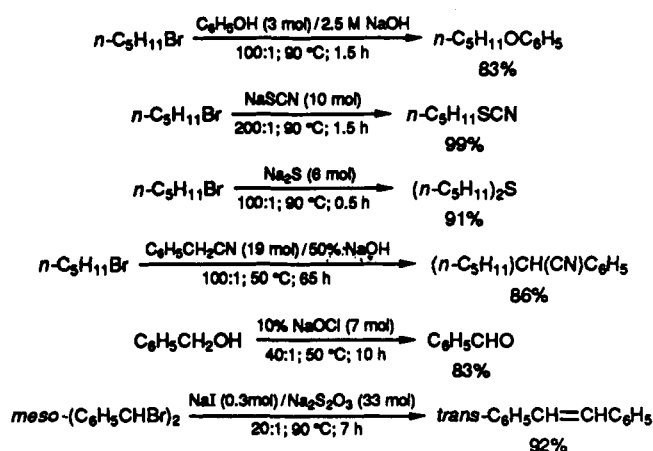


Scheme I



ether, thiocyanate, and sulfide derivatives at the substrate: catalyst molar ratios, temperatures, and reaction times shown in Scheme I. The C-alkylation of a nitrile, oxidation of an alcohol, and dehalogenation of a *vic*-dibromide represent additional facile conversions, as also shown in the scheme.

Finally, we note that organo clays are members of a much larger class of layered materials capable of being intercalated by alkylammonium ions.¹⁹ Onium ion exchange forms of layered phosphates, titanates, vanadates, and niobates, for instances, might also form interfacial assemblies and exhibit useful triphase catalytic properties.

Acknowledgment. The support of this research by the National Science Foundation (DMR-8903579) and by the Michigan State University Center for Fundamental Materials Research is gratefully acknowledged.

Formation of Ultrathin Metal Island Particulate Films by the Transfer of Monolayers of Reversed Micelle Entrapped Colloidal Particles to Solid Supports

Christine Dolan,¹ Youxin Yuan,² Tze-Chi Jao,³ and Janos H. Fendler*²

Department of Chemistry, Syracuse University
Syracuse, New York 13244-4100
and Texaco Research Center
P.O. Box 509, Beacon, New York 12508

Received November 8, 1990

Revised Manuscript Received December 18, 1990

Molecular organization of ultrasmall colloidal particles is an intensively active, current area of research.⁴⁻⁶ The assembly of individual molecules to small clusters, size-quantized particles, and larger crystallites having solid-state properties is inherently interesting and provides an entry to novel materials that have desirable chemical, mechanical, electrical, and electrooptical properties. Molecular beam epitaxy has been used primarily to construct desired structures by atomic, layer-by-layer deposition in ultrahigh vacuum.⁶ An alternative "wet" colloid

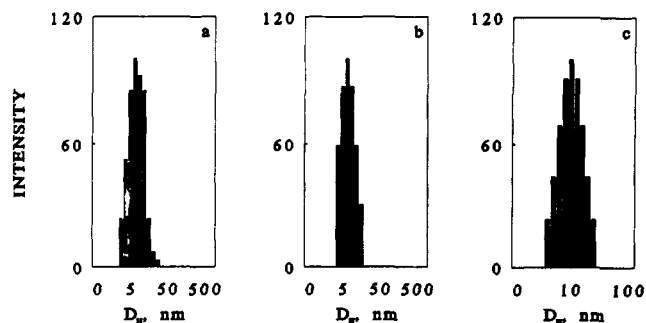


Figure 1. Hydrodynamic diameters, presented in terms of size distributions, of reversed micelles prepared from 1.0×10^{-2} M AOT and 1.0×10^{-2} M H_2O ($w = 20$) in heptane in the absence (a) and in the presence of 7.3×10^{-3} M Ag^+ (b) prior (a and b) and subsequent to exposing sample b to 60 min of repetitive laser pulses (c).

