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, α'-$(ET)_2CuCl_2$, 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 ($2.3 \times 1.8 \times 0.6\ mm^3$) 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, κ-$(ET)_2Cu[N(CN)_2]Cl$, 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] α'-$(ET)_2CuCl_2$.

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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; $N(hexyl)_4Cl$, 5922-92-9; $PPh_4Cu[N(CN)_2]_2$, 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.

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[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 $Cu[N(CN)_2](CH_3CN)$ 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 $N(hexyl)_4Cl$ (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.

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Second Harmonic Generation in Organically Modified Sol-Gel Films

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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

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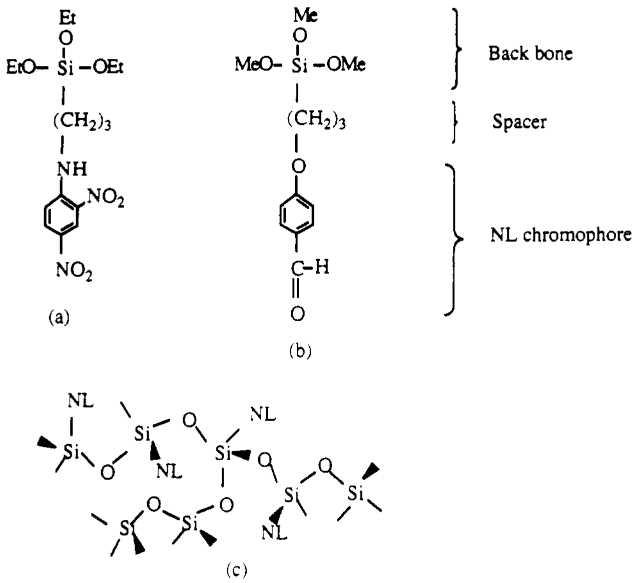

Figure 1. Structure of the organosilane monomers and the organosilicate gel: (a) *N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine; (b) 3-(4-formylphenoxy)propyltrimethoxysilane; (c) organosilicate gel.

can be achieved only in a noncentrosymmetric environment because of the orientational cancellation characteristic of polar, third-rank, tensors. Since Havinga and Van Pelt[4] developed the poling process to align nonlinear chromophores in a polymer matrix, various guest–host systems and poling techniques have been developed. Either physical doping[5] or chemical bonding[6] of the chromophores to the polymer backbone can be used, but the latter, with a cross-linked polymer structure, is preferred because it provides for high densities of optically nonlinear groups and better system stability.[7]

The sol–gel process is a method for producing a three-dimensional inorganic network by chemical reaction at low temperature and is analogous to step reaction polymerizations in organic systems.[8] Recently many novel, composite, optical materials have been prepared by the sol–gel process[9–12] either in bulk or film form. These composite materials possess the large optical nonlinearity of an organic material and the environmental and mechanical stability of an inorganic material.

All the sol–gel derived materials mentioned above have been made by physical blending or doping. Further benefit in the form of higher chromophore concentrations with better orientational stability would be obtained if the organic functionality could be incorporated into the silica networks by chemical bonding. Puccetti et al.[13] have recently used the sol–gel process for attaching the optically nonlinear chromophore directly to the silicon atom during the polymerization and have used corona poling to produce second-order nonlinear films.

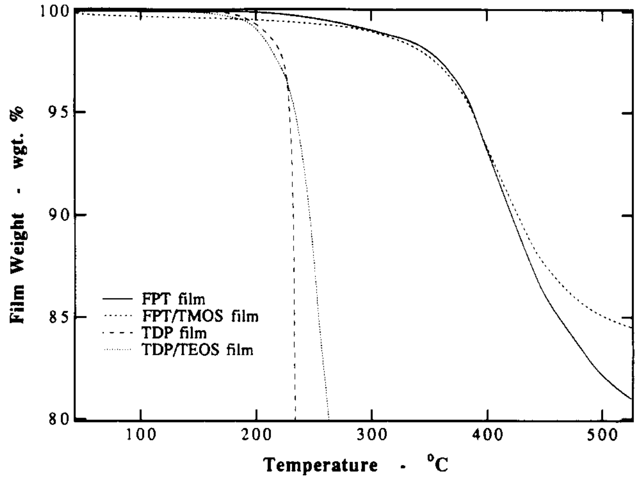

Figure 2. TGA curves for sample TDP and FPT films.

