Chem. Mater. 1992, 4, 247-249

suppresses the rate of corrosion by a factor of about 14. The values of the solution resistance, $R_\Omega$, were 0.7 Ω cm$^2$ at 23 °C and 0.1 Ω cm$^2$ at 95 °C. The time dependence of reciprocal $R_p$ values and values of percent inhibition at 23 °C have been plotted in Figures 2 and 3, respectively. The inhibition efficiency was observed to reach a steady state within 6 h of reaction. The steady-state inhibition efficiency using 0.01% oligomeric methylquinolinium methylsulfate at 23 °C was calculated to be 88%. A similar calculation at a temperature of 95 °C was found to be 90%.

In conclusion, we observed a high anticorrosion efficiency of the quaternary salt of oligoquinolines (**2a** and **2b**) on carbon steel surfaces in aqueous acidic media at both ambient and elevated temperatures. They can be utilized as valuable corrosion inhibitors in the acid-flooding process of oil well exploration. While the exact mechanism of inhibition is unclear, it was hypothesized that positively charged quinoline oligomers being absorbed on the metal surface create an electrostatic field which repels the passage of ferrous ions into solution. If this mechanism is correct, the inhibition action can be extended to other metals.

**Registry No.** MQO–MeSO$_4$, 138629-29-5; carbon steel, 11121-90-7.

---

# Phase Selectivity in the Simultaneous Synthesis of the $T_c$ = 12.8 K (0.3 kbar) Organic Superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl or the Semiconductor (BEDT-TTF)Cu[N(CN)$_2$]$_2$

H. Hau Wang,* Urs Geiser,* Jack M. Williams,*
K. Douglas Carlson, Aravinda M. Kini,
Jean M. Mason, J. Timothy Perry,
Henry A. Charlier, Anneliese V. Strieby Crouch,
James E. Heindl, Michael W. Lathrop,
Bradley J. Love, Diana M. Watkins, and
George A. Yaconi

*Chemistry and Materials Science Divisions*
*Argonne National Laboratory*
*Argonne, Illinois 60439*

*Received November 12, 1991*
*Revised Manuscript Received January 14, 1992*

The discovery of two new radical-cation-based organic superconductors, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, X = Br ($T_c$ = 11.6 K)[1-3] and Cl ($T_c$ = 12.8 K, 0.3 kbar)[4] possessing new records of high $T_c$, was reported recently [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, or simply ET]. The preparation of single-phase materials is essential for the physical characterization of new organic superconductors. Whereas the Br salt is easily produced as a single-phase material by several different routes,[5,6] two distinctly different phases (rhombic platelets for the superconductor and needles for the second nonsuperconducting phase) were observed simultaneously when the isostructural Cl salt superconductor was prepared. The multiphasic nature of the crystal growth that occurred during the preparation of κ-(ET)$_2$Cu[N(CN)$_2$]Cl, **1**, was not unprecedented. Whereas the first organic superconductors [(TMTSF)$_2$X, X$^-$ = PF$_6^-$, AsF$_6^-$, SbF$_6^-$, TaF$_6^-$, ReO$_4^-$, ClO$_4^-$][7] were prepared as single-phase materials during the electrocrystallization process, the second class of organic superconducting materials, based on (ET)$_2$X (X is a monovalent anion), frequently yield multiple crystallographic phases with varying electrical properties.[8] Thus, there often exists a delicate balance of reaction equilibria occurring during electrocrystallization, complicated by the fact that for the preparation of polymeric anions the starting materials frequently do *not* yield the expected anion-containing salts, and these factors must be understood and controlled in order to prepare the desired products.