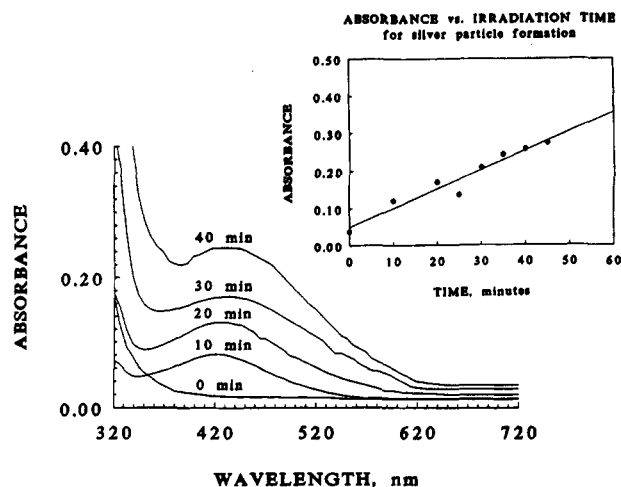


Figure 2. Absorption spectra of reversed micelles prepared from 1.0×10^{-2} M AOT and 1.0×10^{-1} M H_2O ($w = 10$) in heptane in the presence of 7.3×10^{-3} M Ag^+ prior and subsequent to exposure to increasing times of laser pulses. A plot of absorbance at 450 nm vs irradiation is shown in the insert.

chemical approach was launched in our laboratories some years ago. Surfactant vesicles, bilayer lipid membranes, monolayers, and Langmuir-Blodgett films have been used as templates in the in situ generation of nanosized semiconductor and magnetic particles.⁴ These organized assemblies have not only provided a passive size and dimensionality control but, by virtue of electrostatic and hydrophobic interactions, have profoundly influenced the physical and chemical behavior of the given system. We report here that silver particles, in situ formed in the aqueous pools of reversed micelles, can be transferred as a "monolayer" of metal-island particulate films onto solid substrates.

Sodium bis(2-ethylhexyl)sulfosuccinate, aerosol-OT or AOT (Aldrich), and calcium alkylarylsulfonate surfactant, 1 (Texaco),⁷ was used to prepare reversed-micelle solutions in heptane in the absence and in the presence of appropriate concentrations of aqueous silver nitrates (Matheson, Coleman and Bell Co.). Heptane (Aldrich, HPLC grade) was used as received. Water was purified by using a

(1) Participant in the National Science Foundation's Research Experience for Undergraduates Program at Syracuse University, summer 1990.

(2) Syracuse University.

(3) Texaco Research Center.

(4) Fendler, J. H. *Chem. Rev.* 1987, 87, 877.

(5) Henglein, A. *Chem. Rev.* 1989, 89, 1861.

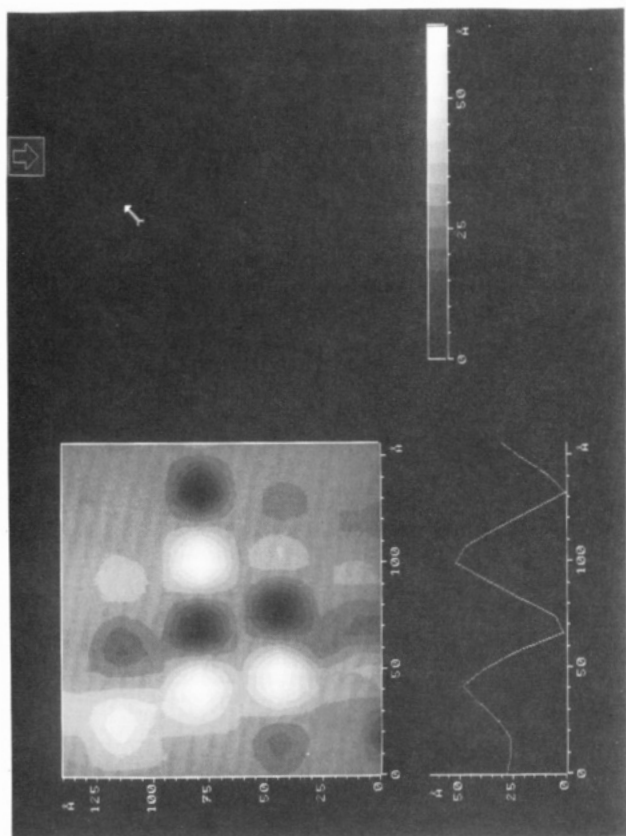
(6) Ploog, K. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 593.

