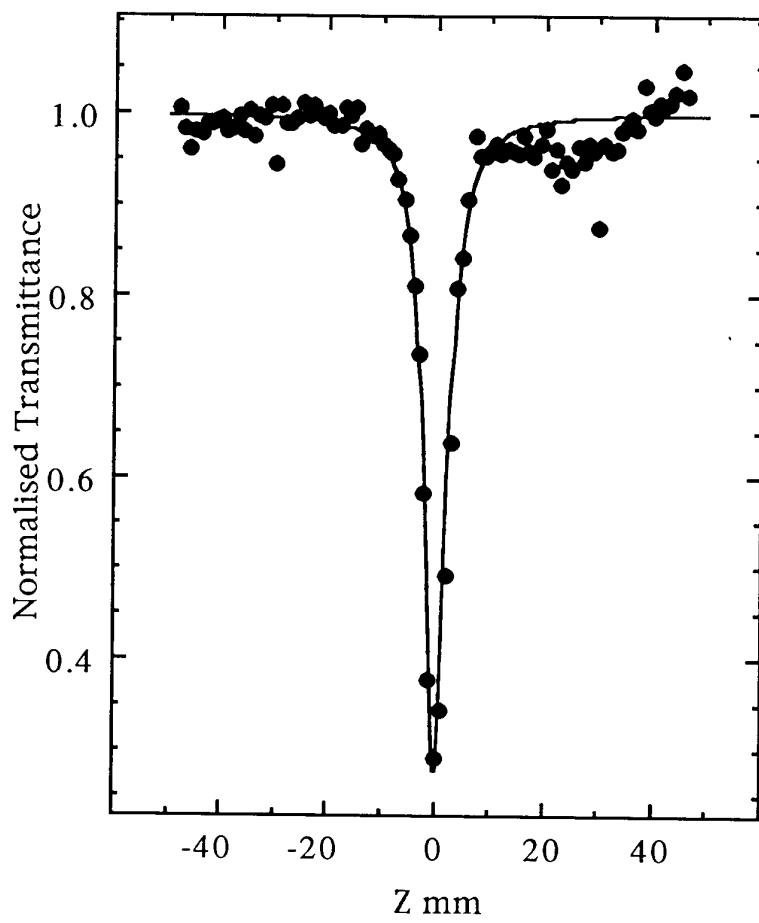
Fig.3 : Normalised transmittance (closed aperture) of PS. The solid line is a fit of data to Equation 3 with $\Delta\phi = 0.92$ and aperture size $S = 0.08$.

References

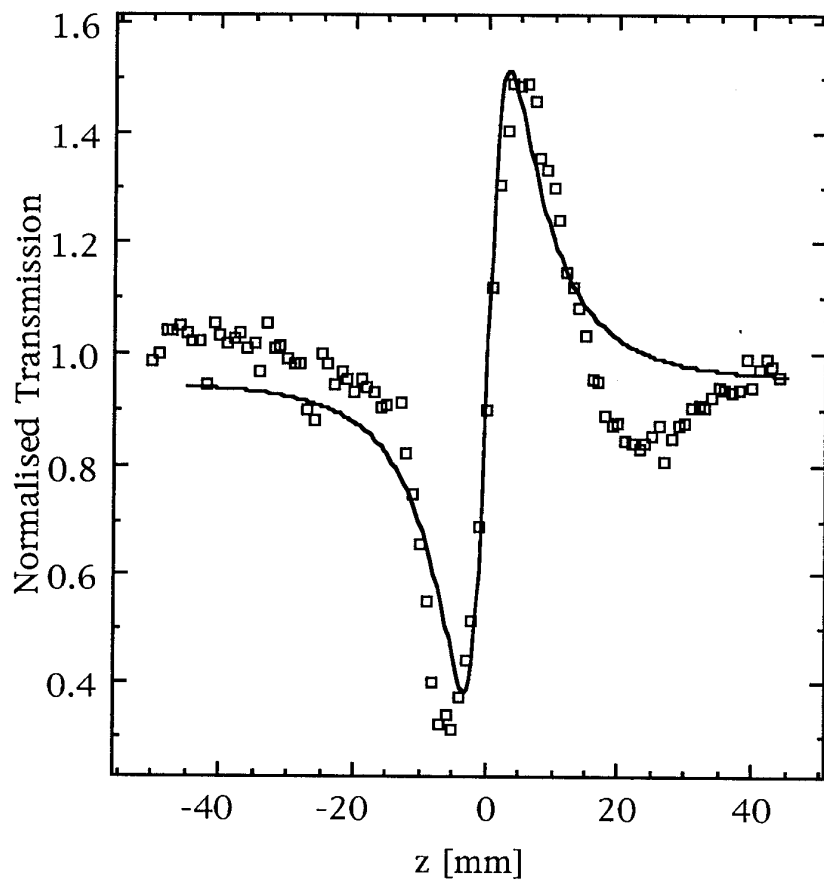
- 1- L. T. Canham, Appl. Phys. Lett. 57, 1046, **1990**.
- 2- V. Lehmann and Gosele Appl. Phys. Lett. 58, 856, **1991**.
- 3- S. Gadelis, J. S. Rimmer, P. Dawson, B. Hamilton, R. A. Kubiak, T. E. Whall and E. H. Parker, Appl. Phys. Lett. 59, 2118, **1992**.
- 4- R. Tsu, H. Shen and M. Dutta, Appl. Phys. Lett, 60, 112, **1991**.
- 5- M. Voos, P. Uzan, C. Delande and G. Bastard, Appl. Phys. Lett, 61, 1213, **1992**.
- 6- V. S. Dneprovskii, V. A. Karavanskii, V. I. Klimove and A. P. Maslove, JETP Lett. 57, 406, **1993**.
- 7- J Wang, H. Jiang, W. Wang and J. Zheng, Phys. Rev. Lett. 69, 3252, **1992**.
- 8- R. Chen, D. L. Lin and B. mendoza Phys Rev. B, 48, 1189, **1993**
- 9- S. Schmitt-Rink, D. A. B. Miller and D. S. Chemla, Phys. Rev. B 35, 8113. **1987**.
- 10- V. I. Klimove, V. S. Dneprovskii and V. A. Karavanskii, Appl. Phys. Lett. 64, 2691, **1994**
- 11- M. Sheik Bahae, A. A Said, T.H. Wei, D.J. Hagan and E.W. Van Stryland, IEEE J. Quantum Electron. 26, 760,**1990**.
- 12- Y. R. Shen The principle of nonlinear optics, (John wiley and sons, Inc., New York 1984) Chap.12, p.202.
- 13- W. Kütt, A. Esser, K. Seibert, U. Lemmer, and H. Kurz,"Application of Ultrashort Laser Pulses in Science and technology, A. Antoneti (ed.), Proc. SPIE 1268, 154 **1990**.
- 14- P. Butcher and D. Cotter The elements of nonlinear optics (Cambridge University Press, Cambridge 1991) chap. 9, p293 .



Henari Fig 1



Henari Fig. 2



Henari Fig. 3

Nearly Resonant Third-order Optical Non-linearity in C₆₀ Cast Films

Fryad Z. Henari,^a Declan N. Weldon^b and Werner J. Blau^a

^aPhysics Department, ^bChemistry Department, Trinity College, University of Dublin, Dublin 2, Ireland

We have carried out measurements of the third-order optical non-linearity $\chi^{(3)}$ of C₆₀ cast films using the z-scan technique. The measurements have shown that two-photon absorption is the dominant non-linear process around the 3.76 eV absorption region. The real and imaginary parts of $\chi^{(3)}$ of C₆₀ films have been measured at 665 nm are found to be 2.8×10^{-8} and -3.2×10^{-8} esu respectively.

KEYWORDS

Numerous studies have shown that fullerenes are interesting non-linear optical materials owing to their unique geometrical and electronic structure (for a review see Ref. 1). Amongst the fullerenes, C₆₀ has attracted considerable attention. The non-linearity of C₆₀ has been studied with various techniques such as THG,² DFWM^{3,4} and EFISH.⁵ None of these studies could distinguish clearly between the non-linear index and the non-linear absorption. We report here, to our knowledge, the first direct measurements of the sign and magnitude of both the real and imaginary parts of the third-order non-linearity $\chi^{(3)}$ of C₆₀ cast films at 665 nm, with 500 ps pulses, using the z-scan technique.

C₆₀ powder was prepared by contact arc evaporation of graphite in a helium gas atmosphere followed by extraction from the soot using CS₂ and chromatographic purification in an oxygen-free N₂ atmosphere. The powder (purity 99%) was dissolved in toluene to a concentration of 4 g l⁻¹. Films were deposited on glass substrates by casting under atmospheric pressure. The absorption coefficient was measured at 665 nm and found to be 2.8×10^4 cm⁻¹ for a 150 nm sample thickness.

The z-scan technique⁶ was used to measure the non-linear susceptibility of C₆₀. The technique relies on the fact that the intensity varies along the axis of a convex lens and is a maximum at the focus. By moving the film through the focus, the intensity-dependent absorption can be measured as the change in the transmission through the

sample (open aperture). The non-linear refraction is determined by the spot size variation at the plane of a finite aperture and detector combination (closed aperture), because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

The laser used in this experiment was a PRA N₂-pumped dye laser operating at a wavelength of 665 nm with a pulse width of 500 ps. The laser output was adjusted to give 12 μJ at the exit face of the substrate. The laser beam was focused to a waist of 25 μm with a lens of focal length 60 mm, giving a typical power of 4.0×10^9 W cm⁻². Each data point plotted corresponds to an average of 10 independent measurements. In the experiment the sample was exposed to laser irradiation at the substrate side to avoid ablation of the deposited C₆₀.

The transmission with and without the aperture was measured in the far field as the sample was moved through the focal point; this enables the separation of the non-linear refractive index from the non-linear absorption. Figure 1 shows the normalised transmission without the aperture as a function of the distance along the lens axis. The transmission is symmetric with respect to the focus ($z = 0$ mm), where there is a minimum. Thus an intensity-dependent absorption effect is observed. For the C₆₀ cluster the energy gap between the highest occupied state h_u and the lowest unoccupied state t_{1u} is about 1.9 eV,⁷ which is an optically forbidden transition. The absorption spectrum of C₆₀ films exhibits a

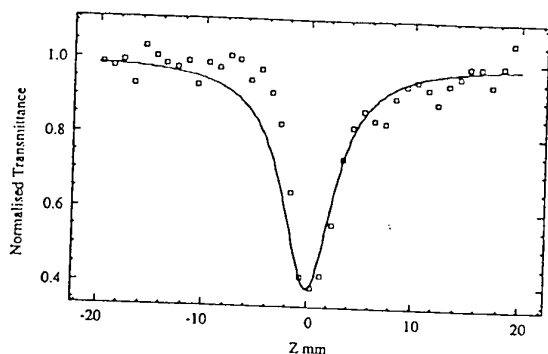


Fig. 1. Normalised transmittance (open aperture) at 665 nm of C₆₀ cast film. The solid curve is a fit of data to Eqn. 1 with $\beta = 33 \text{ cm MW}^{-1}$

further peak at 1.88 eV (Fig. 2). Therefore the observed intensity-dependent absorption may be attributed to a nearly resonant two-photon absorption (TPA) transition around the 3.76 eV absorption region (the excitation energy of one photon is 1.88 eV = 665 nm).

The normalised transmittance for the open aperture condition is given by⁶

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \quad \text{for } |q_0| < 1 \quad 1$$

where

$$q_0 = \frac{\beta I_0 (1 - e^{-\alpha L})}{(1 + z^2/z_0^2)\alpha}$$

Here α is the absorption coefficient, L is the thickness of the sample, I_0 is the intensity of the laser beam at the focus ($z = 0$) and z_0 is the Rayleigh range of the lens. A fit of Eqn 1 to the exper-

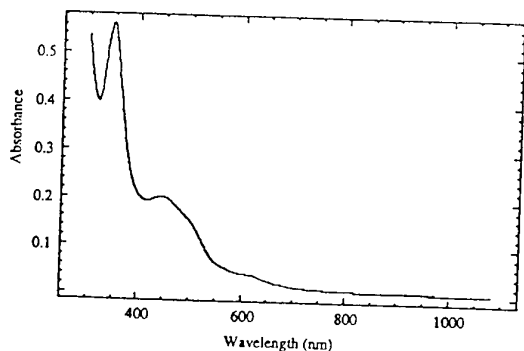


Fig. 2. Absorption spectrum of C₆₀ cast film

imental data is depicted in Fig. 1 and yields a value of $\beta = 33 \text{ cm MW}^{-1}$ for the non-linear absorption. This value should be compared with the value of $\beta = 1.2 \text{ cm kW}^{-1}$ observed for C₆₀ solution at 632 nm.⁸ The latter has more favourable conditions for two-step absorption owing to population of the longer-lived triplet state (0.1 ms). The two-photon event in this case proceeds as a two-step excitation process via a real intermediate triplet state which has a large excited triplet-triplet state absorption cross-section. This is different from the case of solid films, where the two-photon absorption can only proceed through a virtual state. However, one-photon absorption may also contribute to the non-linear effect through the transition $h_g \rightarrow h_u$.⁹ In order to investigate the origin of the effect, intensity-dependent transmission measurements were conducted. Figure 3 shows that the inverse transmission increases with increasing intensity up to an intensity of the order of $6 \times 10^6 \text{ W cm}^{-2}$. As seen from Eqn 2, one would expect this linear behaviour for two-photon absorption. At higher intensities the growth is no longer linear and may be explained as a result of excited state absorption saturation, in this case reverse saturation, which is common for C₆₀. The value of β is estimated by fitting the equation

$$\frac{1}{T} = \frac{1}{T_0} + \frac{\beta I (1 - e^{-\alpha L})}{T_0 \alpha} \quad 2$$

to the experimental data (Fig. 3) and is found to be $20 \times 10^{-5} \text{ cm W}^{-1}$. This value is smaller than

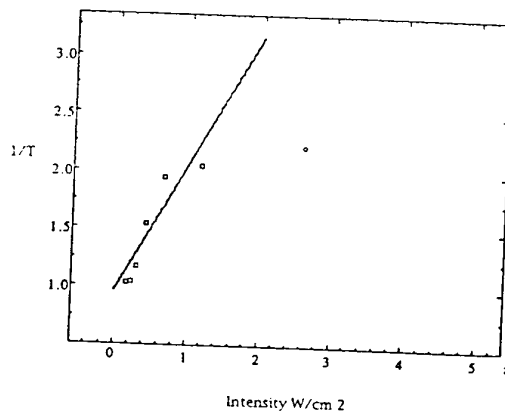


Fig. 3. Dependence of inverse transmission on intensity at 665 nm. The line is a fit to the experimental data

ON ORIGINAL

the value of β obtained from open aperture experiments by one order of magnitude and indicates that at higher intensities there is indeed an additional contribution from excited state absorption to the non-linear measurement.