We report here some of the experimental results using optically nonlinear chromophore containing organosilanes such as *N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine (TDP) and 3-(4-formylphenoxy)propyltrimethoxysilane (FPT).

The sol–gel process is a polymerization route which proceeds according to the simplified reaction mechanism shown in eq 1a–c

hydrolysis

$$\mathrm{SiOR + HOH \rightarrow SiOH + ROH} \qquad (1a)$$

water condensation

$$\mathrm{SiOH + SiOH \rightarrow SiOSi + HOH} \qquad (1b)$$

alcohol condensation

$$\mathrm{SiOH + SiOR \rightarrow SiOSi + ROH} \qquad (1c)$$

To assess the viability of the sol–gel method for fabricating nonlinear optical materials, the two organosilanes shown in Figure 1 were used as monomers. Both were substituted benzene derivatives having the desired donor–acceptor structure for high polarizability. The molecular hyperpolarizabilities (β) of the attached chromophores 2,4-dinitroaniline and *p*-methoxybenzaldehyde are 88×10^{-40} m^4 V^{-1} at 1.06 μm and 35×10^{-40} m^4 V^{-1} at 1.89 μm, respectively, and are comparable to that of *m*-nitroaniline, MNA ($53.6 \sim 188 \times 10^{-40}$ m^4 V^{-1}).[3] TDP was purchased from Huls America Inc. and FPT was purchased from PCR Inc.

The coating solutions (sol) were prepared by mixing the silane, water, and acetone in a polyethylene beaker. Acetone was used as the solvent because TDP was insoluble in ethanol. Tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) were also added to increase the average functionality of the monomers. HCl was used as the catalyst. Stochiometric amounts of water were employed and the molar ratio of solvent to silane was held at 20:1 for the TDP based sols and 15:1 for the FPT-based

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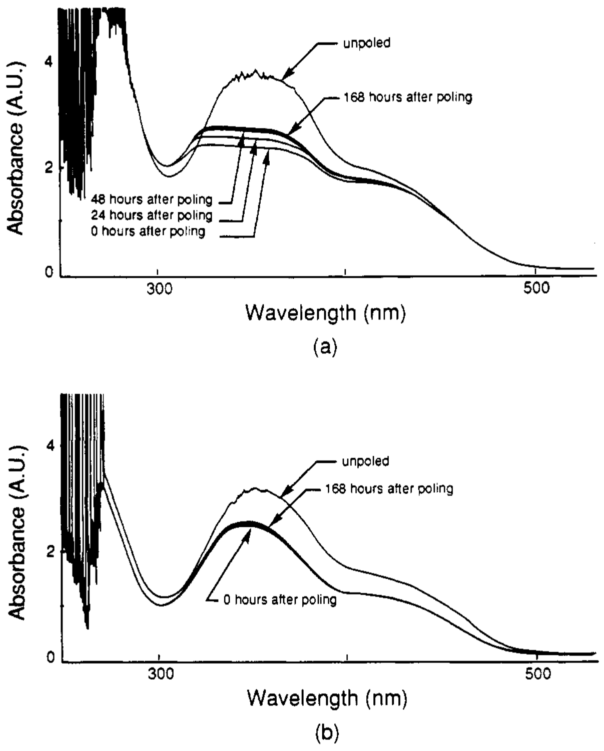

Figure 3. Absorption spectra of (a) TDP film and (b) TDP–TEOS film before and after poling, measured over 1 week.

sols. The solutions were stirred for 1 h at room temperature and then aged another 5 h. The aged sol was passed through a 1-μm filter and spun onto a 1-mm-thick microscope slide or a silicon wafer. The remainder of the sol was allowed to gel for use in thermal analysis.

The chromophore-containing films were further polymerized and poled at 120 °C using a corona discharge technique. The film was placed a distance of 1 cm under the corona wires and a potential of 10 kV was applied across the film. After 3 h of poling, the film temperature was reduced to ambient and the electric field was removed.