(7) 1 = Texaco sulfonate; A = a proprietary branched chain alkylaryl (60-70% monoaryl, 30-40% diaryl) surfactant containing 0.5 mol of $\text{Ca}(\text{OH})_2$ /surfactant.⁸⁻¹⁰

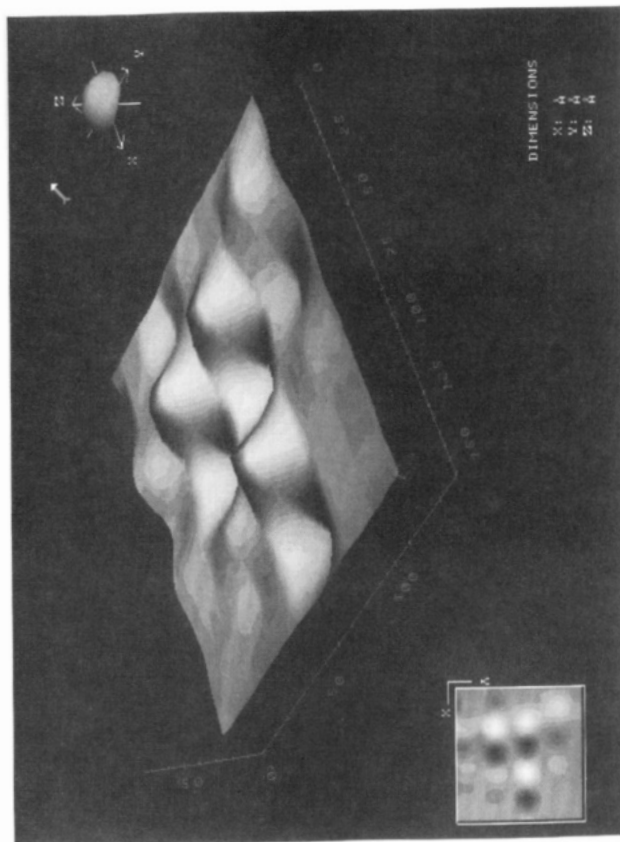
(8) Jao, T.-C.; Kreuz, K. L. *J. Colloid Interface Sci.* 1984, 102, 308.

(9) Jao, T.-C.; Kreuz, K. L. In *Phenomenon in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; American Chemical Society: Washington, DC, 1986; p 90.

(10) Jao, T.-C.; Kreuz, K. L. *J. Colloid Interface Sci.* 1988, 126, 622.



c



d

Figure 3. STM images of silver islands on HOPG. Samples were prepared by the slow vertical transfer of heptane-diluted (ten-fold), 1.0×10^{-2} M AOT and 7.3×10^{-3} M Ag^+ in heptane containing 1.0×10^{-1} M H_2O , $w = 10$ (a and b), and 2.0×10^{-1} M H_2O , $w = 20$ (c and d). Inserts in the three images give bird's-eye views of the same areas. In the

two-dimensional x-y projections (a and c), the dark and white contours correspond to the lowest and highest heights for each image. The heights of each image and their separations can be best ascertained from the z-x plots.

