

Figure 5. Relationship between S and $\log k_w'$ for Pd(II)- α -isonitroso- β -diketone imine chelates.

In this case, the forces holding the substance on the stationary phase should be similar to those responsible for dissolution in a solvent. That is, it is the solubility that determines retention and the solubility behavior is explained in terms of molecular interactions.²⁰ The factors which influence solubility are van der Waals (London dispersion) forces, dipole-dipole, hydrogen bonding, and repulsion forces, etc. In RPLC, the most important factor is a hydrophobic interaction. If the hydrogen bonding and coulombic forces are negligible, the retention of molecules will depend on their size, measured by van der Waals volume. Linear relationship between van der Waals volume and $\log k_w'$ as shown in Figure 4 and linear relationships between S and $\log k_w'$ (Figure 5) for the Pd(II) chelates together indicate that the S index and retention of the Pd(II) chelates increase with increasing van der Waals volume. This seems to indicate that van der Waals volume is the more contributing factor in determining retention of the Pd(II) chelates in RPLC than dipole moment and polarizability.

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References

- Horvath, C.; Melander, W. R.; Molnar, I. *J. Chromatogr.* **1976**, *125*, 129.
- Melander, W. R.; Horvath, C. *Am. Lab.* **1978**, *17*.
- Vtasil, F.; Hamplova, V.; Czecho, C. *Chem. Commun.* **1985**, *50*, 2221.
- Chen, N.; Zhang, Y.; Lu, P. *J. Chromatogr.* **1993**, *633*, 31.
- Kim, I. W.; Shin, C. H.; Lee, M. H.; Yoon, T. K.; Kang, C. H.; Lee, W. *J. Kor. Chem. Soc., Anal. Sci.* **1992**, *5(4)*, 389.
- Sadek, P. C.; Carr, P. W.; Doherty, R. M.; Kamlet, M. J.; Taft, R. W.; Abraham, M. H. *Anal. Chem.* **1985**, *57*,

- 2971.
- Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1981**, *49*, 2877.
- Cheong, W. J.; Carr, P. W. *J. Chromatogr.* **1990**, *499*, 373.
- Johnson, B. P.; Khaledi, M. G.; Dorsey, J. G. *Anal. Chem.* **1986**, *58*, 2354.
- Park, J. H.; Jang, M. D.; Shin, M. J. *J. Chromatogr.* **1992**, *595*, 45.
- Luehersch, D. C.; Chesney, D. J.; Godbole, K. A. *J. Chromatogr.* **1992**, *627*, 37.
- Hellal, F.; Phan-Tan-Luu, R.; Sciouffi, A. M. *J. Liq. Chromatogr.* **1992**, *17(13)*, 2845.
- Lee, W.; Kim, I. W.; Kim, M. K.; Kim, Y. J.; Jung, H. R.; No, K. T.; Kim, S. Y. *J. Kor. Soc. Anal. Sci.* **1995**, *8(4)*, 519.
- Chen, N.; Zhang, Y.; Lu, P. *J. Chromatogr.* **1992**, *603*, 35.
- Chen, N.; Zhang, Y.; Lu, P. *J. Chromatogr.* **1992**, *606*, 1.
- Stadalius, M. A.; Gold, H. S.; Snyder, L. R. *J. Chromatogr.* **1984**, *296*, 31.
- Chen, N.; Zhang, Y.; Lu, P. *Chin. J. Chromatogr.* **1990**, *6*, 325.
- Zou, H.; Zhang, Y.; Lu, P. *J. Chromatogr.* **1990**, *522*, 49.
- Minick, D. J.; Breng, D. A.; Frenz, J. *J. Chromatogr.* **1989**, *461*, 177.
- Hanai, T. *J. Chromatogr.* **1991**, *550*, 313.

Theoretical Study of the Frequency-Dependent First- and Third-Order Polarizabilities of Thiophene Oligomers

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Heterocyclic organic systems have attracted particular attention as the materials with large nonlinear optical properties.^{1,2} In particular, organic compounds containing heterocyclic moieties (thiophene, pyrrole, furan) are well known to exhibit significant NLO behavior.³ The nonlinear optical properties of analogs of heterocyclic molecules, such as hetero-(X=O, S, Se, Te)-TCNQ (tetracyanoquinodimethane) and TTF (tetrathiafulvalene) have been investigated.^{4,5} Polythiophene is one of the most widely investigated π -conjugated systems representing quasi one-dimensional conductors.⁶ In this paper, we present the frequency-dependent first-order polarizabilities, α , and third-order polarizabilities, γ , for the thiophene oligomers with repeating units $n=1-13$. Undoped polythiophene exhibits large third-order nonlinear optical responses.⁷⁻⁹