The normalised transmission through the closed aperture is shown in Fig. 4. The peak-valley sequence of this z-scan is indicative of a self-focusing effect, i.e. C₆₀ has a positive refractive non-linearity.

The normalised transmission for the closed aperture z-scan is given by⁶

$$T(z, \Delta\phi) = \frac{4\Delta\phi x}{(x^2 + 9)(x^2 + 1)} \quad 3$$

where $x = z/z_0$ and $\Delta\phi$ is the phase change. The solid curve in Fig. 4 is obtained by fitting Eqn 3 using $\Delta\phi = 0.92$. The value of $\Delta\phi$ can also be calculated from the peak-valley transmission difference using the equation $\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi|$, where S is the aperture size ($S = 0.08$).

The non-linear index γ is given by⁶

$$\gamma = \frac{\Delta\phi(t)\lambda\alpha}{2\pi I_0(1 - e^{-\alpha L})} \quad 4$$

The real part of the third-order non-linear susceptibility $\chi^{(3)}$ is related to γ through

$$\text{Re}\chi^{(3)} = 2n^2\epsilon_0 c\gamma \quad 5$$

and the imaginary part is related to the TPA coefficient β by

$$\text{Im}\chi^{(3)} = \frac{n^2\epsilon_0 c\lambda\beta}{2\pi} \quad 6$$

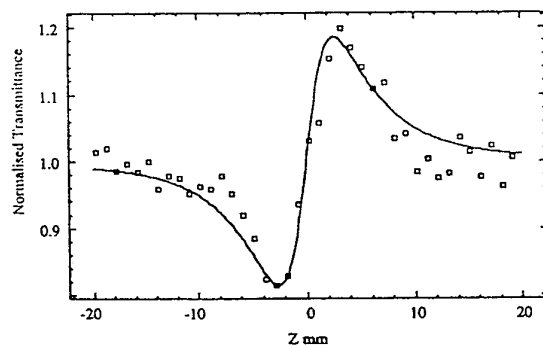


Fig. 4. Normalised transmittance (closed aperture) of C₆₀ cast film. The solid curve is a fit of data to Eqn 3 with $\Delta\phi = 0.92$ and aperture size $S = 0.08$

where n is the linear refractive index, ϵ_0 is the permittivity of free space and c is the velocity of light. The experimentally determined values of $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ at the wavelength 665 nm are 2.8×10^{-8} and -3.2×10^{-8} esu respectively. By comparing the values of $\text{Im}\chi^{(3)}$ and $\text{Re}\chi^{(3)}$ in the wavelength region, one concludes that $\text{Im}\chi^{(3)} > 1.5\text{Re}\chi^{(3)}$, i.e. $\text{Im}\chi^{(3)}$, which is due to a two-photon process, is dominant. The absolute value of $\chi^{(3)}$ was calculated from $[(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2]^{1/2}$ as 4.2×10^{-8} esu. The value of $\text{Re}\chi^{(3)}$ reported here is slightly larger than that quoted for DFWM measurements of C₆₀ made at 1.064 nm (3.3×10^{-9} esu)⁴ owing to the different electronic resonance conditions. The relative value of $\text{Im}\chi^{(3)}$ for C₆₀ agrees with measurements made with 5 ns pulses at 610 nm using the z-scan technique.¹⁰

In conclusion, the sign and magnitude of both the real and imaginary parts of $\chi^{(3)}$ have been directly determined in C₆₀ cast films using the z-scan technique. Two-photon absorption for C₆₀ at 665 nm is the dominant contributor to the non-linear process with 500 ps pulses. Results indicate that the third-order non-linearity is enhanced by a nearly resonant two-photon absorption transition with a band gap energy of 3.67 eV.

ACKNOWLEDGEMENTS

Financial support for this work provided by the European Office of the U.S. Army is gratefully acknowledged.

REFERENCES

1. W. J. Blau and D. J. Cardin, *Mod. Phys. Lett. B*, 1992, 6, 1351.
2. J. S. Meth, H. Vanherzeele and Y. Wang, *Chem. Phys. Lett.*, 1992, 197, 26.
3. Z. H. Kafafi, J. R. Lindle, R. G. S. Pong, F. J. Bartoli, L. J. Lingg and J. Milliken, *Chem. Phys. Lett.*, 1992, 188, 429.
4. Q. Gong, Y. Sun, Z. Xia, Y. H. Zou, Z. Gu, X. Zhou and D. Qing, *J. Appl. Phys.*, 1992, 71, 3025.

5. X. K. Wang, T. G. Zhang, W. P. Lin, S. Z. Liu, G. K. Wong, M. M. Kappes, R. P. H. Chang and J. B. Ketterson, *Appl. Phys. Lett.*, 1992, **60**, 810.
6. M. Sheik Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron*, 1990, **QE-26**, 760.
7. S. Saito and A. Oshiyama, *Phys. Rev. Lett.*, 1991, **66**, 2637.
8. F. Z. Henari, S MacNamara, O. Stevenson, J. Callaghan, D. Welden and W. Blau, *Adv. Mater.*, 1993, **5**, 930.
9. C. Reber, L. Tee, J. MacKiernan, J. Zink, R. Williams, W. Tong, D. Ohlberg, R. Whetten and F. Diederich, *J. Phys. Chem.*, 1991, **95**, 2127.
10. F. Henari, J. Callaghan, H. Stiel, W. Blau and D. J. Cardin, *Chem. Phys. Lett.*, 1992, **199**, 144.

Nonlinear optical properties of a soluble form of polyisothionaphthene

S. J. BURBRIDGE, H. PAGE, A. DRURY, A. P. DAVEY,
J. CALLAGHAN and W. BLAU

Department of Pure and Applied Physics,
Trinity College Dublin, Dublin 2, Ireland

(Received 30 September 1993; revision received and accepted 24 January 1994)

Abstract. The third-order nonlinearity of a low-bandgap conjugated organic polymer has been assessed. Degenerate four-wave mixing experiments (at 1.064 μm using picosecond pulses from a passively mode-locked neodymium-doped yttrium aluminium garnet laser) on solutions of the polymer have permitted the determination of the microscopic third-order nonlinearity γ . The polymer exhibits unusual behaviour which is solution concentration dependent. This behaviour is thought to be due to aggregation effects and strongly suggests that the bulk response of the material is large, the third-order nonlinearity being of the order of ten times greater than that of polythiophene.

Following preliminary studies, a sample of the same polymer with a greater average molecular weight was also measured and was found, within an order of magnitude, to possess the same third-order nonlinearity.

1. Introduction

The third-order nonlinear optical properties of conjugated organic semiconducting polymers has been the subject of intense investigation for the past 15 years. It is hoped that such materials will find use in optical switching devices based on planar waveguides [1].

Many different classes of such polymers have been investigated [2] in the search for a material which exhibits a sufficiently large third-order nonlinear optical response for use in all optical switching devices. To date, a material which meets all device requirements has still not been identified.

Our own work has focused on the development of semiconducting polymers for use in devices which would operate in the near-infrared region. Such devices would find application primarily in optical telecommunications systems. The Kramers-Kronig relationship states that the magnitude and sign of the nonlinear refractive index at a fixed wavelength are strongly dependent on the position of resonance for any sample to be investigated. For the purposes of our own work, this has involved the investigation of narrow-gap semiconducting polymers whose band edge tails into the near-infrared region. In the past, investigations have avoided such systems, concentrating on polymers which exhibit optical transparency in the near infrared. Loss measurements in waveguides have demonstrated, however, that absorption forms only a small fraction of overall losses, scattering in waveguides proving to be a far greater problem.

The work reported here describes investigation of the microscopic third-order nonlinear optical response of a narrow-gap semiconducting polymer based on the polyisothionaphthene (PITN) family (figure 1).

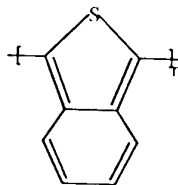
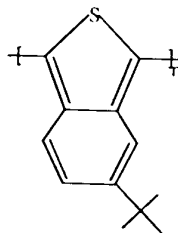


Figure 1. The chemical structure of PITN.

Figure 2. Synthesis of poly(3-*tert*-butyl)isothionaphthene.

The electrical properties of this polymer have been extensively investigated, however, its lack of solubility has prevented any study of the nonlinear optical properties since no form of high optical quality sample has been available. The polymer studied here is a form of PITN which is soluble in common organic solvents (figure 2).

The fact that this material is soluble permits the investigation of its nonlinear optical properties in solution and the fabrication of thin film waveguide structures using spin-coating techniques. This investigation of the microscopic third-order nonlinearity of two different forms of this material in chloroform solutions is described herein.

2. Synthesis of poly(*tert*-butylisothionaphthene)

2.1. Synthesis of 4-*tert*-butyl 1,2-dimethylbenzene

2.1.1. By the method of Larner and Peters [3].

106.2 g (1 mol) *o*-xylene and 92.1 g (1 mol) *tert*-butyl chloride were well mixed (magnetic stirrer). 1.1 g of anhydrous ferric chloride was added slowly (30 min) at room temperature. When the evolution of HCl had stopped, excess *tert*-butyl chloride (20.5 g) was added and the mixture stirred for a further hour. It was then heated in a water bath for 15 min (turning brown at approximately 650°C) and filtered through charcoal (125 g). The resulting yellow solution was distilled and various fractions of colourless liquid were collected (boiling points, 155–1750, 185–2000 and 205–2100°C). The highest boiling fraction was found to be *tert*-butyl 1,2-dimethylbenzene with a yield of 90.6 g (55.8%).

2.1.2. By the method of Nightengale et al. [4]

12.5 g anhydrous ferric chloride was dissolved in 150 ml dry *o*-xylene in a 11 three-necked flask equipped with a reflux condenser. 25 g *tert*-butyl chloride was added slowly (1 h) from dropping funnel while the mixture was stirred and kept cool (with an ice and salt bath at approximately 00°C). It was stirred under reflux for a

further 6 h and the temperature was not allowed to rise above 100°C. It was poured into 100 g of ice in 100 g HCl (to decompose it). The top layer was extracted with petroleum ether (30–40°C) and washed and dried. The solvent and excess *o*-xylene were distilled off (*in vacuo*) and the product collected by vacuum distillation (500°C; 17 mbar) with a yield of 19.6 g (44.7%).

2.2. Preparation of 1,2-bis(bromomethyl)-4-*tert*-butylbenzene

2.2.1. Using the method of Pini et al. [5]

8.125 g *tert*-butyl *o*-xylene (0.05 mol), 17.8 g *N*-bromosuccinimide (0.1 mol), 0.2 g 2-(4-biphenyl)-5-phenyloxazole (BPO) and 50 ml of dry CCl₄ were placed in a 250 ml round-bottomed flask and refluxed with stirring (magnetically) in the dark under nitrogen for 3 h. The mixture was left overnight at room temperature (under the same conditions); then it was filtered (to remove the succinimide) and the solvent removed (*in vacuo*). The product was collected by vacuum distillation (116–1180°C at 0.12 Torr) with a yield of 4.66 g (29%).

2.3. Preparation of 1,3-dihydro-4-*tert*-butylisothionaphthene

2.3.1. Using the method of Cava and Deana [6]

1.05 g (0.013 mol) sodium sulphide dehydrate was dissolved in 75 ml of dry ethanol in a 250 ml round-bottomed two-necked flask fitted with a magnetic stirrer and condenser. 3.98 g (0.012 mol) 1,2-bis(bromomethyl)-4-*tert*-butylbenzene was added dropwise during 30 min. The solution went from pale blue to bright yellow. It was refluxed for 1 h and the ethanol removed *in vacuo*. The remaining brown-black oil was dissolved in methylene chloride and filtered to remove sodium bromide. The CH₂Cl₂ was removed *in vacuo* and the final product obtained by vacuum distillation ($p = 6 \times 10^{-2}$ Torr; $T = 880^\circ\text{C}$) with a yield of 1.53 g (64%).