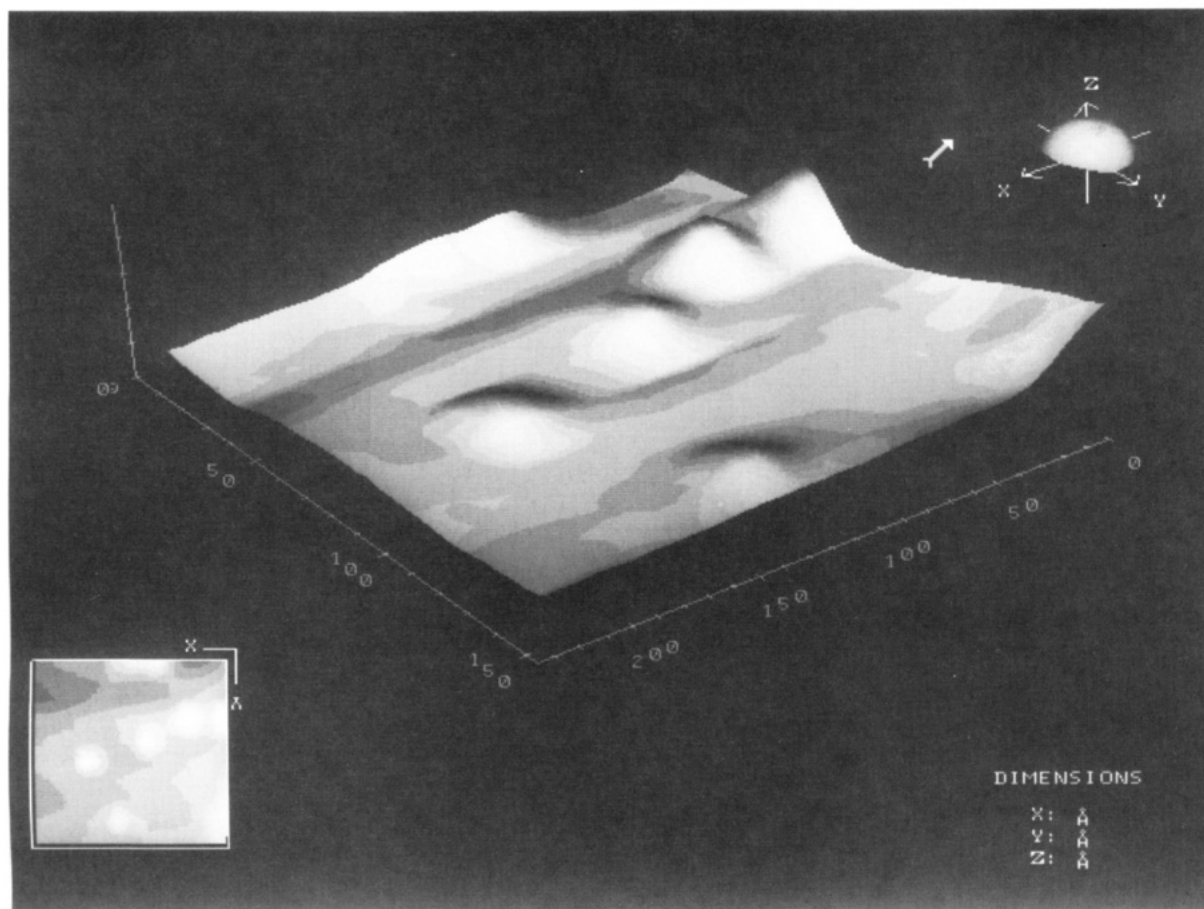


Figure 4. STM images of silver islands on HOPG. Samples were prepared by the slow vertical transfer of heptane-diluted (ten-fold), irradiated (60 min), 1.0×10^{-2} M I and 7.0×10^{-4} M Ag^+ in heptane containing 1.0×10^{-1} M H_2O ($w = 10$). The insert gives a bird's-eye view of the same area.

Millipore, Milli-Q filter system provided with a $0.2\text{-}\mu\text{m}$ Millistack filter at the outlet. Absorption spectra were taken on a Hewlett-Packard 8450 A diode-array spectrophotometer. Reversed-micelle-entrapped silver ions were photoreduced by irradiation by 3-mJ, 20-ns, 353-nm repetitive (10 Hz) laser pulses using a Lambda Physik EMG 101 MSC excimer-FL-2002 dye laser system.¹¹ Hydrodynamic diameters of reversed micelles were determined by dynamic light scattering using a Brookhaven BI 2030 AT system. Samples, placed in a thermostated (25.0°C) and refractive-index-matched compartment, were illuminated by a continuous-wave (CW) argon-ion laser (Spectra Physics, Model 2020; 514.5 nm, 200 mW). Fluctuations of the scattered light intensity, determined at 90° to the incident light, were autocorrelated. The data were analyzed by an exponential sampling program to present mean particle size and size distributions. Standard polystyrene particles were used to verify the system. The determined sizes and size distributions agreed well with accepted values. Scanning tunneling microscopic images were acquired by means of an Angstrom Technology (Mesa, AZ) TAK 2.0 instrument operated in the constant-current mode. A Pt-Ir wire was used for the tunneling tip. Images were scanned at 5 lines/s with a 0.5–1.0-V tip bias. Images were plotted on a CP 200U Mitsubishi video processor. Images were taken on samples in 50–100 different areas.

Size distributions, in terms of hydrodynamic diameters (D_H values), of reversed micelles formed in 1.0×10^{-2} M AOT in heptane in the presence of 1.0×10^{-1} M