The component in the i -th molecular fixed-coordinate dire-

ction of the electric field induced dipole moment (the dipole polarization) for an isolated molecule can be written:¹⁰

$$P_i(\omega) = \alpha_{ij}(-\omega; \omega_1) E_j(\omega_1) + \beta_{ijk}(-\omega; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) + \gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) + \dots$$

where $\alpha_{ij}(-\omega; \omega_1)$ is the first-order molecular polarizability, and $\beta_{ijk}(-\omega; \omega_1, \omega_2)$ and $\gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)$ are the second- and third-order polarizability, respectively. The subscripts i , j , and k refer to a molecule-based coordinate system.

In this study, the time-dependent Hartree-Fock (TDHF) method combined with semiempirical AM1¹¹ and PM3¹² calculations is employed to obtain the first- and third-order polarizabilities for the thiophene oligomers shown in Figure 1. Thiophene oligomers were assumed to be planar structures. All the structures were fully optimized and have all the positive vibrational frequencies. Thiophene oligomers with an odd number of rings belong to the C_{2v} representation, while the oligomers with an even number of the thiophene ring belong to the C_{2h} representation.

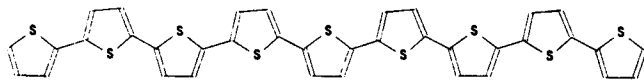


Figure 1. Structure of the nine-ring thiophene oligomer.

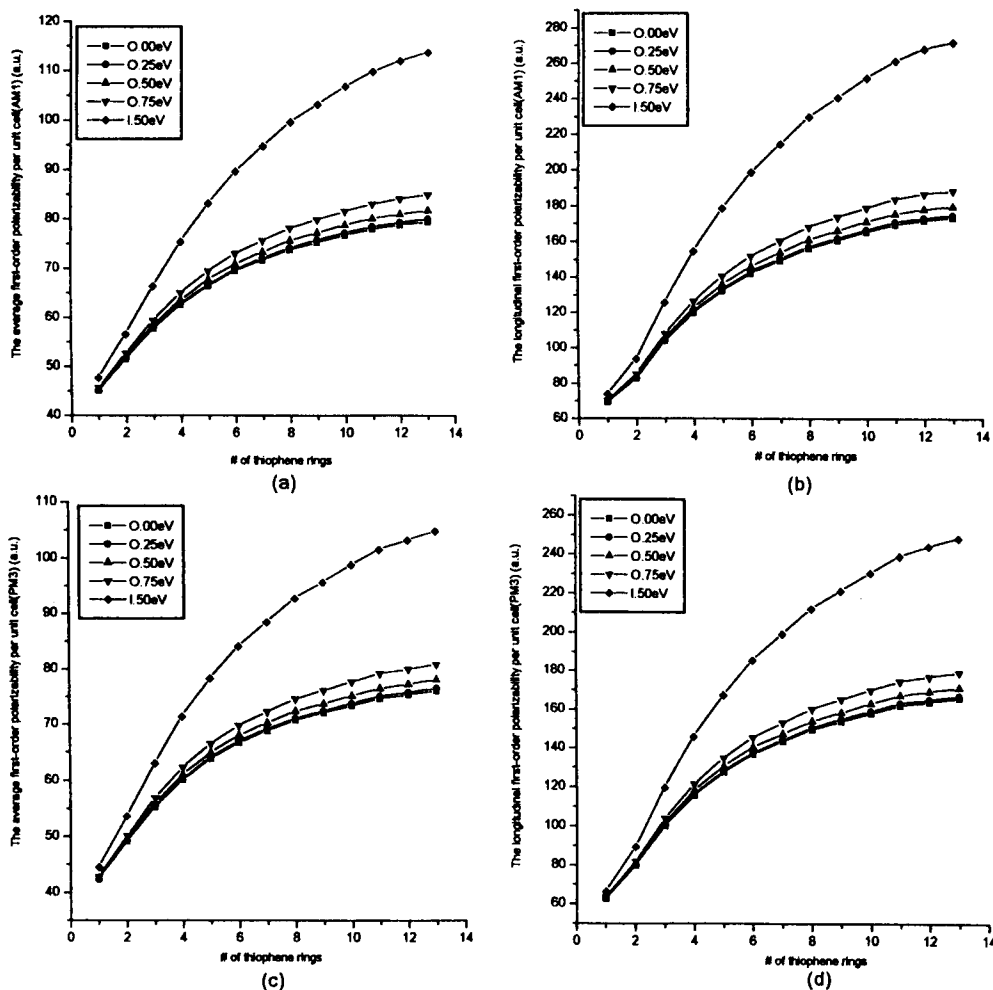


Figure 2. The average and longitudinal first-order polarizabilities per thiophene ring.