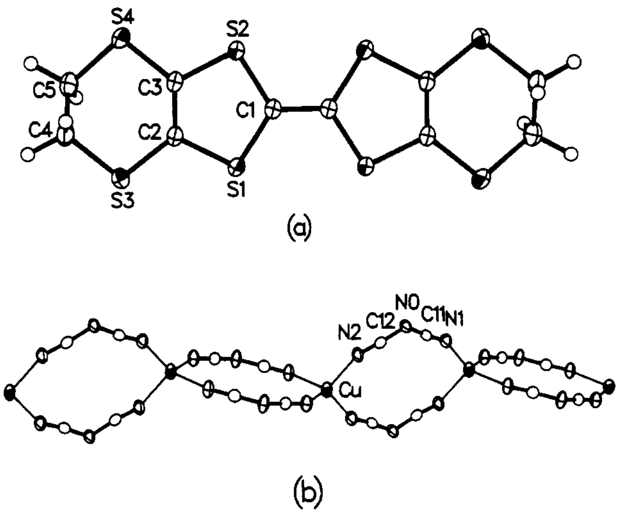


**Figure 1.** (a) ET molecule with atomic labels. A 2-fold rotation axis perpendicular to the plane of the drawing relates the two halves of the molecule, (b) infinite chain-like polymeric Cu[N(CN)$_2$]$_2^-$ anion with atomic labels. In both parts of the figure, the atoms (except hydrogen) are drawn with 50% probability ellipsoids, but the scale of (a) is different from that of part (b).

Superconducting κ-(ET)$_2$Cu[N(CN)$_2$]Cl, **1**, was initially prepared from the electrocrystallization of the ET donor molecule in the presence of CuCl and PPh$_4$[N(CN)$_2$].[4] Crystals of the rhombic shaped Cl salt, **1**, are usually smaller than those of the isostructural Br salt grown under identical conditions, and in addition, a second competing needle-shaped product frequently grows simultaneously. In this communication, we report the first characterization of the needle phase, (ET)Cu[N(CN)$_2$]$_2$, **2**, by use of X-ray diffraction, ESR spectroscopy, four-probe conductivity measurements, and the synthetic procedures required for

---

[1] Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555.

[2] Williams, J. M.; Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Organic Superconductivity*; Kresin, V. Z., Little, W. A., Eds.; Plenum Press: New York, 1990; pp 39–50.

[3] Wang, H. H.; Beno, M. A.; Carlson, K. D.; Geiser, U.; Kini, A. M.; Montgomery, L. K.; Thompson, J. E.; Williams, J. M. *Organic Superconductivity*; Kresin, V. Z., Little, W. A., Eds.; Plenum Press: New York, 1990; pp 51–66.

[4] Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins, D. M.; Kommers, J. M.; Boryschuk, S. J.; Strieby Crouch, A. V.; Kwok, W. K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3262.

[5] Wang, H. H.; Kini, A. M.; Montgomery, L. K.; Geiser, U.; Carlson, K. D.; Williams, J. M.; Thompson, J. E.; Watkins, D. M.; Kwok, W. K.; Welp, U.; Vandervoort, K. G. *Chem. Mater.* **1990**, *2*, 482.

[6] Wang, H. H.; Carlson, K. D.; Geiser, U.; Kini, A. M.; Schultz, A. J.; Williams, J. M.; Montgomery, L. K.; Kwok, W. K.; Welp, U.; Vandervoort, K. G.; Boryschuk, S. J.; Strieby Crouch, A. V.; Kommers, J. M.; Watkins, D. M.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Novoa, J. J.; Whangbo, M.-H. *Synth. Met.* **1991**, *42*, 1983.

[7] Bechgaard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1.

[8] Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Progress In Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1987; Vol. 35, pp 51–218.

0897-4756/92/2804-0247$03.00/0

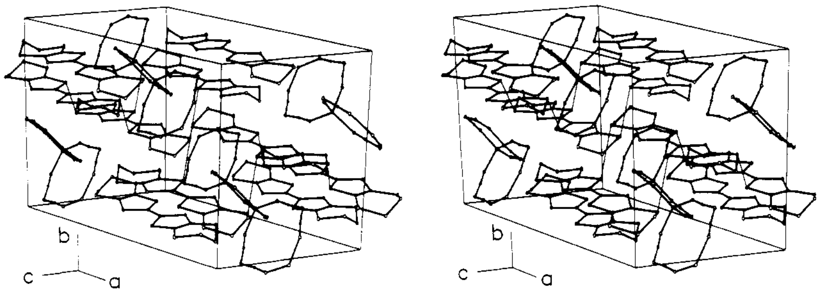


**Figure 2.** Stereoview of the unit cell of (ET)Cu$[N(CN)_2]_2$. No well-developed S···S network exists in this salt, and the shortest intermolecular S···S contacts, at a distance of 3.63 Å, are drawn with thin lines. The atoms are shown with ellipsoids of an arbitrary scale, and the hydrogen atoms are omitted for clarity.