($[\text{H}_2\text{O}]:[\text{AOT}] = w = 10$) and 2.0×10^{-1} M ($[\text{H}_2\text{O}]:[\text{AOT}] = w = 20$) H_2O were determined by dynamic light scattering. Typical light scattering data, presented in terms of size distributions, are shown in Figure 1. The obtained mean D_H values (7.0 ± 0.2 nm for $w = 10$ and $D_H = 11.0 \pm 0.2$ nm for $w = 20$) agreed well with corresponding values reported for AOT reversed micelles in isooctane ($D_H = 7.4$ nm at $w = 10$; $D_H = 10$ nm at $w = 20$).¹² Introduction of 7.3×10^{-3} M AgNO_3 increased D_H values of the $w = 10$ and $w = 20$ AOT reversed micelles to 10.0 ± 0.1 and 14.0 ± 0.1 nm, respectively. Irradiation of reversed-micelle-entrapped silver ions resulted in silver particle formation, which manifested in the development of a broad absorbance with a maximum at around 450 nm¹³ (see Figure 2 for typical development of silver particle absorption). Absorption maxima at wavelengths longer than 400 nm are indicative of colloidal silver particles that are in the 8–10-nm range and which may have relatively broad size distributions. Reduction of silver ions to silver particles changed the hydrodynamic diameters of their reversed-micellar hosts to 13.0 ± 0.1 nm for $w = 10$ and 13.0 ± 0.2 for $w = 20$. However, sizes of silver-particle-containing reversed micelles remained stable for days if kept in the dark.

Silver-particle-containing reversed micelles were transferred to freshly cleaved, highly oriented, pyrolytic graphite (HOPG, Union Carbide Corp.). The transfer was effected by vertically pulling the HOPG substrate from the silver-particle-containing, reversed-micellar solutions at a slow speed (1 mm/min). Slow deposition was found to be

(11) Jao, T.-C.; Beddard, G. S.; Tundo, P.; Fendler, J. H. *J. Phys. Chem.* **1981**, *85*, 1963.

(12) Zulauf, M.; Eicke, H.-F. *J. Phys. Chem.* **1979**, *83*, 480.

(13) Henglein, A. *J. Phys. Chem.* **1979**, *83*, 2209.

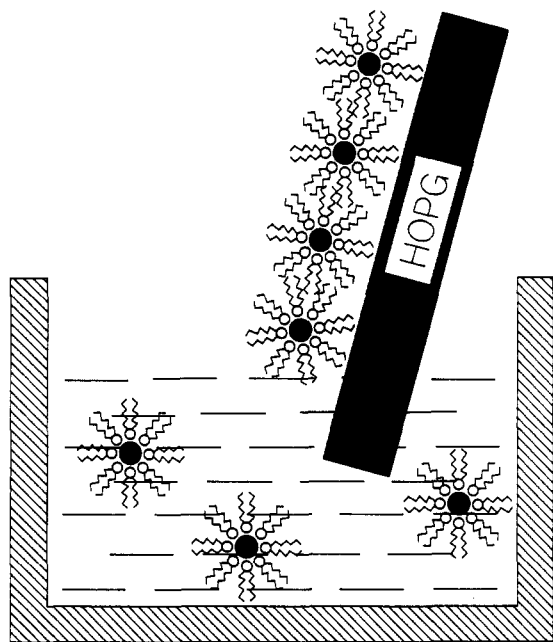


Figure 5. Schematic diagram (not drawn to scale) of the proposed mode of transfer of reversed-micelle-entrapped silver particles to a solid support.

critical for good deposition of one layer of reversed micelles. STM images of reversed-micelle-coated HOPG substrates were taken subsequent to drying in air for 1 h.

STM images revealed the presence of silver islands on atomically smooth HOPG (Figure 3). Concentrations of reversed micelles affected the interisland separation distance. In undiluted (1.0×10^{-2} M AOT) samples, the substrate was fairly completely covered by interconnected silver islands (not shown). Ten-fold dilution of the silver-particle-containing reversed micelles by heptane (prior to transfer) appeared to be optimal for assessing interisland distances (Figure 3). At further dilutions, it became increasingly difficult to find images. Most significantly, heights of silver islands were consistently the same (4.0 ± 0.5 nm; see z - x plots in Figure 3a,c), thus indicating the effective transfer of only one layer of reversed micelles on HOPG. A similar behavior was observed for the transfer of silver particles, in situ generated in reversed micelles, prepared from 1 (Figure 4). Hydrophobic interactions between HOPG and the surfactant tails appear to be stronger than the reversed micelle-reversed micelle interactions. Interisland distances (5.5–6.5 nm for $w = 10$ and 4.5–5.5 nm for $w = 20$) were, however, smaller than the hydrodynamic diameter of the reversed micelles. Apparently, the hydrocarbon tails of the micelles are well intercalated. The proposed mode of transfer is illustrated in Figure 5.