The average α and γ value are defined as $\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ and $\langle \gamma \rangle = 1/5[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$, respectively. The $\log A(n) = a + b/n + c/n^2 + d/n^3$ formula is applied to predict the asymptotic value (for $n = \infty$). Also, to calculate the saturation, the first- and third-order polarizabilities are usually expressed as a function of the chain lengths (n):

$$A(n) = n^k$$

Here n is the number of thiophene rings and $A(n)$ stands for the first- and third-order polarizabilities. The bigger the exponent value (k) shows, the slower the saturation becomes.

Figure 2 shows a plot of $\langle \alpha \rangle/n$ and α_{xx}/n as a function of n , where n is the number of thiophene rings. The asymptotic average (longitudinal) first-order polarizabilities per thiophene ring at the optical wavelengths of 4959.37 nm, 2479.68 nm, 1653.12 nm, and 826.56 nm are 199.61(86.81), 205.58(88.88), 216.61(92.71), and 317.70(127.27) a.u. at PM3 level, 209.33(90.97), 216.15(93.34), 228.87(97.74), and 352.71(139.98) a.u. at AM1 level, respectively.

The average first-order polarizabilities values of monomer (dimer) for the static frequency are 42.24 (98.16) and 45.01 (102.83) a.u. at PM3 and AM1 levels, respectively. Compared

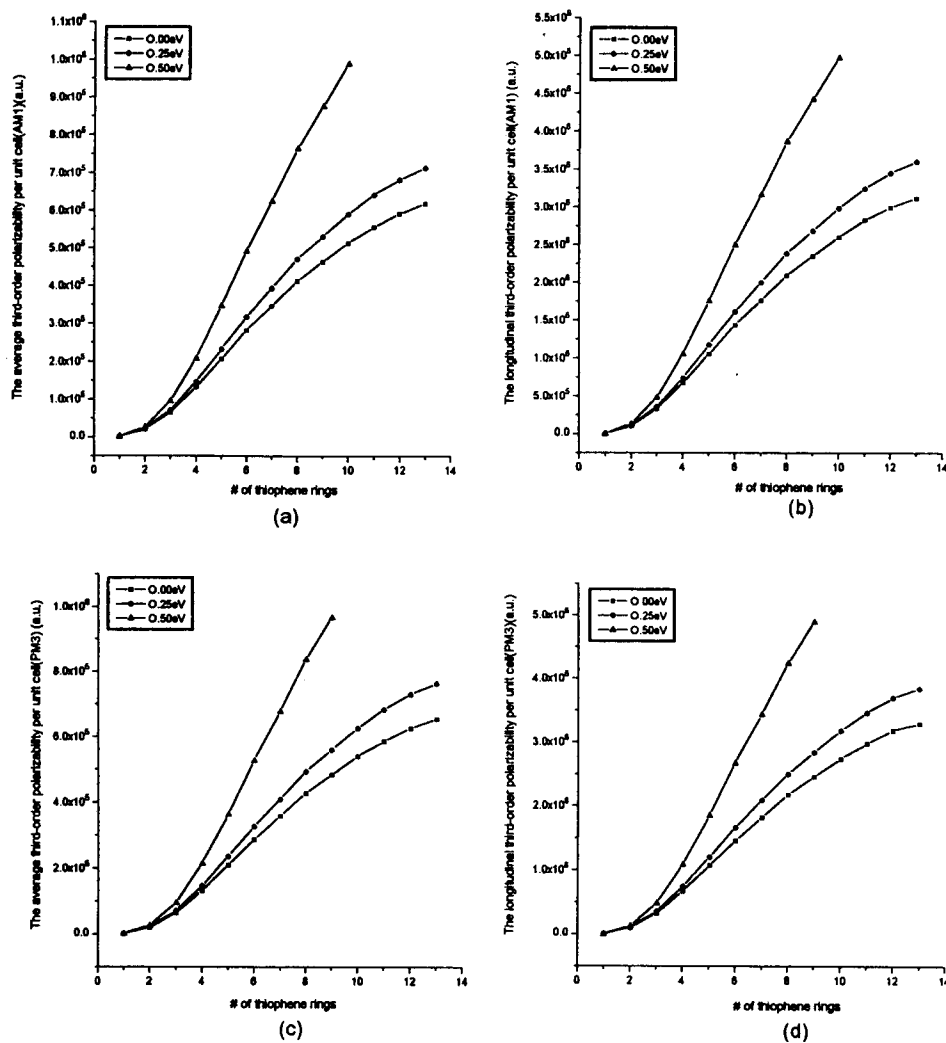


Figure 3. The average and longitudinal third-order polarizabilities per thiophene ring.