2.4. Polymerization of 4-*tert*-butyl-1,3-dihydroisothionaphthene

2.4.1. Oxygen-promoted solid-state polymerization

1 g of the monomer (4-*tert*-butyl-1,3-dihydroisothianaphthene) was left uncovered in air in a glove-box for 3 weeks. Infrared spectra were taken at regular intervals and finally ultraviolet and nuclear magnetic resonance (NMR) spectra after washing with methanol to remove monomer. Gas-phase chromatography (GPC) indicated a polymer of weight-averaged molecular weight 13 091 and number-averaged molecular weight 5569.

2.4.2. Chemical cationic oxidative polymerization with ferric chloride (using the method of Pomerantz et al. [7])

3.6 mmol thiophene (0.7 g) was placed into a three-necked flask equipped with a condenser and drying tube, a dropping funnel and an inlet for dry air. 0.5 g anhydrous FeCl₃, dissolved in 50 ml chloroform was added (20 min). The solution was then warmed to 500°C and stirred for 24 h, with air bubbling through. The black solution was then washed with water to remove the FeCl₃. 20 ml concentrated NH₃ was added and the solution stirred for 30 min at room temperature. It was then washed several times with water and dried over MgSO₄. The solvent was removed *in vacuo* and the low-molecular-weight fractions removed by Soxhlet extraction with methanol, giving a yield of 0.25 g (36.48%).

The experiment was repeated using monomer recovered from the methanol wash, giving a total yield of 53.11%.

GPC showed a high-molecular-weight polymer of weight-averaged molecular weight and number-averaged molecular weight 10 842. The structure was confirmed by NMR.

2.4.3. Chemical cationic free-radical polymerization

0.75 g 4-*tert*-butyl-1,3-dihydroisothionaphthene was dissolved in 200 ml CCl_4 . A pinch (0.1 g) of BPO was added and the mixture heated under reflux (in a nitrogen atmosphere) for 24 h. Upon filtration a black powder was obtained. This was washed with methanol and dried *in vacuo*.

GPC indicated a polymer of weight-averaged molecular weight 3901 and number-averaged molecular weight 3862.

3. Experimental details

The experimental method employed in these studies was that of forced light scattering from laser-induced gratings, a technique which may be viewed as a degenerate four-wave mixing process in the forward direction [8]. The light source is an amplified, passively mode-locked Nd^{3+} -doped yttrium aluminium garnet laser emitting linearly polarized pulses of 50 ± 25 ps duration and of wavelength $\lambda = 1.064 \mu\text{m}$ at a repetition rate of 3 Hz. Peak powers of up to 50 MW were readily available. The experimental method is described in detail elsewhere [9] and the set-up is depicted schematically in figure 3. It is based on the interference at the sample of two spatially and temporally overlapped beams, producing a spatial modulation of the intensity dependent refractive index of the material. This modulation acts as a diffraction grating from which the pulses may self-diffract. Under thin-grating conditions [8], satisfied experimentally by keeping the angle between the two beams small (less than 1°), an expression relating the diffraction efficiency, η into the first order, to the third-order material nonlinearity may be derived:

$$|\chi^{(3)}| = \frac{4\epsilon_0 c n^2 \lambda \eta^{1/2}}{3\pi d I_0}, \quad (1)$$

where c is the speed of light, ϵ_0 is the permittivity of free space, n is the refractive index of the sample, d is the sample thickness and I_0 is the input pulse intensity. In the experiments reported here, $d = 1$ mm and n is taken to be the refractive index of the solvent, because of the low fractional volume of solute. Equation (1) holds for materials which are transparent at the operating wavelength. Although there is some

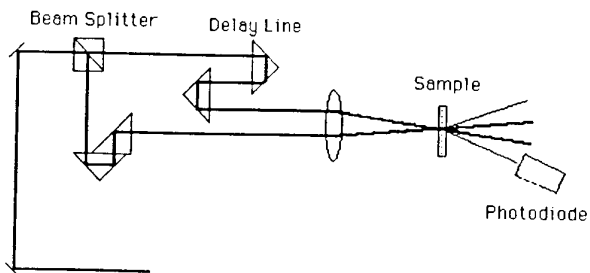


Figure 3. Experimental set-up for the self-diffraction technique.

small absorption at the operating wavelength, the effective refractive index and thus the effective sample thickness may be considered to be that of the refractive index of the solvent and the sample cell path length respectively.

It can be seen from equation (1) that verification of the presence of a true third-order nonlinear process may be performed by monitoring the intensity dependence of the diffraction efficiency. For a true third-order process,

$$\eta = \frac{I_1}{I_0} \alpha I^2, \quad (2)$$

where I_1 is the intensity diffracted into the first order. Such verification is important as fifth- and seventh-order processes, originating in two- and three-photon resonant enhancement of the material nonlinearities, have been observed in organic conjugated materials [9, 10].

$|\chi^{(3)}|$ may have both real and imaginary components originating from the solute as well as a contribution $\chi_{\text{solv}}^{(3)}$ from the solvent, which is purely real and positive in the case of most organic solvents, including chloroform [11]. For the concentration range employed in this work the solute fractional volume is negligible. Thus,

$$|\chi^{(3)}| = [(\chi_{\text{solv}}^{(3)} + \text{Re } \chi_{\text{sol}}^{(3)})^2 + (\text{Im } \chi_{\text{sol}}^{(3)})^2]^{1/2}, \quad (3)$$

where $\text{Re } \chi_{\text{sol}}^{(3)}$ and $\text{Im } \chi_{\text{sol}}^{(3)}$ are the real and imaginary components of the material nonlinearity. By monitoring the concentration dependence of $|\chi^{(3)}|$, the contribution $\chi_{\text{solv}}^{(3)}$ due to the solvent may be extracted and the magnitudes of $\text{Re } \chi_{\text{sol}}^{(3)}$ and $\text{Im } \chi_{\text{sol}}^{(3)}$ may be determined. Furthermore the sign of $\text{Re } \chi_{\text{sol}}^{(3)}$ may be determined from the concentration dependence of the real part of $|\chi^{(3)}|$.

The second molecular hyperpolarizability γ is given by

$$|\gamma| = \frac{|\chi^{(3)}|}{N_A C L_L^4}, \quad (4)$$

where C is the oligomer concentration, N_A is Avogadro's constant and L_L is the Lorentz local field factor, which for practical purposes is taken to be that of a linear molecule and is given by $L_L = 1$ [12].

4. Results

4.1. Linear absorption

Two different types of sample were studied: one of low molecular weight (with an average of five repeat units per chain), and one of far higher molecular weight (of the order of 80 repeat units on average) [13]. The absorption spectrum of the higher-molecular-weight sample is shown in figure 4.

4.2. Nonlinear optical response of the low-molecular-weight sample

Figure 5 shows the concentration dependence of diffraction efficiency. As already described, theory predicts a parabolic behaviour. It is clear, however, that there is a deviation from such behaviour in this case. At low concentrations the dependence of the diffraction efficiency is parabolic. At a certain limit, however, this dependence begins to deviate before returning at higher concentrations to a second parabolic behaviour. Such behaviour is not well understood but is clearly due to some form of interaction between polymer chains. However, this behaviour has been

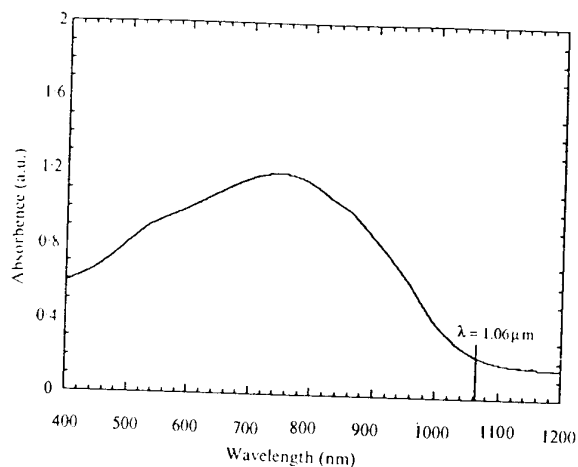


Figure 4. Absorption spectrum of higher-molecular-weight poly(*tert*-butylisothionaphthene) (a.u., arbitrary units). (Note that the absorption bandtail for the lower-molecular-weight material disappears at 950 nm.)

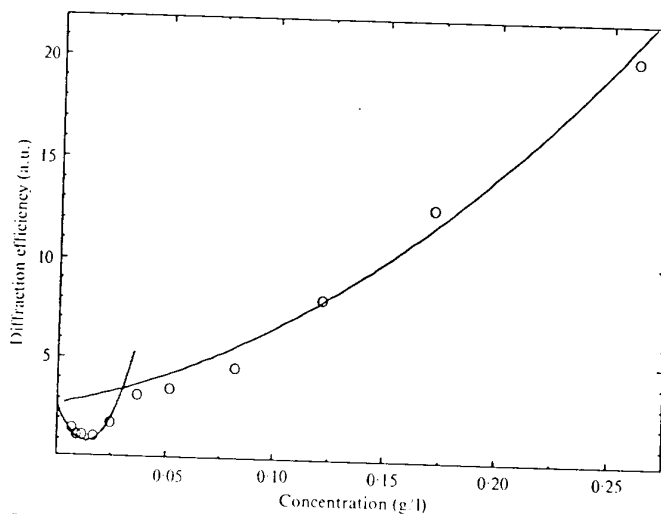


Figure 5. Concentration dependence of the diffraction efficiency for the low-molecular-weight sample (a.u., arbitrary units).

consistently observed in a variety of organic materials both monomeric and polymeric [14].

For the purposes of calculating a microscopic nonlinearity γ , points in the low-concentration region (where no interchain interaction occurs) are used. The fit employed in this case along with the points is shown in figure 6. It should be noted that errors (including scattering) are minimized by sampling each data point over 100 shots. The best fits in each case were found to be parabolic.

The values of γ obtained from this fit are given in the table. As can be seen by comparison with the values given for polythiophene (a structurally related conjugated polymer), the nonlinear optical response is quite large.

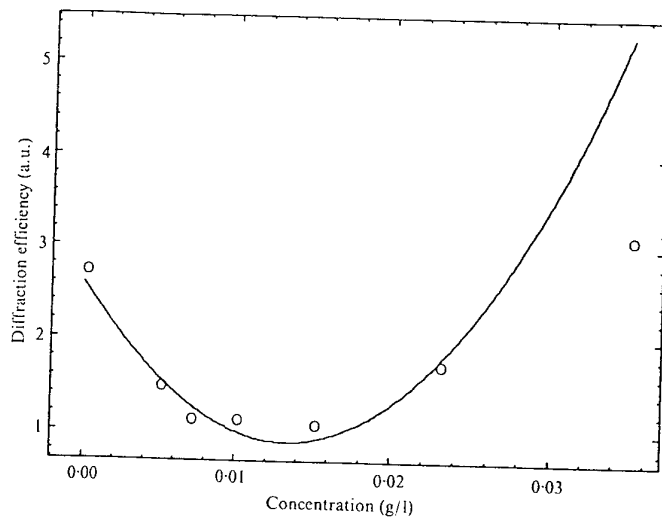


Figure 6. Fit of concentration to the diffraction efficiency for the low-molecular-weight sample (a.u., arbitrary units).

γ values.

Compound	γ_{Re} ($m^5 V^{-2}$)	$ \gamma _{Im}$ ($m^5 V^{-2}$)	$ \gamma $ ($m^5 V^{-2}$)
Poly(3- <i>tert</i> -butyl)isothionaphthene (low molecular weight)	-9×10^{-45}	6×10^{-45}	1×10^{-44}
Poly(3- <i>tert</i> -butyl)isothionaphthene (high molecular weight)	-1×10^{-45}	3×10^{-45}	4×10^{-45}
Polythiophene [15]	-6×10^{-46}	1×10^{-45}	1×10^{-45}

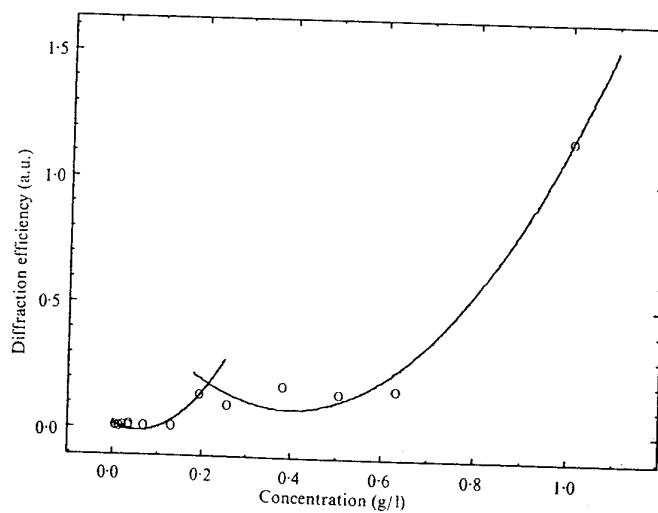


Figure 7. Concentration dependence of the diffraction efficiency for the high-molecular-weight sample (a.u., arbitrary units).