The hydrolysis step of the TDP and FTP monomers was studied using ^{1}H NMR and the structure of the gelled organosilicates was studied using IR spectroscopy to determine if the nonlinear chromophore survived the polymerization.[14] Both the IR and the NMR data indicate that the nonlinear chromophores were not degraded or hydrolyzed during the polymerization process and that the silane underwent almost complete hydrolysis in about 30 min.[14]

Figure 2 shows TGA curves for the TDP- and FPT-based films. The decomposition temperatures for the TDP and FPT films were 230 and 350 °C, respectively. If the Si–C bond were to break during decomposition, one would expect about the same decomposition temperature for each material. The chromophore in the TDP sample breaks apart first, perhaps at the weak C–N linkage.[15]

The absorption characteristics and the order parameter for the films were also measured for some select samples. The order parameter is a measure of the degree of orientation of the chromophore inside the network and is defined by[16]

$$\Phi = 1 - A_\perp/A_0 \qquad (2)$$

where $A_\perp$ is the absorbance of a poled sample measured with the light polarized perpendicular to the poling direction and A_0 is the absorbance of an unpoled sample. The absorbances are measured at λ_{max}, the wavelength of maximum absorption.[17] The refractive indexes of the films were measured using a standard interference technique and the film thicknesses were measured using a DekTak profilometer.

Table I. Second Harmonic Generation Experiments

sample	intensity (2ω) I_s/I_q	film thickness, μm	$\eta(\omega)$	$\eta(2\omega)$	$(d_{33})_{exp}$,[a] pm/V
100% TDP	1.10	1.65	1.70	1.83	11.7
75:25 TDP/TEOS	0.60	1.10	1.64	1.80	10.9
50:50 TDP/TEOS	0.53	1.0	1.61	1.74	9.1
100% FPT	5.3E-2	2.16	1.64	1.67	1.3
50:50 FPT/MOS	2.5E-2	2.12	1.60	1.64	0.8

[a] d_{33} for unpoled and pure TEOS samples were effectively 0 (indistinguishable from system noise).

Absorption spectra for TDP-based films were taken regularly over the course of 1 week to investigate the relaxation of the nonlinear chromophore and are shown in Figure 3. A hypochromic shift and a blue shift were observed in the spectrum after poling. This was due to dichroism and electrochromism resulting from the induced dipole alignment.

The order parameter for the pure TDP film measured immediately after poling was 0.35 and stabilized after 2 days at 0.28. The order parameter for a composite 50:50 TEOS–TDP film was 0.21 immediately after poling and relaxed only to 0.19 after 1 week at ambient temperature. The pure TDP film was easier to align than the TDP–TEOS film, but the latter gave a more stable system. The order parameter for the FPT film will be presented at a later date. These films must be cast on fused silica substrates for measurement since the wavelength of maximum absorption for FPT lies within the absorption edge of commercial microscope slides.

Second harmonic generation (SHG) measurements of the sol–gel films at 532 nm were carried out using the Q-switched Nd:YAG laser in the p-polarized geometry right after poling. SHG coefficients, d_{33}, were calculated from the angular dependence of the second harmonic intensity and the formalism of Jerphagnon and Kurtz for uniaxial materials, assuming that $d_{31} = d_{24} = d_{15} = (^1/_3)d_{33}$.[5,16] A 0.5-mm-thick, y-cut, quartz single crystal (d_{11} = 0.5 pm/V) was used as a reference. The TDP-based films showed d_{33} = 9.1–11.7 pm/V and FPT-based films showed d_{33} = 0.8–1.3 pm/V (Table I). These values (TDP) are approaching that of $LiNbO_3$ (d_{33} = 30 pm/V) and are 3 orders of magnitude larger than the results reported by Puccetti et al.[13]

Absorption by the chromophores was not a problem at either the 1064-nm fundamental wavelength or the 532-nm harmonic.[17] The sol–gel solutions used here and the resulting films are homogeneous on a molecular scale and contain no particulates. The only scattering losses which would be observed are Rayleigh losses due to compositional and density fluctuations. These would be very small due to the uniformity and thickness of the films and should be at least as small as losses obtained using PMMA impregnated composites which had 15.6-nm pore diameters

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[17] The TDP samples showed two absorption peaks at approximately 350 and 420 nm. These are absorptions from the two nitro groups. The FTP samples had an absorption peak at 390 nm and maximum absorption was in the UV, below the cutoff wavelength (≈300 nm) for the glass substrate.

and sharp changes in density and refractive index at the pore boundary.[18] The PMMA sol-gel composites showed transmissivities of 0.992 (at 500 nm). Absorptivities of our films were unmeasurable and were buried within the absorption of the substrate glass.