to the CPHF results obtained with the medium-polarized basis set of Sadlej¹³ [$\langle\alpha\rangle = 63.1(131.2)$ a.u.] ($\omega = 0$) and the experimental values measured by Zaho *et al.*⁸ [$\langle\alpha\rangle = 66.9(168.7)$ a.u.], these values are underestimated. At PM3 level, the longitudinal first-order polarizability of thiophene monomer for the static frequency is 62.50 a.u.. This value shows small differences obtained by using the 3-21G(61.16 a.u.), 6-31G**(65.62 a.u.) and 6-311G**(68.95 a.u.) atomic basis sets at CPHF level.¹⁴

The exponent values (PM3 and AM1 level) of the average first-order polarizability at the optical wavelengths of 4959.37 nm-826.56 nm to be in the range of 1.23-1.35. On the other hand, the exponent values (PM3 and AM1 level) of the longitudinal first-order polarizability at the optical wavelengths of 4959.37 nm-826.56 nm are 1.38-1.55. These results were close to the exponent value (~ 1.0) predicted by the *ab initio* calculation.⁸ On the other hand, the exponent value predicted by a free electron model¹⁵ and a PPP model¹⁶ show 3 and 2.3, respectively. The average and longitudinal third-order polarizabilities per thiophene unit for thiophene oligomers are shown in Figure 3. We obtain that the average and longitudinal third-order polarizabilities (at PM3 and AM1 level) are slightly higher than those of the INDO/MRD-CI SOS

approach.¹⁴ As shown in Figure 3, we have observed a strong length dependence of $\langle\gamma\rangle$ up to the pentamer but a weak one for $n > 6$.

The average (longitudinal) limiting third-order polarizabilities at the optical wavelengths of 4959.37 nm and 2479.68 nm are 1.62×10^7 (8.15×10^7) and 1.87×10^7 (9.44×10^7) at AM 1 level, 1.51×10^7 (7.61×10^7) and 1.69×10^7 (8.51×10^7) at PM 3 level, respectively. These values are ~ 2 and ~ 5 times smaller than those of thiophene-TCNQ (TTF) and -polyene systems. In this paper, we find that the exponent values of the average third-order polarizabilities at the optical wavelengths of 4959.37 nm and 2479.68 nm are ~ 3.21 and ~ 3.74 at PM3 level, ~ 3.37 and ~ 3.96 at AM1 level, respectively, which are in agreement with the experimental degenerate four wave mixing (DFWM) values (4.05) obtained by Zaho *et al.* for thiophene oligomers (recorded at 602 nm).⁸ On the other hand, these values are about 1.5 and 2 times larger than those of thiophene-TCNQ (TTF) and -polyene systems. Therefore, the limiting average third-order polarizabilities of thiophene oligomer are smaller, while the regime of saturation is faster than those of thiophene-TCNQ (TTF) and -polyene systems. The exponent value k , at AM1 level, goes from 5.08 to 2.05 at static electric field, which is similar

to the VEH (Valence effective Hamiltonian) results¹⁸ (4.8-2.8) for PPV (polyparaphenylene vinylene) oligomers. In contrast, VEH calculations¹⁹ for polyene predict the exponent value from 6.0 for $n=6$ to 3.3 for $n=30$, while for the SSH (Su-Schrieffer-Heeger)-SOS (Sum-Over-States) calculations,¹⁸ it varies from 5.7 to 1.6.

The exponent values of the longitudinal third-order polarizabilities at the optical wavelengths of 4959.37 nm and 2479.68 nm predicted by PM3(AM1) level are 4.15 (3.89) and 4.32 (4.09), respectively. These results are qualitatively similar to previously observed results for polyenes.^{20,21}