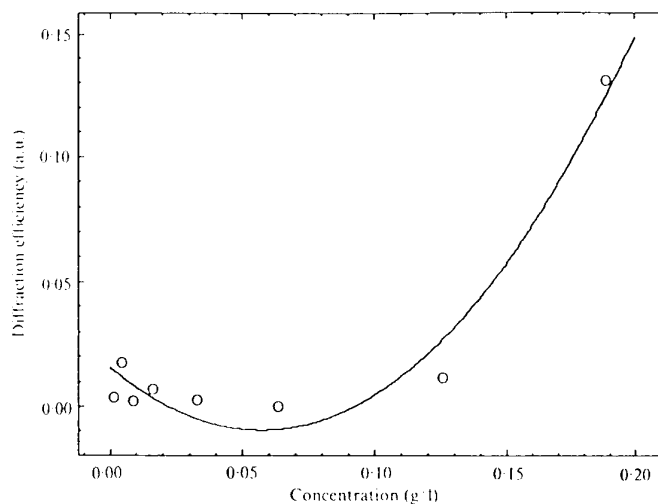


Figure 8. Fit of concentration to the diffraction efficiency for the high-molecular-weight sample (a.u., arbitrary units).

4.3. Nonlinear optical response of the high-molecular-weight sample

Figure 7 shows the variation in diffraction efficiency with concentration. As before, there is a significant deviation from the behaviour predicted by theory. It is interesting to note that the deviation is quite similar to that of the low-molecular-weight sample.

Figure 8 shows the fit employed to calculate the values of γ for the high-molecular-weight sample. The γ values obtained (given in the table) are similar to those for the other polymers listed. It should be noted, however, that for this sample the wavelength of measurement lies in the band edge, whereas for the other compounds in the table the measurement may be considered to have been performed off resonance.

5. Conclusions

Nonlinear optical properties of high- and low-molecular-weight narrow-bandgap conjugated organic polymers were studied. The concentration dependence of the diffraction efficiency shows an unusual behaviour. In the sample where the primary absorption is shifted towards the wavelength of measurement, no increase in the real and imaginary components of nonlinearity was observed. Further work aims to probe the change in nonlinearity through the wavelength region of 1.0–1.5 μm .

Acknowledgment

This work was funded by the RACE 2017 (HIPOS) project, sponsored by the European Communities Commission

References

- [1] STEGEMAN, G. I., and STOLEN, R. H., 1989, *J. opt. Soc. Am. B*, **6**, 652.
- [2] NALWA, H. S., 1993, *Adv. Mater.*, **5**, 341.
- [3] LARNER, B., and PETERS, A., 1952, *J. chem. Soc.*, **1**, 680.
- [4] NIGHTENGALE, D., et al., 1944, *J. Am. chem. Soc.*, **66**, 154.

- [5] PINI, D., *et al.*, 1987, *Macromolecules*, **20**, 58.
- [6] CAVA, M., and DEANA, A., 1958, *J. Am. chem. Soc.*, **81**, 4266.
- [7] POMERANTZ, M., TSENG, J. J., ZHU, H., SPROULL, S. J., REYNOLDS, J. R., UITZ, R., ARNOTT, H. J., and HAIDER, M. I., 1991, *Synth. Metals*, **41-43**, 825.
- [8] EICHLER, H. J., GUNTER, P., and POHL, D. W., 1986, *Laser Induced Gratings*, Springer Series in Optical Sciences, Vol. 50 (Berlin: Springer), p. 28.
- [9] BYRNE, H. J., BLAU, W., and JEN, K. Y., 1989, *Synth. Metals*, **32**, 229.
- [10] NUNZI, J. M., and GREC, D., 1987, *J. appl. Phys.*, **62**, 2198.
- [11] MAKER, P. D., TERHUNE, R. W., and SAVAGE, C. M., 1964, *Phys. Rev. Lett.*, **12**, 507.
- [12] SHEN, Y. R., 1984, *The Principles of Nonlinear Optics* (New York: Wiley-Interscience), p. 212.
- [13] DRURY, A., 1993, M.Sc. Thesis, Trinity College, Dublin.
- [14] BYRNE, H. J., and BLAU, W., 1992, *Electronic Properties of Polymers*, Springer Series in Solid-State Sciences, Vol. 107 (Berlin: Springer), p. 190.
- [15] BYRNE, H. J., 1989, Ph.D. Thesis, Trinity College, Dublin.

Nonlinear optical studies of Group 10 transition-metal thienyl systems

A. P. Davey^{a,b}, H. J. Byrne^b, H. Page^b, W. Blau^b and D. J. Cardin^a

^aDepartment of Chemistry, ^bDepartment of Pure and Applied Physics, Trinity College Dublin, Dublin 2 (Ireland)

(Received February 27, 1992; accepted in revised form October 15, 1992)

Abstract

trans-Square-planar Group 10 metal thienyl complexes were synthesized and characterized. The linear and nonlinear optical properties were studied in solution, the latter by forward degenerate four-wave mixing at 1.064 μm . A strong dependence of the linear and nonlinear optical properties on the metal centre was observed, both the lowest energy absorption wavelength and second hyperpolarizability decreasing down the metal group. A benzothienyl analogue of the nickel complex was similarly synthesized and characterized, both structurally and optically. The fused ring is seen to have a favourable influence on the second hyperpolarizability. Polymeric analogues of the two nickel complexes were prepared by copolymerization. The lowest energy optical transitions are substantially higher than those of purely organic analogues and the measured second hyperpolarizabilities compare very favourably, being up to 25 times larger than poly[(3-butyl)thiophene].

Introduction

In the investigation of nonlinear optical materials for application to all-optical signal processing, the incorporation of transition metals into conjugated organic systems has recently been demonstrated as a possible route towards considerably increased off-resonant nonlinear optical response [1]. The presence of polarizable transition metals which possess occupied d-orbitals in a conjugated backbone should increase the density of polarizable electrons. Furthermore, the linear structure imposed on the molecule by the incorporation of selected square-planar metal systems as well as the increased processability provided by solubilizing phosphine groups must be viewed as favourable, as must the environmental and photochemical stability of these systems. In our previous study, the incorporation of Group 10 transition metal complexes into alkynyl systems was shown to enhance considerably the nonlinear optical properties of the organic system [1]. The nature of the interaction of the metal centre with the conjugated organic system is as yet unclear, as is the trend of metal dependence although a strong dependence on metal size is apparent. In an effort to elucidate further the nonlinear optical nature of such systems, thiophene and benzothiophene complexes incorporating the Group 10 transition metals have been synthesized and studied. As a reference point, the terthiophene oligomer (an organic analogue of comparable con-

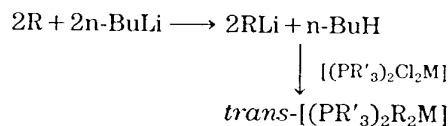
jugated length) is also studied and measured nonlinearities of the metal complexes are found to compare favourably.

Polythiophene is of interest as a stabilized form of *cis*-polyacetylene [2], but both the linear and nonlinear responses are diminished by the influence of free rotation about the inter-ring σ -bond. One approach to limiting this free rotation is the inclusion of a benzene ring on the thiophene moiety, in the form of polyisothionaphthene [3]. The fused ring acts to reduce the electron density of the 2,3- π -bond inducing an increase in π -character of the bond connecting adjacent rings. In order to investigate the influence of such a fused ring on the optical and nonlinear optical properties of the Group 10 thienyl systems, a nickel benzothienyl analogue was synthesized and characterized. This system should provide an understanding of the degree of π -character of the metal-carbon bond in this family of compounds.

In order to study larger metal-containing systems, polymers of thiophene and benzothiophene incorporating nickel centres in their backbone were also synthesized and investigated. The purposes of this exercise were twofold; first, to extend the understanding of the nature of the nonlinear optical processes of the monomer complexes, secondly to determine the magnitude of their third-order nonlinear response and hence evaluate the potential of such systems in terms of device applications.

Chemical synthesis

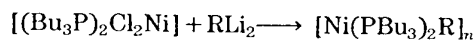
The thienyl complexes were synthesized by the reaction of lithiothiophene (formed by the reaction of *n*-butyllithium with thiophene at 0 °C) with the appropriate dihalometal phosphine compound to afford the product complexes in reasonable yields according to



for R = thiophene, R' = ethyl, M = Ni (1), Pd (2) and Pt (3); R = benzothiophene, R' = *n*-butyl, M = Ni (4).

Single crystal X-ray analysis reveals that these complexes are square-planar [4]. Whereas π -coordination of thiophene to transition metals has been reported [5], this constitutes the first structural data for Group 10 metal 2-thienyl species. Comparison of X-ray structural data [4] of the thiophene and benzothiophene complexes shows that the metal-carbon σ -bond distance is greater in the case of the benzothienyl complex, indicative of a lesser degree of π -character.

Polymers 5 and 6 were also prepared via lithium reagents according to



for **5**, R=thiophene and for **6**, R=isothionaphthene, the stoichiometry being 1:1 with respect to conjugated ligand and bis(phosphine)dichlorometal complex [2]. Although yields of both polymers were poor (of the order of 4–5% [4]), **5** proved to possess a remarkably high average degree of polymerization (c. 1100 repeat units) [4]. This represents the largest known example (in terms of average number of repeat units) of a conjugated organometallic polymer. ^{31}P NMR in solution [4] indicates that both polymers are linear with respect to the metal centre and hence are considered to be essentially one dimensional.

Nonlinear optical studies

The experimental method employed for nonlinear optical studies was that of forced light scattering from laser-induced gratings, a technique which may be viewed as a degenerate four-wave mixing process in the forward direction [6] and the experimental conditions are described in detail elsewhere [7]. The light source is an amplified, passively mode-locked Nd^{3+} :YAG laser emitting linearly polarized pulses of 70 ± 25 ps duration and of wavelength $\lambda = 1.064 \mu\text{m}$ at a repetition rate of 3 Hz. Under thin grating conditions [6], the diffraction efficiency η to the first order may be related to the third-order material nonlinearity, $|\chi^{(3)}|$ [6]. For a true third-order process, $|\chi^{(3)}|$ is a bulk material constant and the diffraction efficiency η is proportional to the square of the input intensity I_0 . Verification of the nature of the nonlinear process is important as fifth- and seventh-order processes, originating in multiphoton resonant enhancement of the material nonlinearities, have been observed in organic conjugated materials [7, 8].

$|\chi^{(3)}|$ may possess both real and imaginary components originating from the solute as well as a contribution from the solvent, $\chi_{\text{solv}}^{(3)}$, which is purely real and positive in the case of most organic solvents including the solvent used in this study, chloroform [9]. For the concentration range employed in this work, the solute fractional volume is negligible. Thus

$$|\chi^{(3)}| = \{(\chi_{\text{solv}}^{(3)} + \text{Re } \chi_{\text{sol}}^{(3)})^2 + (\text{Im } \chi_{\text{sol}}^{(3)})^2\}^{1/2} \quad (1)$$

where $\text{Re } \chi_{\text{sol}}^{(3)}$ and $\text{Im } \chi_{\text{sol}}^{(3)}$ are the real and imaginary components of the solute nonlinearity. By monitoring the concentration dependence of $|\chi^{(3)}|$, the contribution $\chi_{\text{solv}}^{(3)}$ due to the solvent may be extracted and the magnitude of $\text{Re } \chi_{\text{sol}}^{(3)}$ and $\text{Im } \chi_{\text{sol}}^{(3)}$ thus determined. Furthermore the sign of $\text{Re } \chi_{\text{sol}}^{(3)}$ may be determined from the concentration dependence of the real component of $|\chi^{(3)}|$.

For the purposes of comparison of material nonlinearities, the third-order molecular hyperpolarizability, given by

$$|\gamma| = \frac{|\chi^{(3)}|}{N_A C L_L^4} \quad (2)$$

should be used, where C is the solute molar concentration, N_A is Avogadro's constant and L_L is the Lorentz local field factor, which for these compounds

is taken to be that of a rigid rod, one-dimensional system given by $L_{11} = 1$ [10]. $|\gamma|$ may similarly be resolved into real and imaginary components, γ_R and γ_i , and as already mentioned provides the most accurate means of comparing the nonlinearities of systems on a molecular scale. When considering the polymeric systems, γ is calculated per repeat unit.

Results and discussion

Optical properties of the monomer complexes

All of the metal systems were found to be soluble in chloroform, as was the terthiophene oligomer. In Fig. 1, the UV/Vis absorption spectra of the complexes are plotted along with that of terthiophene. Of interest is the positioning of the longest wavelength absorption maximum, which is seen to vary from 374 nm for **1**, through 330 nm for **2**, to 320 nm for **3**. It should be noted that this trend of decreasing maximum absorption wavelength with increasing metal atomic number has also been observed in alkynyl complexes of the Group 10 metals [1]. Terthiophene has its longest wavelength absorption maximum at an intermediate value of 355 nm.

A series of chloroform solutions of graded concentration was prepared for each metal complex. Maximum concentrations used were 0.93, 3.5 and 3.4 g/l for **1**, **2** and **3**, respectively, and 0.9 g/l for **4**. Solutions of terthiophene were prepared in chloroform to a maximum concentration of 2.2 g/l. Measurements of diffraction efficiency as a function of pump intensity and solution concentration were performed by monitoring the pump and first-order diffracted beams with calibrated photodiodes and a digital storage oscilloscope.