**Table I. Electrocrystallization of $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$, 1, and $(ET)Cu[N(CN)_2]_2$, 2, by Various Routes**

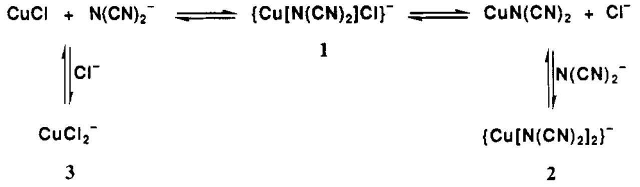
| electrolyte[a,b] | current density, $\mu A/cm^2$ | crystal morphology | ESR line width,[b] G | product[c] |
|---|---|---|---|---|
| CuCl, $PPh_4[N(CN)_2]$[d] | 0.1–0.2 (30 days) | rhombic plates | 55–75 | 1 (major)[e] |
| | | needles | 7.8–10.3 | 2 (minor)[e] |
| $Cu[N(CN)_2]$, $N(hexyl)_4Cl$ | 0.2 (28 days) | rhombic plates | 60–68 | 1 |
| $PPh_4Cu[N(CN)_2]_2$, $N(hexyl)_4Cl$ | 0.1 (28 days) | rhombic plates | 56–61 | 1 |
| $N(n\text{-}Bu)_4CuCl_2$, $PPh_4[N(CN)_2]$ | 0.2 (55 days) | thick rhombic plates | ~60 | 1 (major) |
| | | rectangular plates | 39 | 3 (minor) |
| CuCl, $PPh_4[N(CN)_2]$, $N(hexyl)_4Cl$ | 0.2 (29 days) | rhombic plates | ~60 | 1 (major) |
| | | rectangular plates | 47 | 3 (minor) |
| | | needles | ~9 | 2 (trace) |
| CuCl, $PPh_4[N(CN)_2]$, 0.5 equiv $N(hexyl)_4Cl$[f] | 0.2 (27 days) | rhombic plates | ~60 | 1 |
| $Cu[N(CN)_2]$, $PPh_4[N(CN)_2]$ | 0.2 (32 days) | needles | 12.9 | 2 |

[a] Solvent: 1,1,2-trichloroethane + 10% (vol) absolute ethanol. [b] Ambient temperature. [c] 1: $\kappa$-$(ET)_2Cu[N(CN)_2]Cl$. 2: $(ET)Cu[N(CN)_2]_2$. 3: $\alpha'$-$(ET)_2CuCl_2$. [d] ET (8 mg), CuCl (15.4 mg) and $PPh_4[N(CN)_2]$ (63 mg) in 15 mL of solvent. [e] See text. [f] ET (8.6 mg), CuCl (15.5 mg), $PPh_4[N(CN)_2]$ (63.5 mg), and $N(hexyl)_4Cl$ (30.8 mg), in 15 mL of solvent.

the *selective* growth of single crystals of the superconducting salt 1.