References

1. Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers*; Wiley Interscience: New York, 1991.
2. Reinhardt, B. A.; Unroe, M. R.; Evers, R. C.; Zaho, M.; Samoc, M.; Prasad, P. N.; Sinsky, M. *Chem. Mater.* **1991**, *3*, 864.
3. Choi, U.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 61.
4. Choi, U.-S.; Lee, W. R.; Kim, C. J. *Bull. Korean Chem. Soc.* **1994**, *15*, 814.
5. Choi, U.-S. *J. Electrical and Electronic Materials* **1996**, *2*, 21.
6. McIntyre, E. F.; Hameka, H. F. *J. Chem. Phys.* **1978**, *68*, 3481.
7. (a) de Melo, C. P.; Silbey, R. S. *Chem. Phys. Lett.* **1987**, *140*, 537. (b) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696.
8. Zhao, M. T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.
9. Pierce, B. M. *J. Chem. Phys.* **1989**, *91*, 791.
10. Kaminow, I. *An Introduction to Electrooptic Devices*; Academic Press: New York, 1974; p 56.
11. Dewar, M. J. S.; Zebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
12. Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 210.
13. Sadlej, A. J. *Theor. Chim. Acta* **1991**, *79*, 123.
14. Champagne, B.; Mosley, D. H.; Andre, J.-M. *J. Chem. Phys.* **1994**, *100*, 2034.
15. Boggard, M. P.; Orr, B. J. *Int. Rev. Sci., Phys. Chem. Ser.* **2**, 149.
16. (a) McIntyre, E. F.; Hameka, H. F. *J. Chem. Phys.* **1978**, *68*, 3481. (b) Zamani-Khamiri, O.; Hameka, H. F. *ibid.* **1980**, *72*, 5903.
17. Beljonne, D.; Shuai, Z.; Bredas, J. L. *J. Chem. Phys.* **1993**, *98*, 8819.
18. Shuai, Z.; Bredas, J. L. *Phys. Rev. B* **1991**, *44*, 5962.
19. Shuai, Z.; Bredas, J. L. *Phys. Rev. B* **1992**, *46*, 4395.
20. Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O.; Gartio, A. F. *Phys. Rev. B* **1988**, *38*, 1573.
21. de Melo, C. P.; Silbey, R. *Chem. Phys. Lett.* **1987**, *140*, 537.

Sulfur(IV) Catalysis on the Aquation of Cyanopentaaquochromium(III) Ion

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Since the unusual effect of nitrate ion on the aquation of aquopentamine-chromium(III) complex was observed,¹ other oxyanion catalyses of substitution reactions of chromium(III) complex ion have been the subjects of several papers.²⁻⁹

Duffy and Early² reported a catalytic effect on the part of sulfate in the aquation of $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ without any mechanistic explanation. Matts and Moore⁵ observed nitrate catalysis of the aquation of several halochromium(III) complexes.

Zinato, *et al.*⁶ reported the *cis* labilizing effect of coordinated acetate in amminechromium(III) complexes, and Guastalla and Swaddle⁷ reported that coordinated nitrate in amminechromium(III) complexes also strongly labilizes the ligand *cis* to it.

Sulfite catalyses of the aquation of $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$, $\text{Cr}(\text{H}_2\text{O})_5\text{NCS}^{2+}$, *cis*- and *trans*- $\text{Cr}(\text{H}_2\text{O})_4(\text{NCS})_2^+$, $\text{Cr}(\text{H}_2\text{O})_5\text{N}_3^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})^{2+}$ were studied by Carlyle *et al.*^{8,9} They suggested that the sulfite ion coordinates to the oxygen atom of a water molecule bound to chromium in a labile equilibrium, and then the sulfite ion labilizes the other ligand in the *trans* position to the coordinated sulfite ion.

Sulfite catalysis of cyanochromium(III) was studied to learn whether there are any mechanistic differences from the chromium(III) complexes with neutral or weakly basic ligands that have been previously studied.

Experimental

Materials. Water used in all solutions was redistilled from laboratory distilled water.

Potassium hexacyanochromate(III), $\text{K}_3\text{Cr}(\text{CN})_6$, was prepared by using Bigelow's method.¹⁰ Cyanopentaaquochromium(III) perchlorate, $[\text{Cr}(\text{H}_2\text{O})_5\text{CN}](\text{ClO}_4)_2$ was prepared by using Wakefield and Schaap's method¹¹; a 0.008 M solution of $\text{K}_3\text{Cr}(\text{CN})_6$ with 0.04 M perchloric acid was prepared. The low initial acidity of 0.04 M was used in order to prevent acid hydrolysis of the cyanopentaaquochromium(III) complex during the subsequent ion exchange separation. The hydrolysis solution was kept in the dark at room temperature until the pH of the solution rose to *ca.* 2, which took approximately 44 hours. A stream of nitrogen was continuously bubbled through the solution to sweep out the liberated molecular hydrogen cyanide. The deep red solution was cooled to 0 °C and the precipitated potassium perchlorate was removed by filtration. The solution was then absorbed on a column of Dowex 50W-X8 cation-exchange resin (100-200 mesh) in the sodium ion form, and $\text{Cr}(\text{H}_2\text{O})_5\text{CN}^{2+}$ ion was eluted from