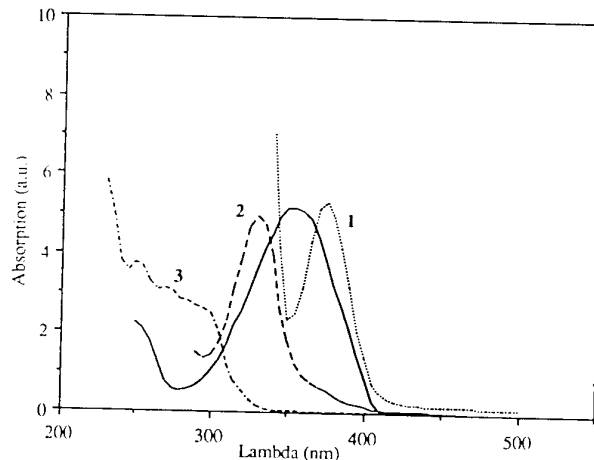


Fig. 1. UV/Vis absorption spectra of the thienyl complexes (**1**, **2** and **3**) and terthiophene (—).

For solutions of both **2** and **3**, the intensity dependence of the diffraction efficiency is found to be characteristic of a third-order nonlinear optical process, as is that of terthiophene and of neat chloroform. In solutions of **1**, however, an intensity dependence characteristic of a higher-order nonlinear process is observable at low concentrations. Such an intensity dependence is associated with the contribution to the nonlinear process of a multiphoton resonance enhancement [7, 8]. Figure 2 shows, for example, the intensity dependence of the diffraction efficiency of a 0.0675 g/l solution of **1** which exhibits a slope of approximately 4. At higher concentrations, however, the influence of the multiphoton resonance disappears and the intensity dependence of the diffraction process is indicative of a purely third-order nonlinearity. Figure 3 shows the variation of the order α of input intensity (I^α) dependence of diffraction efficiency with concentration in solutions of **1**. In solutions of *trans*-[M(C₄H)₂(PEt₃)₂], where again M is a Group 10 transition metal, the nonlinear optical process giving rise to self-diffraction is also seen to be strongly influenced by a multiphoton process and, furthermore, a concentration dependence of the degree of influence similar to that shown in Fig. 3 is observed [1a]. In poly[(3-butyl)thiophene] solutions, in which multiphoton processes are also prominent at 1.064 μm , a strong variation with concentration of the intensity dependence of the diffraction process has also been observed [7]. This concentration dependence may be associated with solvent-mediated interchain interactions which cause a variation in backbone electron correlations, a strong determining factor in the positioning of multiphoton absorption levels [11]. The observation of this multiphoton absorption at low concentrations is indicative of a reasonable degree of delocalized electron correlation, suggesting a significant interaction of the metallic d-electrons with the organic π -conjugated system in the excited state. It is interesting to note that when the polarity of the solvent is reduced (for example, if hexane is used instead of chloroform) no multiphoton effects are observed.

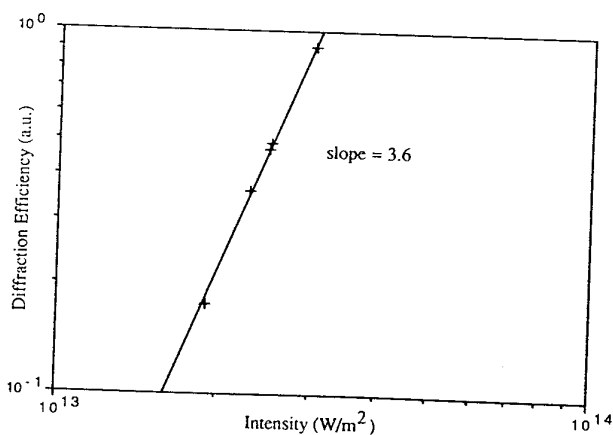


Fig. 2. Input intensity dependence of diffraction efficiency for a 0.0675 g/l solution of **1**.

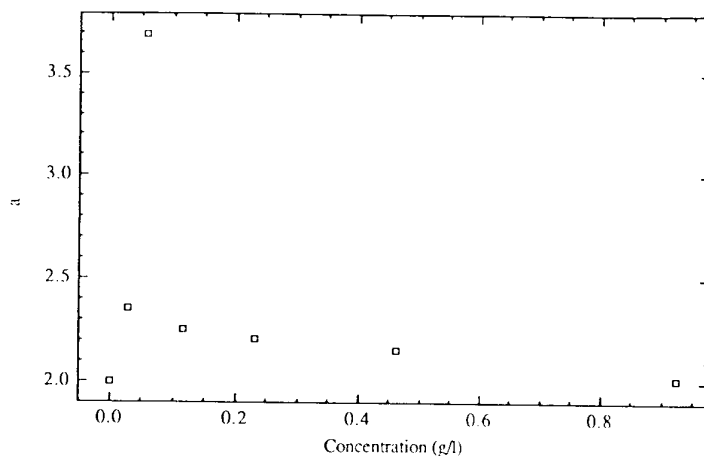


Fig. 3. Variation of the order α of input intensity (I^{α}) dependence of diffraction efficiency with concentration in solutions of **1**.

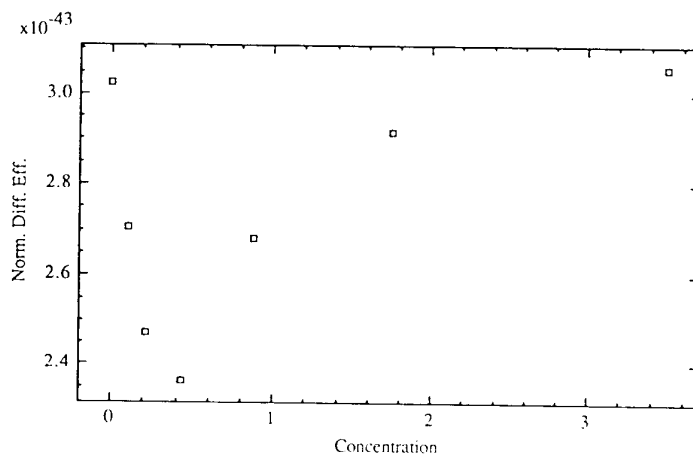


Fig. 4. Concentration dependence of normalized diffraction efficiency for solutions of **2**.

This observation tends to suggest that aggregation effects shift the energy positioning of the multiphoton absorption.

For the other metal complexes as well as solutions of terthiophene, although no influence of multiphoton effects are apparent, the concentration dependence of diffraction efficiency is far from the parabolic dependence predicted by a sum over the response of individual molecules. Figure 4 shows, for example, the concentration dependence of normalized diffraction efficiency (η/I^2) of solutions of **2**. A dependence close to parabolic may be seen at low concentrations, the initial decrease indicating a negative real component of the nonlinear susceptibility of the solute, but with increasing concentration the dependence deviates strongly from the theoretically pre-

dicted parabolic behaviour. A similar behaviour is observed for **1** and **3** as well as for terthiophene. Whereas this behaviour has been frequently observed for polymers [12], our results indicate that aggregation also plays a significant role in these monomeric systems, producing effects analogous to those associated with interchain coupling in polymers. This point is discussed in greater detail elsewhere [13].

Although this deviation from ideal behaviour complicates matters, an estimate of the molecular hyperpolarizability may be made by fitting a parabolic concentration dependence (eqn. (1)) to the low concentration regions where no multiphoton effects are observed. The measured values for the respective components of the molecular hyperpolarizabilities for each metal complex are given in Table 1. Clearly a trend of increasing molecular hyperpolarizability with decreasing atomic number may be seen. Indeed this is consistent with the increase in maximum absorption wavelength observed in the linear optical spectra, indicating that the positioning of this primary resonance may be correlated with the off-resonant nonlinear optical properties of the molecule in a similar way to purely organic π -conjugated systems [13]. It should also be noted that the magnitudes of the imaginary component of the nonlinearity are large despite the fact that no multiphoton absorption is necessarily observed and, where it is, its contribution to the nonlinearity is extracted in the fitting process. This observation is not uncommon and may be explained by the fact that any polarization induced in a system will result in electron-lattice coupling giving rise to dissipative processes. Hence, appreciable imaginary components are invariably observed in conjugated systems where the degree of polarization may be large.

Significantly the trends of the metal dependence of both the linear and nonlinear optical properties observed in these systems confirm the trends observed in previous studies of the linear and nonlinear optical properties of Group 10 metal alkynyl species [1]. Although simple models, such as CNDO/SCF, may easily account for the differences between the properties of nickel complexes and those of the larger metals palladium and platinum from size effects, a consistent difference is observed between the optical properties of conjugated organic systems incorporating palladium and plat-

TABLE 1
Experimentally deduced values of γ for the thienyl systems

Compound	Re γ (m^5/V^2)	Im $ \gamma $ (m^5/V^2)	$ \gamma $ (m^5/V^2)
1	-5.1×10^{-46}	4.6×10^{-46}	6.8×10^{-46}
2	-6.9×10^{-47}	1.3×10^{-46}	1.5×10^{-46}
3	-2.5×10^{-47}	6.0×10^{-47}	6.5×10^{-47}
4	-2×10^{-46}	1×10^{-45}	1×10^{-45}
Terthiophene	-3.4×10^{-47}	7.8×10^{-47}	8.5×10^{-47}
5	-1.7×10^{-44}	2.0×10^{-44}	2.6×10^{-44}
6	-3×10^{-45}	1×10^{-45}	3×10^{-45}
Poly[(3-butyl)thiophene]	-6×10^{-46}	1×10^{-45}	1×10^{-45}

inum. Such differences may not simply be accounted for by size effects and an understanding of the trends in the metal dependence of the linear and nonlinear optical properties of these systems may be central to a complete understanding of the incorporation of metal centres into conjugated organic systems. Future modelling will be based on Fenske–Hall calculations of crystallographic data which should provide an insight into the transitions which provide the origin of the nonlinear behaviour of this family of systems. The value of $|\gamma|$ for terthiophene is one order of magnitude lower than previously reported [14], probably due to the fact that the original measurements were performed closer to resonance (602 nm). In terms of magnitude of response, **3** compares well with the purely organic terthiophene system, although the lower value of its longest wavelength absorption would suggest a lesser degree of electron delocalization in the $d_{\pi}-p_{\pi}$ system. Both **1** and **2** exhibit second molecular hyperpolarizabilities which are significantly higher than that of terthiophene. Indeed that of **1** is almost one order of magnitude greater.

The absorption spectrum of **4** is shown in Fig. 5. The longest wavelength absorption maximum is at 395 nm. This is consistent with a decrease in the $d_{\pi}-p_{\pi}$ character of the metal–carbon bond compared to **1**, also manifest as a longer bond in the X-ray structure [4]. In terms of nonlinear behaviour, the response of **4** is seen to be purely third order in nature over the concentration range employed. It is somewhat surprising that no multiphoton influence is observed in solutions of **4** and emphasizes the fact that the origin of such multiphoton phenomena are not well understood. The second hyperpolarizability was measured and is given in Table 1. Significantly, the value is higher than that of **1** despite the reduction of π -character in the metal–carbon bond. This points to an origin of the nonlinear process in these materials similar to that suggested by Cheng *et al.* [15] whereby the third-order nonlinear optical response of transition-metal conjugated organic

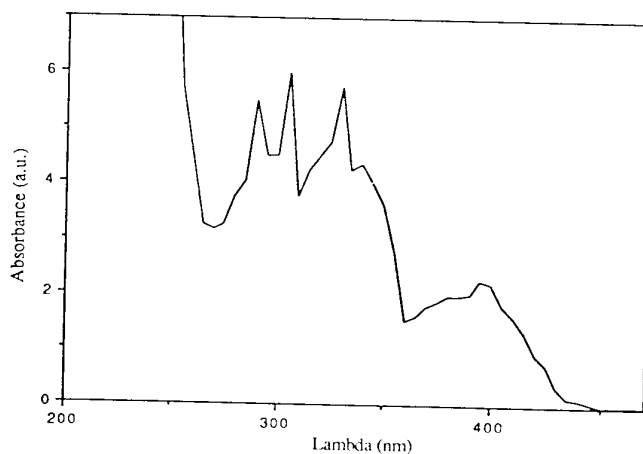


Fig. 5. UV/Vis absorption spectrum of **4**.

complexes is dominated by a metal–ligand charge transfer. The effect of the electron-withdrawing fused ring therefore seems to be to increase the degree of charge transfer to the most proximate antibonding π -orbital and, thus, increase the polarizability of the complex. $|\gamma|$ for complex **4** is in excess of one order of magnitude greater than terthiophene and possesses a remarkably high third-order nonlinearity approaching that of poly[(3-butyl)thiophene] [2].