A shiny black needle-shaped crystal of 2 (0.02 × 0.08 × 1.4 mm$^3$) was mounted on a Syntex $P2_1$ four-circle diffractometer, and its structure determined by use of X-ray diffraction methods.[9] The atomic labeling of the molecular constituents is shown in Figure 1, and atom coordinates are given in the supplementary material (see paragraph at end of paper). In contrast to most conducting salts containing ET radical cations, the structure of 2 does *not* consist of alternating layers but rather contains a three-dimensional network of ET donor-radical cations interwoven with unprecedented tetrahedrally coordinated $\{Cu[N(CN)_2]_2^-\}_\infty$ infinite chains; see Figure 2. The only other examples of such three-dimensional networks in ET salts are $(ET)Ag_4(CN)_5$,[10] $(ET)AuBr_2Cl_2$,[11] and $(ET)_3[V(C_3S_5)_3]_2$,[12] and of these only $(ET)Ag_4(CN)_5$ contains a polymeric anion. The ET molecules are located on a 2-fold rotation axis perpendicular to the plane of the molecule. The shortest intermolecular S···S contact (known to be important for electronic conduction pathways if orbital overlap exists) is 3.63 Å, i.e., longer than the van der Waals distance[13] of 3.60 Å. Thus, no well developed S···S network exists in this salt. Contact distances shorter than van der Waals sum that occur between the sulfur atoms of the ET molecule and nitrogen and carbon atoms of the anion are 3.17 Å ($r_{vdW}$ = 3.35 Å) and 3.19 Å ($r_{vdW}$ = 3.50 Å), respectively. The significantly short contacts between the donor molecule and anion might indicate that unfavorable strain exists in compound 2 (strain indexes,[14] are 5% and 9% for the two short contacts, respectively). This observation is consistent with the fact that compound 1 is preferentially formed under slow growth conditions (vide infra). The polymeric anion, $\{Cu[N(CN)_2]_2^-\}_\infty$, contains chains of distorted tetrahedrally coordinated copper(I) atoms connected by doubly bridged dicyanamide anions. Only the terminal nitrogen atoms are coordinated to the copper atoms. A 2-fold rotation axis penetrates the chains through the copper atoms perpendicular to the chain direction ($a + b$).

**Scheme I**



The resistivity of 2 was measured along the needle axis ($c$) and indicated semiconductive behavior over the entire temperature range measured (295–80 K). The resistivity was 3.2 × 10$^3$ Ω cm at 295 K with an activation energy of 0.13 eV (between 300 and 200 K). The ESR measure-

---

(9) X-ray data were collected on a Syntex $P2_1$ diffractometer, and the monoclinic unit cell data (space group $C2/c$, $Z = 4$) are (295 K) $a = 16.723$ (3) Å, $b = 13.941$ (3) Å, $c = 10.279$ (2) Å, $\beta = 124.02$ (1)°, $V = 1986.1$ (7) Å$^3$. 3061 diffraction data were collected ($\theta/2\theta$ scans, 2.1° + $\alpha_1$–$\alpha_2$ splitting, 1.5–4.5° min$^{-1}$) in the range $4° \leq 2\theta \leq 55°$ (all $h$, $k \geq -2$, $l \geq 0$). Reflections were corrected for absorption ($\mu = 19.27$ cm$^{-1}$, $T_{min} = 0.842$, $T_{max} = 0.962$) and averaged ($R_{av} = 0.010$) to 2288 unique, allowed reflections. Structure solved by direct methods, 132 variables refined by full-matrix least-squares to 2059 observed reflections ($F_o > 3\sigma$), with $R(F) = 0.038$, $R_w(R) = 0.035$, GOF = 1.81. The programs used in the analysis of the diffraction data were modified versions of: Strouse, C. *UCLA Crystallographic Program Package*; University of California: Los Angeles, CA, 1986.

(10) Geiser, U. W.; Wang, H. H.; Gerdom, L. E.; Firestone, M. A.; Sowa, L. M.; Williams, J. M.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1985**, *107*, 8305.

(11) Porter, L. C.; Wang, H. H.; Beno, M. A.; Carlson, K. D.; Pipan, C. M.; Proksch, R. B.; Williams, J. M. *Solid State Commun.* **1987**, *64*, 387.

(12) Broderick, W. E.; McGhee, E. M.; Godfrey, M. R.; Hoffmann, B. M.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2902.