The coefficient, d_{33}, can be calculated using the oriented gas model:[19]

$$d_{33} = \tfrac{1}{2} N \beta f^{2\omega} (f^{\omega})^2 \langle \cos^3 \theta \rangle \qquad (3)$$

where N is the chromophore density (mol/cm^3), f is the Lorentz local field factor, and θ is the angle between the dipole moment of the chromophore and the poling direction. This angle can be estimated from the order parameter:[20]

$$\Phi = \tfrac{1}{2}(3\langle \cos^2 \theta \rangle - 1) \qquad (4)$$

The calculated value for d_{33} using the pure TDP film as an example was 15.4 pm/V, close to the measured value of 11.7 pm/V. Further work comparing calculated and experimentally determined values for d_{33} is premature and will be undertaken once film processing procedures have been optimized.

In conclusion, the sol-gel process can be used to incorporate nonlinear chromophores directly into an inorganic network to make nonlinear optical materials possessing properties of both organic and inorganic materials. Since each Si atom contains an attached chromophore, the nonlinear susceptibilities of the films are higher than physically doped sol-gels and are within the range of commercially available inorganic crystals. By mixing trifunctional organo-substituted silanes with TEOS, the physical properties of the films can be improved without sacrificing their optical properties. Future work will involve optimizing the film fabrication and poling process and synthesizing new silane monomers with chromophores of higher susceptibility than those used here.

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Registry No. TDP, 71783-41-0; FPT, 72136-46-0; 2,4-dinitroaniline, 97-02-9; p-methoxybenzaldehyde, 123-11-5.

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Incorporation of C_{60} in Langmuir-Blodgett Films

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Developments in the synthesis of macroscopic quantities of buckminsterfullerene[1] (C_{60}) have led to numerous studies of the properties of this new and exciting material. In this paper, we describe the preparation of an ultrathin mixed film of C_{60} and 1-octadecanol, $C_{18}H_{37}OH$ (abbreviated here as $C_{18}OH$) on fused silica using the Langmuir-Blodgett (L-B) method.[2,3] Thin films of C_{60} are of interest for several reasons. Most noteworthy is the recent discovery that superconducting films are produced when films of C_{60} are exposed to alkali-metal vapor.[4] In addition, thin films of C_{60} have been used in electrochemical studies[5] and in nonlinear optical (NLO) experiments.[6] Recently, Obeng and Bard[7] have reported results of L-B experiments on pure C_{60} and C_{60} mixed with arachidic acid ($C_{19}H_{39}COOH$).

Table I. Spreading Solutions

film type	concn, M	added,[a] μL
C_{60}	3.583×10^{-4}	750
	1.250×10^{-4}	1500
	5.972×10^{-5}	200
$C_{18}OH$	1.831×10^{-3}	300
$C_{60}/C_{18}OH$	2.986×10^{-4} (C_{60}) 3.051×10^{-4} ($C_{18}OH$)	500

[a] Added in 5.0-μL increments.

Film pressure vs area (π-A) isotherms were determined for three Langmuir film types: (1) C_{60}, (2) $C_{18}OH$, and (3) a 1:1 mole ratio mixture of the two compounds. C_{60} was prepared following the procedures described by Haufler et al.[8] and Aije et al.[9] The C_{60}:C_{70} ratio was greater than 99:1 as determined by negative ion chemical ionization mass spectrometry. C_{60} for these studies was recrystallized from benzene prior to preparation of the spreading solutions described in Table I. Octadecanol (99.5%, LaChat) was used as received. The more dilute (5.972×10^{-5} M) solution of C_{60} was used to check for dependence of π-A characteristics on concentration. Results for the low-concentration run were similar to the runs using higher concentration solutions. The 1.250×10^{-4} M C_{60} solution was from a different preparation batch and was recrystallized from chlorobenzene. Triply distilled water (second and third distillations from a quartz still) used as the subphase was changed for each run.

π-A studies and depositions of L-B multilayer films were carried out in a constant-temperature room at 25 °C using a KSV 5000 Langmuir-Blodgett system (KSV Instruments, Helsinki, Finland). The system had a 10-mm-deep Teflon Langmuir trough with a water surface area of 150 mm × 510 mm. Surface tension (γ) was measured with a Wilhelmy plate. Film pressure is the difference between the surface tension of the clean water and the film-covered water, i.e., $\pi = \gamma_w - \gamma_f$. Solutions were spread on the trough by adding drops in 5-μL increments at different locations on the water surface. Films were compressed at a rate of 1 mN/(m min), resulting in a slowing of the rate of change of area as pressure increased. Fused silica slides 25 mm × 50 mm × 1 mm were cleaned in sulfuric acid/sodium dichromate solution and rinsed with

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