Optical properties of the polymeric systems

Polymer 5

The polymer was dissolved in chloroform; the maximum concentration studied was 1.63 g/l. Figure 6 illustrates the visible absorption spectrum of **5** and **6**. The spectrum exhibits a broadband absorption with the maximum wavelength peak situated at 515 nm. This would suggest that, compared to **1**, the polymer possesses a far greater degree of π -conjugation. Polymer **5** does not, however, strongly absorb at longer wavelengths where, for example, poly[(3-butyl)thiophene] (a comparable totally organic polymer) absorbs, suggesting that at least in the ground state, the presence of the transition metal centres in the organic backbone seems to act as a defect to extended π -conjugation. It should be noted, however, that a similar observation has previously been made in the case of Group 10 metal alkynyl polymers [1], where it was found that the third nonlinear optical properties of a conjugated polymeric system were significantly enhanced compared to analogous totally organic systems by the presence of Group 10 metal centres, particularly nickel, in the backbone despite relatively shorter maximum absorption wavelengths.

In contrast to complex **1**, monitoring the pump intensity as a function of diffraction efficiency revealed that polymer **5** exhibits no behaviour char-

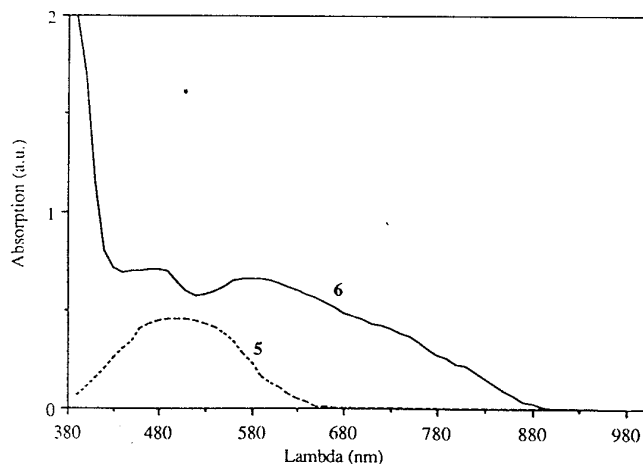


Fig. 6. Visible absorption spectra of polymers **5** and **6**.

acteristic of concentration-dependent multiphoton resonance effects. This is probably not altogether surprising since the energy positioning of such resonances is thought to be strongly dependent on the electron distribution within a system, this distribution being likely to differ dramatically when comparing monomer to polymer.

A parabolic fit of concentration to $|\chi^{(3)}|^2$ for **5** leads to values of γ listed in Table 1 along with those of poly[(3-butyl)thiophene] [16] for comparison. Clearly, the presence of nickel centres in the conjugated backbone of the polymer enhances the third-order hyperpolarizability of the system. It should be noted that this enhancement of nonlinearity occurs despite a smaller relative maximum absorption wavelength in the UV/Vis spectrum. That is to say, the metal would appear to behave as a defect to electronic conjugation in the ground state. In the excited state, the reverse situation appears to hold, the metal centre acting as an efficient conjugation linkage. This point emphasizes the need for excited state spectroscopic study of these systems using techniques such as pump and probe experiments in order to achieve a better understanding of the nature of the nonlinear processes which occur in these materials.

Polymer 6

Chloroform solutions of the polymer of maximum concentration 1.05 g/l were prepared and measured in the normal manner. As was the case for **5**, the visible spectrum of **6** consists of a broadband absorption with a maximum absorption wavelength peak at 580 nm (see Fig. 6).

The four-wave mixing experiment was performed in the usual manner. Monitoring of diffraction efficiency as a function of pump intensity showed that the nonlinear behaviour of the polymer was close to third order throughout the concentration range employed in the experiment. Parabolic fitting provided values of third-order molecular nonlinearity given in Table 1. $|\gamma|$ for **6** is somewhat lower than that of **5** implying that the presence of the fused benzene moiety does not enhance the hyperpolarizability of the polymer. The large imaginary component of the nonlinearity of **6** is in agreement with observations of the behaviour of **4** and would again perhaps suggest a large degree of coupling of the polarization to vibronic states giving rise to nonlinear dissipative phenomena.

In terms of extrapolation of monomer nonlinearity to the polymer, the latter would appear to behave optically as a system somewhat smaller than truly polymeric. This is likely to be due to a limited degree of polymerization ($n_{av}=9$) [4].

Conclusions

In this work, previous studies of the incorporation of Group 10 transition metal complexes into organic conjugated systems have been extended to the much studied thiophene system. This illustrates the scope available for

the incorporation of metal centres into well-characterized organic conjugated systems. The study of the metal dependence of molecular hyperpolarizabilities of the metal thiophene complexes confirms the trends observed in previous studies, indicating that optimum interaction of metal d-electrons with the organic conjugated system occurs in the case of nickel. The magnitudes of the nonlinear response for both the nickel and palladium thiophene complexes are substantially larger than that of terthiophene, a purely organic conjugated analogue. This result is also consistent with previous studies and confirms that, in the search for organic materials for nonlinear optical applications, incorporation of metallic centres is a worthwhile pursuit. The effect of the fused benzene ring in the benzothienyl complex (4) is seen to reduce the degree of π -character of the metal-carbon bond. The observed increase in the nonlinear optical response points towards transfer of charge from a non-bonding metal d-orbital to the most proximate antibonding ligand π -orbital as dominating the third-order nonlinear process and provides a guideline for the optimization of the nonlinear optical characteristics of these materials. Studies on two thiophene-based polymers incorporating nickel centres into the backbone have shown that very large nonlinearities are possible for such systems, values obtained comparing very favourably with similar organic systems.

Acknowledgements

This work has been funded in part by the United States Army and by the Irish Government Department of Social Welfare. The terthiophene oligomer was supplied by Dr D. Fichou of CNRS, Thiais, France.

References

- 1 (a) W. J. Blau, H. J. Byrne, D. J. Cardin and A. P. Davey, *J. Mater. Chem.*, **1** (1991) 245; (b) S. Guha, C. C. Frazier, W. P. Chen, P. Porter, K. Kang and S. E. Finbberg, *Materials for Optical Switches, Isolators and Limiters, Proc. SPIE*, **1105** (1989).
- 2 R. Dorsinville, L. Yang, R. R. Alfano, R. Zamboni, R. Danieli, G. Ruani and C. Taliani, *Opt. Lett.*, **14** (1989) 1321.
- 3 F. Wudl, M. K. Kobayashi and A. J. Heeger, *J. Org. Chem.*, **49** (1984) 3382.
- 4 A. P. Davey, D. J. Cardin, M. Convery, C. J. Cardin, H. J. Byrne, H. Page and W. Blau, *J. Mater. Chem.*, to be submitted.
- 5 R. J. Angelici, *Coord. Chem. Rev.*, **105** (1990) 61.
- 6 H. J. Eichler, P. Gunter and D. W. Pohl, *Laser Induced Gratings, Springer Series in Optical Sciences*, Vol. 50, Springer, Berlin, 1986.
- 7 H. J. Byrne, W. Blau and K. Y. Jen, *Synth. Met.*, **32** (1989) 229.
- 8 J. M. Nunzi and D. Grec, *J. Appl. Phys.*, **62** (1987) 2198.
- 9 P. D. Maker, R. W. Terhune and C. M. Savage, *Phys. Rev. Lett.*, **12** (1964) 507.
- 10 Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley-Interscience, New York, 1984.
- 11 C. Grossman, J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri and A. F. Garito, in J. Messier, F. Kajzar, P. Prasad and D. Ulrich (eds.), *Nonlinear Optical Effects in Organic Polymers, Nato ASI Series*, Vol. 162, Kluwer, Dordrecht, 1989.

- 12 H. J. Byrne and W. Blau, *Synth. Met.*, 37 (1990) 231.
- 13 W. Blau and H. J. Byrne, in H. Kuzmany, M. Mehring and S. Roth (eds.), *Electronic Properties of Polymers; Orientation and Dimensionality of Conjugated Systems*, Springer Series in Solid State Sciences, Vol. 107, Springer, Berlin, 1992, p. 183.
- 14 M.-T. Zhao, B. P. Singh and P. N. Prasad, *J. Chem. Phys.*, 89 (1988) 5535.
- 15 L.-T. Cheng, W. Tam, G. R. Meredith and S. R. Marder, *Mol. Cryst. Liq. Cryst.*, 189 (1990) 137.
- 16 K. C. Rustagi and J. Ducuing, *Opt. Commun.*, 10 (1974) 258.

Nonlinear optical properties of some mono- and bimetallic organometallic systems

H. Page, W. Blau and A.P. Davey

Department of Pure and Applied Physics, Trinity College Dublin, Dublin 2 (Ireland)

X. Lou

Department of Chemistry, Trinity College Dublin, Dublin 2 (Ireland)

D.J. Cardin

Department of Chemistry, University of Reading, Reading (UK)

(Received June 26, 1993; accepted in revised form December 1, 1993)

Abstract

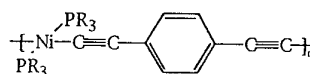
The second molecular hyperpolarizabilities (γ) of a group of conjugated organometallic systems have been measured off-resonance (1.064 μm) using forward degenerate four-wave mixing. The effect on the optical properties of introducing more than one metal centre into a conjugated organic backbone was studied. The effect of changing the size of solubilizing substituents was also investigated. Results demonstrate that the presence of two metals in the backbone of a conjugated organic compound serves to enhance the third-order nonlinearity in comparison to monometallic systems.

Introduction

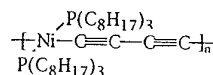
The nonlinear optical properties of organometallic compounds have recently attracted a great deal of attention [1]. The presence of transition metals in the backbone of conjugated organic systems has already been shown to enhance substantially the electronic third-order nonlinearity [2]. In this paper we present a study of mono- and bimetallic compounds similar in structure to those studied previously. Group 10 transition-metal compounds are probably the most well-studied organometallic systems for electronic third-order nonlinearity. It is therefore possible to compare the second molecular hyperpolarizabilities (γ) of these compounds with values for those reported in the literature for structurally related species.

The geometry of these molecules (with respect to the metal) is *trans*-square-planar. The conjugated organic fragments utilized here are the diethynyl and *p*-diethynylbenzene moieties. The structures of the compounds are illustrated in Fig. 1.

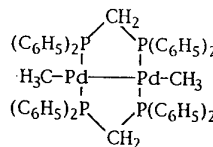
The chemical synthesis and characterization of these compounds are reported elsewhere [3]. Due to the geometry of the metal coordination and the conjugated organic ligands employed, the electronic structure in these molecules is linear or quasi-one-dimensional. This is an important consideration in the context of correction



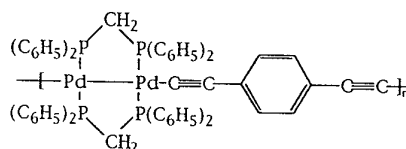
For Compound 1; R = n-Butyl
For Compound 2; R = n-Octyl



Compound 3



Compound 4



Compound 5

Fig. 1. Structures of the compounds studied.

for local field effects in calculation of hyperpolarizabilities.

The compounds were studied for two purposes: compounds 1, 2 and 3 in order to assess the effect of larger solubilizing substituents (PR_3 groups); and compounds 4 and 5 in order to assess the effect of two metal centres (bonded to each other) present in a conjugated organic polymer backbone.

Experimental

The experimental method employed for nonlinear optical studies was that of forced light scattering from laser-induced gratings, a technique which may be viewed as a degenerate four-wave mixing process in the forward direction [4] and the experimental conditions are described in detail elsewhere [5a]. The light source is an amplified, passively mode-locked $\text{Nd}^{3+}:\text{YAG}$ laser emitting linearly polarized pulses of 70 ± 25 ps duration and of wavelength $\lambda = 1.064 \mu\text{m}$ at a repetition rate of 3 Hz. Under thin grating conditions [4], the diffraction efficiency (η) with respect to first order may be related to the third-order material nonlinearity, $|\chi^{(3)}|$ [4]. For a true third-order process, $|\chi^{(3)}|$ is a bulk material constant and the diffraction efficiency, η , is proportional to the square of the input intensity, I_0 . Verification of the nature of the nonlinear process is important as fifth- and seventh-order processes, originating in multiphoton resonant enhancement of the material nonlinearity, have been observed in conjugated materials [5].

$|\chi^{(3)}|$ (the measured bulk susceptibility) possesses both a real and an imaginary component originating from the solute ($|\chi^{(3)}|_{\text{sol}}$) as well as a contribution from the solvent ($|\chi^{(3)}|_{\text{solv}}$), which is purely real and positive in the case of common organic solvents including the one used in this study, chloroform [6]. For the concentration range employed in this work, the solute fractional volume is negligible. Thus:

$$|\chi^{(3)}| = [(\chi_{\text{solv}}^{(3)} + \text{Re } \chi_{\text{sol}}^{(3)})^2 + (\text{Im } \chi_{\text{sol}}^{(3)})^2]^{1/2} \quad (1)$$

where $\text{Re } \chi_{\text{sol}}^{(3)}$ and $\text{Im } \chi_{\text{sol}}^{(3)}$ are the real and imaginary components of the solute nonlinearity. By monitoring the concentration dependence of $|\chi^{(3)}|$, the contribution $\chi_{\text{solv}}^{(3)}$ may be extracted and the magnitude of $|\text{Re } \chi_{\text{sol}}^{(3)}|$ and $|\text{Im } \chi_{\text{sol}}^{(3)}|$ thus determined. Furthermore, the sign of $\text{Re } \chi_{\text{sol}}^{(3)}$ may be determined from the concentration dependence of the real component of $|\chi^{(3)}|$.