(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(14) The strain index, *SI*, was defined as $SI = 100\% (r_{vdW} - r)/r_{vdW}$ in: Whangbo, M.-H.; Novoa, J. J.; Jung, D.; Williams, J. M.; Kini, A. M.; Wang, H. H.; Geiser, U.; Beno, M. A.; Carlson, K. D. In *Organic Superconductivity*; Kresin, V. Z., Little, W. A., Eds.; Plenum Press: New York, 1990; pp 243–266.

ments[15] on a single crystal of **2** were carried out with the $c$ axis oriented vertically in the microwave cavity. Rotation about the $c$ axis at room temperature revealed that the peak-to-peak line width ranged from 7.8 to 10.3 G with associated $g$ values of 2.0021 and 2.0119, respectively.

The coexistence of **1** and **2** during synthesis can be understood in terms of Scheme **I**. When the reaction between CuCl and PPh$_4$[N(CN)$_2$] is carried out in refluxing acetonitrile, the product isolated is the solvated Cu[N(CN)$_2$] which readily loses solvent in air.[16] With the formation of Cu[N(CN)$_2$] and the presence of excess N(CN)$_2^-$ anion during electrocrystallization, the growth of **2**, which does not contain any Cl, can occur. Various reaction conditions for the selective electrocrystallization of **1** were tested in order to verify Scheme I. On the basis of the chemical formula of **2**, i.e., (ET)Cu[N(CN)$_2$]$_2$, two strategies were taken to avoid its formation. First, since the formal oxidation state of ET in **2** is +1, high current density during electrocrystallization or any chemical oxidant such as a Cu(II) impurity, both of which promote the oxidation of ET, should be rigorously avoided. Second, we chose to include excess Cl$^-$ in order to shift the equilibrium in favor of CuCl and N(CN)$_2^-$ in Scheme I. The test results are summarized in Table I.[17] The detailed experimental procedure for electrocrystallization has been reported in the literature.[8] The structural phases were then easily identified by use of their characteristic room-temperature ESR peak-to-peak line widths. A line width near 60 G is indicative of **1**, while a linewidth near 10 G is ascribed to **2**. In the first table entry, under inert atmosphere with rigorously dried solvent and freshly recrystallized electrolytes, the only product is the superconductor, **1**. With undried or slightly impure chemicals or higher current density (>1 $\mu$A/cm$^2$), the semiconductor **2** is notably increased in content. In the second entry, without the presence of N(CN)$_2^-$ anion, **1** is the only product observed; however, the crystals are small which might be caused by the facile nucleation due to the very insoluble and highly suspended Cu[N(CN)$_2$] powder in the solution during electrocrystallization. The result that the use of Cu[N(CN)$_2$]$_2^-$ and Cl$^-$ (entry 3) also leads to **1** is somewhat unexpected. It suggests that under slow growth conditions, such as low current density and with no extra chemical oxidant (or Cu(II) impurity), the growth of superconducting **1** is favored. This result is consistent with the presence of unfavorable strain in compound **2** (vide supra). Entries 4 and 5 were designed to test the effect of excess Cl$^-$. Semiconducting **2** is mostly eliminated under these conditions but a second nonsuperconducting phase contaminant, **3**, $\alpha'$-(ET)$_2$CuCl$_2$, forms.[18,19] Entry 6 is a modified route with 0.5 equiv of Cl$^-$ added with respect to CuCl to reduce the CuCl$_2^-$ concentration, and compound **1** is formed exclusively. In fact, the largest crystal of **1** (2.3 × 1.8 × 0.6 mm$^3$) was grown in a moderate time period under these conditions (entry 6). Finally compound **2** can also be prepared selectively in the absence of Cl$^-$ as indicated in the last entry.

In conclusion, electrocrystallization of ET with CuCl and PPh$_4$[N(CN)$_2$] leads to two products, $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl, **1**, and (ET)Cu[N(CN)$_2$]$_2$, **2**, depending on the experimental conditions. **1** is the highest-$T_c$ radical-cation-based organic superconductor ($T_c$ = 12.8 K, 0.3 kbar) known, and **2** is a semiconductor. The product distribution is controlled by chemical equilibrium with the selective preparation of **1** achieved under inert atmosphere by use of CuCl and [N(CN)$_2$]$^-$ (entry 1) or the same reagents and a small amount of added Cl$^-$ (<0.5 equiv/CuCl, entry 6). Oxidizing chemical impurities must be strictly avoided as they increase the concentration of ET$^{\bullet+}$ and favor the growth of **2**. A large excess of Cl$^-$ should also be avoided as it leads to a second nonsuperconducting product,[18,19] $\alpha'$-(ET)$_2$CuCl$_2$.