For the purposes of comparison of molecular nonlinearities, the nonlinearity per molecule, i.e., the second hyperpolarizability:

$$|\gamma| = \frac{|\chi^{(3)}|}{N_A C L^4} \quad (2)$$

should be used, where C is the solute molar concentration and N_A is Avagadro's constant. The Lorentz

local field factor, L_L , is taken to be that of a rigid rod, one-dimensional system given by $L_L = 1$ [7]. Similarly to $|\chi^{(3)}|_{\text{sol}}$, $|\gamma|$ may be separated into real and imaginary components, γ_R and γ_I , and, as already mentioned, provides the most accurate means of comparing the nonlinearities of systems on a molecular scale. When considering the polymeric systems, γ is calculated per repeat unit.

Results

All of the compounds discussed here are soluble in chloroform and so, for the sake of consistency, this solvent was employed throughout the experiments. A series of solutions of graded concentration was prepared for each compound.

Nonlinear optical properties of compounds 1, 2 and 3

For these compounds, the maximum concentrations employed were: compound 1, 0.95 g l^{-1} ; compound 2, 0.22 g l^{-1} ; compound 3, 1.00 g l^{-1} .

The intensity dependence of diffraction efficiency was monitored for the compounds throughout their concentration ranges. The behaviour of all three was found to be purely third order. This observation agrees with previously reported work [2, 8] on similar polymeric systems and is discussed in greater detail therein.

First, the concentration dependence of $|\chi^{(3)}|^2$ for all three compounds reveals a negative real component of the nonlinearity indicated by an initial decrease of $|\chi^{(3)}|^2$ induced by a negative real component initially cancelling a positive contribution from the solvent (see Fig. 2). Secondly, the minima of these plots for all three compounds are found to be non-zero indicating that all three possess a finite imaginary component. All three compounds exhibit a non-ideal concentration-dependent behaviour. At low concentrations, $|\chi^{(3)}|^2$ varies

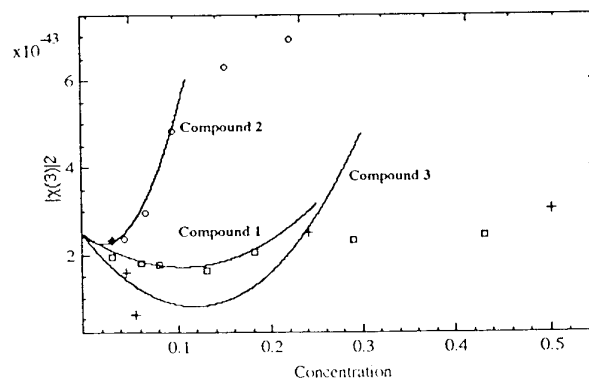


Fig. 2. Concentration (g l^{-1}) dependence of $|\chi^{(3)}|^2$ ($\text{m}^4 \text{V}^{-4}$) for compounds 1, 2 and 3.

parabolically as a function of concentration (as theory predicts, see eqn. (1)). At higher concentrations, however, a saturation of the nonlinearity is apparent (Fig. 2). This behaviour has been reported for both organic polymers and for organometallic molecules [2]. This saturation is thought to arise from molecular aggregation and represents a severe limitation for practical application in solid devices because it implies a reduction of the nonlinearity in the solid state compared to the case of a low-concentration solution where there is no interaction.

A fit to the low-concentration regions (where parabolic behaviour is observed) of the concentration dependence of $|\chi^{(3)}|^2$ gives values of second molecular hyperpolarizability (γ) for the three compounds. These values are listed in Table 1 along with values reported for similar compounds. It can be seen by comparison of the γ values of 1, 2 and 3 and of the previously reported $[\text{Ni}(\text{PBu}_3)_2\text{C}_4]_n$, that an increase in the size of the PR_3 substituent leads to an increase in the magnitude of the third-order nonlinearity. This is somewhat surprising since the size of the solubilizing substituent should not affect the electronic structure. It is possible that, by increasing the bulk of the substituent, there is some form of reduction of intermolecular interaction. Further studies are in progress which aim to extend the understanding of the nature of intermolecular interaction in the nonlinear regime for such systems.

Nonlinear optical properties of compounds 4 and 5

As already mentioned, the purpose of studying compounds 4 and 5 was to establish whether the presence of a bimetallic moiety in the backbone of a conjugated organic polymer serves to enhance the third-order nonlinearity to a greater degree than for monometallic systems. In this case, a comparison of the nonlinearity of 4 with 5, and of 5 with related monometallic polymeric

TABLE 1. Second molecular hyperpolarizabilities^a for the compounds studied along with those of related polymers for comparison

Compound	γ_{Re} ($\text{m}^5 \text{V}^{-2}$)	$ \gamma_{\text{Im}} $ ($\text{m}^5 \text{V}^{-2}$)	$ \gamma $ ($\text{m}^5 \text{V}^{-2}$)
1	-1×10^{-45}	2×10^{-45}	2×10^{-45}
2	-4×10^{-45}	1×10^{-44}	1×10^{-44}
3	-4×10^{-45}	3×10^{-45}	5×10^{-45}
4	-1×10^{-46}	2×10^{-46}	2×10^{-46}
5	-2×10^{-45}	2×10^{-45}	2×10^{-45}
$[\text{Pt}(\text{PBu}_3)_2\text{C}_4]_n$ [8]	-1×10^{-45}	2×10^{-45}	2×10^{-45}
$[\text{Ni}(\text{PBu}_3)_2\text{C}_4]_n$ [8]	-3×10^{-45}	2×10^{-45}	4×10^{-45}
4BCMU (polydiacetylene-chloroform solution [5a])			2×10^{-45}

^aTo convert values to e.s.u., divide by 1.4×10^{-8} .

systems provides a reasonable relative measure of the nonlinearity arising from the bimetallic palladium unit.

The samples were measured in the same manner as already described for 1, 2 and 3. The values of γ for the two compounds are listed in Table 1 along with values (previously measured and reported [8]) for two related monometallic polymers. It seems from these values that the bimetallic unit contributes significantly to the real component of the electronic nonlinearity. The values of γ for 5 are significantly greater than those of 4. This indicates that the nonlinearity of 5 arises from electron delocalization in the excited state which may be enhanced by the presence of the bimetallic palladium moiety. Ideally, one would like to be able to compare the nonlinearity of 5 with the purely organic equivalent, poly(*para*-phenylene ethynylene). Unfortunately, this polymer is intractable which explains the absence of any measurement of nonlinearity in the literature. The synthesis of an alkyl-substituted soluble form is a major synthetic task which is beyond the scope of this paper.

In comparing the nonlinearity of compound 5 with the monometallic nickel-containing polymers, it should be noted that previous work [8] has shown that, in general, the latter tend to exhibit a greater real component of the nonlinear response than equivalent palladium-containing compounds. The nonlinearity of compound 5 does, however, compare favourably with a monometallic platinum-containing polymer, suggesting that the presence of more than one metal centre in the polymer backbone may well enhance the third-order nonlinearity.

Conclusions

Two factors which affect the third-order nonlinearity of conjugated organometallic polymers have been investigated; first, the effect of larger polymer side groups and, secondly, the effect of the presence of bimetallic (as compared to monometallic) moieties in the polymer backbone. The results of four-wave mixing experiments indicate that the presence of bulkier substituents enhances the third-order nonlinearity, perhaps by reducing the degree of intermolecular interaction. Also, it seems clear that bimetallic units serve to increase the nonlinearity in such systems when compared to related monometallic polymers.

In view of these results, studies on conjugated metal-organic polymers which employ small cluster frameworks with large substituent groups should be studied, with a view to further increasing the third-order nonlinearities of such systems.

Acknowledgements

The authors acknowledge financial support for this work from the European Office of the US Army and from the European Commission Directorate XIII (RACE 2012 HIPOS project).

References

- 1 (a) A.P. Davey, H. Page, W. Blau, H.J. Byrne and D.J. Cardin, *Synth. Met.*, 55-57 (1993) 3980; (b) L.T. Cheng, W. Tam, G.R. Meredith and S.R. Marder, *Mol. Cryst. Liq. Cryst.*, 189 (1990) 137; (c) C.S. Winter, C.A.S. Hill and A.E. Underhill, *Appl. Phys. Lett.*, 58 (1991) 107.
- 2 A.P. Davey, H. Page, H.J. Byrne, W. Blau and D.J. Cardin, *Synth. Met.*, 58 (1993) 161.
- 3 X. Lou, *Ph.D. Thesis*, University of Dublin, 1992.
- 4 H.J. Eichler, P. Gunter and D.W. Pohl, *Laser Induced Gratings, Springer Series in Optical Sciences*, Vol. 50, Springer, Berlin, 1986.
- 5 (a) H.J. Byrne, W. Blau and K.Y. Jen, *Synth. Met.*, 32 (1989) 229; (b) J.M. Nunzi and D. Grec, *J. Appl. Phys.*, 62 (1987) 2198.
- 6 P.D. Maker, R.W. Terhune and C.M. Savage, *Phys. Rev. Lett.*, 12 (1964) 507.
- 7 Y.R. Shen, *The Principles of Nonlinear Optics*, Wiley-Interscience, New York, 1984.
- 8 W.J. Blau, H.J. Byrne, D.J. Cardin and A.P. Davey, *J. Mater. Chem.*, 1 (1991) 245.

LINEAR AND THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF ONE-DIMENSIONAL ORGANOMETALLIC SYSTEMS.

A. P. DAVEY, H. PAGE, W. BLAU*

*Department of Pure and Applied Physics, Trinity College Dublin, Dublin 2, Ireland.

H. J. BYRNE**

**Max Planck Institut für Festkörperforschung, Stuttgart, Germany.

D. J. CARDIN***

***Department of Chemistry, Trinity College Dublin, Dublin 2, Ireland.

ABSTRACT

The optical properties (both linear and nonlinear) of a series of conjugated group 10 transition-metal (Ni, Pd, and Pt) organometallic systems have been studied. A strong dependence of the maximum absorption wavelength (λ_{max}) on metal centre for a fixed conjugated organic system is observed in the visible absorption spectrum. The same trends are observed for the values of second molecular hyperpolarisability (γ) measured using forward degenerate four wave mixing at 1.064 μm . A strong dependence of γ on conjugated organic system for a fixed metal is also observed. Larger organometallic polymeric systems have been shown to possess large second molecular hyperpolarisabilities which are remarkably large and compare very well with analogous organic systems such as polydiacetylene or polythiophene. The established trends in optical properties have led to a good understanding of the nature of the interaction of metal with organic system in this family of compounds in the nonlinear regime.

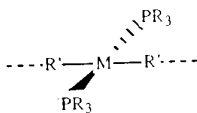
INTRODUCTION

Over the last few years, as an extension to studies of conjugated organic systems for potential application in the field of nonlinear optics, conjugated organometallic systems have begun to be investigated [1]. Intuitively, one would expect that the presence of low oxidation state transition-metals situated in the backbone of a conjugated organic polymer might serve to enhance the polarisability of such systems as compared to purely organic analogues. One family of such organometallic systems are the group 10 transition metal diethynyl polymers first synthesised by Hagihara *et al* [2]. In these polymers, a group 10 transition metal (nickel, palladium or platinum) is σ -bonded to a carbon-carbon triple bond. The coordination geometry with respect to the metal is *trans* square-planar leading to a linear, rigid-rod conjugated polymer backbone.

Elsevier Sequoia

DTIC QUALITY INSPECTED

As an extension to this series, we have produced and studied a family of group 10 metal/2-thienyl systems whose structure is depicted in Figure 1 which are similarly linear in structure to the organometallic diethynyl systems previously produced.



For Monomers ($(M(PR_3)_2R'_2)$): $R' = C_8H_5$ (Phenylethynyl); $M = Ni, Pd, Pt$; $R = C_2H_5$
 $R' = C_4$ (Diethynyl); $M = Ni, Pd, Pt$; $R = C_2H_5$
 $R' = C_4H_3S$ (Thienyl); $M = Ni, Pd, Pt$; $R = C_2H_5$
 and $R' = C_8H_5S$ (Benzothienyl); $M = Ni$; $R = C_4H_9$

For Polymers ($(M(PR_3)_2R'_n)$): $R' = C_4$ (Diethynyl); $M = Ni, Pt$; $R = C_4H_9$
 $R' = C_4H_3S$ (Thienyl); $M = Ni$; $R = C_4H_9$
 $R' = C_8H_4S$ (Benzothienyl); $M = Ni$; $R = C_4H_9$

Figure 1. Structure of the group 10 transition-metal polymers.

The question then is what is the precise nature of the metal centre and conjugated system required to optimise the third order nonlinear response of this family of systems. In order to establish this, we have investigated series of such systems where, firstly the metal and secondly the conjugated organic fragment is systematically varied in order to gain an understanding of the nature of the interaction between the metal centre and the conjugated system in the nonlinear regime. The second molecular hyperpolarisabilities (γ) of these systems have been probed off-resonance (at $1.064\mu m$) using the technique of forward degenerate four-wave mixing. The absolute values of nonlinearity obtained are presented here along with the observed trends linking linear absorption to third order nonlinear optical response.