**Acknowledgment.** Work at Argonne National Laboratory is sponsored by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38. J.M.M. and J.T.P. are DOE teacher research associates, sponsored by the Argonne Division of Educational Programs, from St. Martin De Porres, H.S., Chicago, IL, and Mt. Hebron H.S., Ellicott City, MD, respectively. H.A.C., A.V.S.C., J.E.H., M.W.L., B.J.L., D.M.W., and G.A.Y. are undergraduate student research participants also sponsored by the Argonne Division of Educational Programs, from the University of Wisconsin—Stevens Point, Stevens Point, WI; Aurora University, Aurora, IL; Knox College, Galesburg, IL; Western Montana College, Dillon, MT; Miami University, Oxford, OH; Florida Institute of Technology, Melbourne, FL; and Pennsylvania State University, State College, PA, respectively.

**Registry No.** **1**, 129265-30-1; **2**, 139277-07-9; **3**, 108447-94-5; ET, 66946-48-3; CuCl, 7758-89-6; PPh$_4$[N(CN)$_2$], 51501-04-3; Cl, 16887-00-6; Cu[N(CN)$_2$], 21962-69-6; N(hexyl)$_4$Cl, 5922-92-9; PPh$_4$Cu[N(CN)$_2$]$_2$, 129215-62-9.

**Supplementary Material Available:** Tables of crystal structure data collection and refinement parameters (Table S1), final atom positional parameters (Table S2), anisotropic thermal parameters (Table S3), and bond lengths and angles (Table S4) (4 pages); observed and calculated structure factors (Table S5) for (ET)Cu[N(CN)$_2$]$_2$ (8 pages). Ordering information is given on any current masthead page.

---

[15] ESR measurements were carried out on an IBM ER-200 spectrometer with 9.5 GHz microwave frequency (X-band) and a TE$_{102}$ rectangular cavity.

[16] On the basis of the weight lost, the solvated product corresponds to Cu[N(CN)$_2$](CH$_3$CN) which readily loses acetonitrile in air. Cu[N(CN)$_2$] was verified from satisfactory elemental analyses.

[17] ET was purchased from Strem Chemicals, Inc.; CuCl (99.995%) and N(hexyl)$_4$Cl (reagent grade and recrystallized from ethyl acetate) were from Aldrich Chemical Co., Inc.; PPh$_4$[N(CN)$_2$] was prepared according to: Köhler, H.; Lischko, T. P.; Hartung, H.; Golub, A. M. *Z. Anorg. Allg. Chem.* **1974**, *403*, 35.

[18] Geiser, U.; Wang, H. H.; Hammond, C. E.; Firestone, M. A.; Beno, M. A.; Carlson, K. D.; Nuñez, L.; Williams, J. M. *Acta Crystallogr.* **1987**, *C43*, 656.

[19] Obertelli, S. D.; Friend, R. H.; Talham, D. R.; Kurmoo, M.; Day, P. *J. Phys.: Condens. Matter* **1989**, *1*, 5671.

---

## Second Harmonic Generation in Organically Modified Sol-Gel Films

Jongsung Kim and Joel L. Plawsky*

*Department of Chemical Engineering*
*Rensselaer Polytechnic Institute*
*Troy, New York 12180*

Richard LaPeruta and G. M. Korenowski

*Department of Chemistry*
*Rensselaer Polytechnic Institute*
*Troy, New York 12180*

*Received November 25, 1991*
*Revised Manuscript Received January 9, 1992*

Thin films of organic or polymeric materials with large second-order optical nonlinearities have been developed because of their potential use in communication and optical signal processing.[1-3] The second-order nonlinearities

---

* To whom correspondence should be addressed.