RESULTS

Linear Optical Properties of the Organometallic Systems

The principal features of the electronic absorption spectra of such systems are a) absorptions associated with electron transfer within the organic ligand ($\pi-\pi^*$ transitions) and b) absorptions associated with transfer of charge from the metal to the conjugated organic ligand.

Monomer Complexes. In general, for the monomer complexes, a clear trend of increasing maximum absorption wavelength (λ_{max}) with decreasing metal atomic number may be seen for a fixed conjugated organic ligand. Figure 2 illustrates this point; the electronic spectra of the bis(2-thienyl) complexes $[M(PEt_3)_2(C_4H_3S)_2]$ are given along with terthiophene (a thiophene oligomer of comparable size).

The most reasonable assignment for this transition is to the transfer of charge from metal to ligand. If one assumes such an assignment then it is clear that the energy associated with this transition increases with increasing atomic number. This is perhaps not surprising since as the size of the metal increases, so to does the degree of back-bonding between the metal and the conjugated

organic ligand [3]. This higher degree of back-bonding in turn leads to a relative increase in the energy of the π^* molecular orbital and hence greater energy associated with transfer of charge from the metal to the ligand π^* orbital. This point will be further discussed later in the correlation between the linear absorption and the third order nonlinear response of the monomer systems.

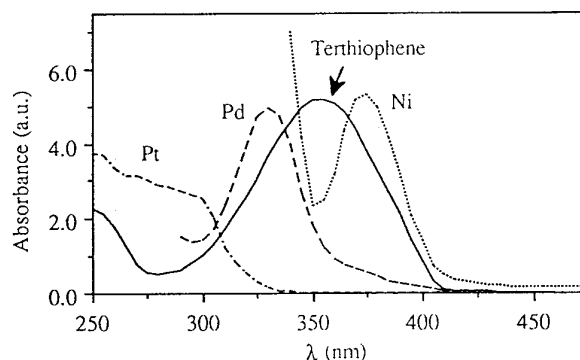


Figure 2. Electronic absorption spectra of the group 10 metal 2-thienyl monomer complexes.

Organometallic polymers. The electronic absorption spectra of the polymers is broadband and red-shifted compared to the analogous monomer complexes due to an increase in the conjugation length. It is interesting to note that in comparison to related purely organic polymers, the maximum absorption wavelength of these polymers is somewhat shorter. This tends to suggest that at least in the ground state, the presence of a metal centre in the polymer backbone acts as a defect in terms of conjugation length. Figure 3 illustrates this, the absorption spectrum of the polymer $[\text{Ni}(\text{PBu}_3)_2(\text{C}_4\text{H}_2\text{S})_2]_n$ is given. In comparison, the maximum absorption wavelength for poly(3-Butyl)thiophene is 530 nm (see Table 2).

The maximum absorption wavelength of related polymers has been assigned to a $\pi-\pi^*$ transition [4] which tends to agree with the observation that the introduction of a metal centre widens the energy gap of this transition and hence gives rise to a blue-shift of the λ_{max} compared to analogous purely organic polymers.

Second Molecular Hyperpolarisability (γ) of the Organometallic Systems

The experimental method employed for determination of second molecular hyperpolarisability (γ) is reported elsewhere[5]. When considering the polymeric systems, γ is calculated per repeat unit. For the sake of consistency in these studies, all samples were dissolved in chloroform.

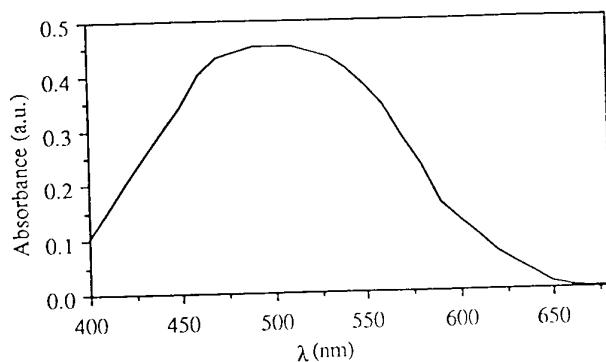


Figure 3. Visible absorption spectrum of the polymer $[\text{Ni}(\text{PBu}_3)_2(\text{C}_4\text{H}_2\text{S})_2]_n$ ($\lambda_{\text{max}} = 515\text{nm}$).

Organometallic Monomers. All the monomer complexes studied were found to possess large values of γ for systems of their size. In comparison to analogous organic systems of similar size, the third order nonlinear response proves to be highly favourable. Values of the real and imaginary components of these systems as well as the overall second molecular hyperpolarisability are given in Table 1 along with those of analogous purely organic systems of similar size for comparison.

TABLE 1
Second molecular hyperpolarisabilities (γ) of the monomer complexes

Compound	λ_{max} (nm)	γ_{Re} ($\text{m}^5 \text{V}^{-2}$)	$ \gamma_{\text{Im}} $ ($\text{m}^5 \text{V}^{-2}$)	$ \gamma $ ($\text{m}^5 \text{V}^{-2}$)
$[\text{Ni}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4)_2]$	336	-7.9×10^{-47}	1.7×10^{-46}	1.9×10^{-46}
$[\text{Pd}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4)_2]$	290	-3.9×10^{-47}	9.2×10^{-48}	4.0×10^{-47}
$[\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4)_2]$	318	-1.9×10^{-47}	7.7×10^{-48}	2.1×10^{-47}
$[\text{Ni}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_8\text{H}_5)_2]$	370	-2.8×10^{-46}	1.5×10^{-46}	3.1×10^{-46}
$[\text{Pd}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_8\text{H}_5)_2]$	370	-2.1×10^{-46}	3.4×10^{-47}	2.1×10^{-46}
$[\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_8\text{H}_5)_2]$	332	-1.1×10^{-46}	2.2×10^{-47}	1.1×10^{-46}
Terdiacetylene	-	-	-	1.0×10^{-47}
$[\text{Ni}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4\text{H}_3\text{S})_2]$	374	-5.1×10^{-46}	4.6×10^{-46}	6.8×10^{-46}
$[\text{Pd}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4\text{H}_3\text{S})_2]$	330	-6.9×10^{-47}	1.3×10^{-46}	1.5×10^{-46}
$[\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_4\text{H}_3\text{S})_2]$	320	-2.5×10^{-47}	6.0×10^{-47}	6.5×10^{-47}
$[\text{Ni}\{\text{P}(\text{C}_4\text{H}_9)_3\}_2(\text{C}_8\text{H}_5\text{S})_2]$	388	-2×10^{-46}	1×10^{-45}	1×10^{-45}
Terthiophene	356	-3.4×10^{-47}	7.8×10^{-47}	8.5×10^{-47}

It is interesting to note that as well as comparing favourably to organic systems, two clear trends also emerge. Firstly, for a given conjugated organic ligand, the trend of decreasing γ for varying metals is $\text{Ni} > \text{Pd} > \text{Pt}$. Interestingly, this trend follows that of the electronic absorption spectrum for each complex. Secondly, for the case of nickel at least, varying the conjugated organic ligand gives

the trend of decreasing γ as isothionaphthene (C_8H_5S) > thiophene (C_4H_3S) > Phenylacetylide (C_8H_5) > Diacetylide (C_4). Once again, the same trend is observed in the electronic absorption spectrum. These trends tend to suggest that the origin of the third order nonlinear process in these systems is dominated by the electronic transition which gives rise to absorption of maximum wavelength in the electronic spectrum. If one assumes an assignment for this absorption to metal ligand (π^*) charge transfer, then the evidence tends to suggest that the third order nonlinear process originates in transfer of charge from metal to conjugated organic ligand. Such an origin has been suggested in work reported by Cheng *et al* [6] in which both the second and third order nonlinearities of some related transition-metal systems are suggested to arise from metal-ligand charge transfer. This point is illustrated in Figure 4, the maximum absorption wavelength for each monomer complex is plotted as a function of the size of the real component of second molecular hyperpolarisability (γ_{Re}).

The exact nature of the relationship between linear absorption and third order nonlinearity is not clear however, it is clear that as the energy associated with metal-ligand charge transfer increases, so does γ .

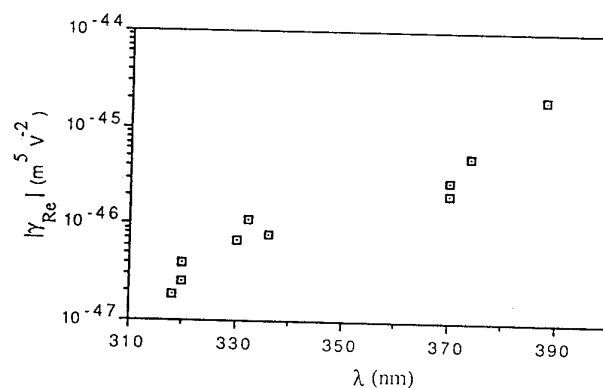


Figure 4. Size of real component of second molecular hyperpolarisability (γ_{Re}) versus maximum absorption wavelength (λ_{max}) for the group 10 monomer systems.

Organometallic Polymers. All of the organometallic polymers studied here proved to possess large nonlinearities which compare favourably with analogous purely organic polymers. The values of γ for each system relative to the corresponding monomer complexes are consistently larger inferring an enhanced degree of conjugation with the exception of the polymer $[Ni(PBu_3)_2(C_8H_5S)_2]_n$ which consists of rather small chains ($n_{av} = 9.5$) limiting the degree of polarisation in the system. Values of γ for the polymers studied are given in Table 2 along with analogous organic polymers measured using the same technique for comparison.

It is clear that despite the fact that the organometallic polymers possess relatively shorter maximum absorption wavelengths, their nonlinearities compare very favourably with organic

systems. The presence of metal centres in the backbone of extended conjugated organic backbones would then seem to enhance the degree of polarisation in the excited state despite limiting it in the ground state.

TABLE 2

Values of second molecular hyperpolarisability for the group 10 metal polymers

Compound	λ_{max} (nm)	γ_{RC} ($\text{m}^5 \text{V}^{-2}$)	$ \chi _{\text{Im}}$ ($\text{m}^5 \text{V}^{-2}$)	$ \chi $ ($\text{m}^5 \text{V}^{-2}$)
$[\text{Ni}\{\text{P}(\text{C}_4\text{H}_9)_3\}_2(\text{C}_4)]_n$	410	-2.63×10^{-45}	2.41×10^{-45}	3.57×10^{-45}
$[\text{Pt}\{\text{P}(\text{C}_4\text{H}_9)_3\}_2(\text{C}_4)]_n$	360	-1.48×10^{-45}	1.74×10^{-45}	2.28×10^{-45}
P4BCMU (Yellow Form)	440	-	-	2×10^{-45}
P3BCMU (Blue Form)	630	-4×10^{-45}	1×10^{-44}	1.1×10^{-44}
$[\text{Ni}\{\text{P}(\text{C}_4\text{H}_9)_3\}_2(\text{C}_4\text{H}_2\text{S})]_n$	515	-1.7×10^{-44}	2.0×10^{-44}	2.6×10^{-44}
Poly(3-Butyl)Thiophene	530	-5.7×10^{-46}	1.2×10^{-45}	1.4×10^{-45}
$[\text{Ni}\{\text{P}(\text{C}_4\text{H}_9)_3\}_2(\text{C}_8\text{H}_4\text{S})]_n$	580	-3×10^{-45}	1×10^{-45}	3×10^{-45}
Poly(2-t-butyl)Isothionaphthene	945	-9×10^{-45}	6×10^{-45}	1×10^{-44}

CONCLUSIONS

A series of systematic studies of the effect on third order nonlinearity of introducing group 10 transition metal centres into conjugated organic systems has been undertaken. Results suggest that the third order response is dependent on the nature of the metal-carbon bond. Studies on smaller systems (monomeric complexes) suggest that for the case of this family of compounds at least, the smaller the metal centre, the greater the degree of enhancement of the third order nonlinearity. Furthermore, conjugated organic systems in which the degree of back-bonding from metal to carbon is minimised provide larger third order nonlinearities. Both of these deductions may be rationalised by consideration of molecular orbital pictures in which the smaller the metal and the less π -character (back-bonding) there is in the metal-carbon bond, the smaller the energy associated with metal-ligand charge transfer (the process which appears to dominate the origin of the third order nonlinearity).

ACKNOWLEDGEMENT

This work was carried out as a part of the RACE 2012 collaborative project.

REFERENCES

- [1] W. J. Blau, H. J. Byrne, D. J. Cardin and A. P. Davey, *J. Mater. Chem.*, **1**, (1991), 245.
- [2] N. Hagihara, S. Takahashi, K. Ogha and K. Sonagashira, *Journal of Organometallic Chemistry*, **188**, (1980), 237.
- [3] H. Masai, K. Sonagashira and N. Hagihara, *Journal of Organometallic Chemistry*, **26**, (1971), 271.
- [4] A. E. Dray, F. Wittman, R. H. Friend, A. M. Donald, M. S. Khan, J. Lewis and B. F. G. Johnson, *Synthetic Metals*, **41-43**, (1991), 871.
- [5] H. J. Byrne, W. Blau and K. Y. Jen, *Synth. Metals*, **32**, (1989), 229.
- [6] L. T. Cheng, W. Tam, G. R. Meredith and S. Marder, *Mol. Cryst Liq Cryst.*, **189**, (1990), 137.