The convenient preparation of ultrathin metal-island films, described in the present report, opens the door to a new approach for solid-state device construction. Additionally, STM images of particles generated in the cavities of reversed micelles could provide important information on the structure of the surfactant-aqueous interface. This is particularly important for the characterization of the complex surfactant systems used in the lubricant industry.

Acknowledgment. Support of this work by grants from the National Science Foundation and Texaco, Inc. is gratefully acknowledged.

Registry No. AOT, 577-11-7; Ag, 7440-22-4.

Third-Order Nonlinear Optical Properties of Thin Films of Polyanilines and Poly(*o*-toluidines)

John A. Osaheni and Samson A. Jenekhe*

Department of Chemical Engineering
University of Rochester, Rochester, New York, 14627

Herman Vanherzeele and Jeffrey S. Meth

E.I. Du Pont de Nemours and Co.
Central Research & Development Department
P.O. Box 80356, Wilmington, Delaware 19880-0356

Received November 26, 1990
Revised Manuscript Received January 10, 1991

Organic nonlinear optical (NLO) materials with large third-order electronic susceptibility $\chi^{(3)}$ are currently of interest for diverse applications in photonic switching devices.¹⁻⁸ The third-order nonlinear optical properties of some of the well-known conjugated polymers have thus been investigated, including polyacetylene,³ polydiacetylenes,^{3e} polythiophenes,^{5,6} poly(*p*-phenylene vinylenes),⁴ poly(thiophene vinylene),^{4d} conjugated rigid-rod and ladder polymers,^{7,8} and their derivatives and composites.^{7,8a} Although polyanilines⁹⁻¹³ represent a versatile family of

- (1) (a) Heeger, A. J.; Orenstein, J.; Ulrich, D. R., Eds. *Nonlinear Optical Properties of Polymers*; Materials Research Society Proceedings; Materials Research Society: Pittsburgh, PA, 1988; Vol. 109. (b) Prasad, P. N.; Ulrich, D. R., Eds. *Nonlinear Optical and Electroactive Polymers*; Plenum: New York, 1988. (c) Chemla, D. S.; Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2. (d) Messier, J.; Kajzar, F.; Prasad, P.; Ulrich, D., Eds. *Nonlinear Optical Effects in Organic Polymers*; Kluwer Academic Publishers: Dordrecht, Holland, 1989.
- (2) Gibbs, H. M.; Khitrova, G.; Peyghanbarian, N., Eds. *Nonlinear Photonics*; Springer-Verlag: Berlin, 1990.
- (3) (a) Sinclair, M.; Moses, D.; Heeger, A. J.; Vilhelmsson, K.; Valk, B.; Salour, M. *Solid State Commun.* 1987, 61, 221. (b) Drury, M. *Solid State Commun.* 1988, 68, 417. (c) Krausz, F.; Wintner, E. *Phys. Rev. B* 1989, 39, 3701. (d) Neher, D.; Wolf, A.; Bubeck, C.; Wegner, G. *Chem. Phys. Lett.* 1989, 163, 116. (e) Sautret, C.; Hermann, J. P.; Frey, R.; Pradere, F.; Ducuing, J.; Baughman, R. H.; Chance, R. R. *Phys. Rev. Lett.* 1976, 36, 956.
- (4) (a) Kaino, T.; Kubodera, K. I.; Tomura, S.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Electron. Lett.* 1987, 23, 1095. (b) Bubeck, C.; Kaltbeitzel, A.; Lenz, R. W.; Neher, D.; Stenger-Smith, J. D.; Wegner, G. In ref 1d, pp 143-147. (c) Kaino, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Appl. Phys. Lett.* 1989, 54, 1619. (d) Kaino, T.; Kubodera, K.; Kobayashi, H.; Kurihara, T.; Caito, S.; Tsutsui, T.; Tokito, S.; Murata, H. *Appl. Phys. Lett.* 1988, 53, 2002.
- (5) (a) Houlding, V. H.; Nahata, A.; Yardley, J. T.; Elsenbaumer, R. L. *Chem. Mater.* 1990, 2, 169. (b) Sugiyama, T.; Wada, T.; Sasabe, H. *Synth. Met.* 1989, 28, C323.
- (6) (a) Jenekhe, S. A.; Lo, S. K.; Flom, S. R. *Appl. Phys. Lett.* 1989, 54, 2524. (b) Jenekhe, S. A.; Chen, W. C.; Lo, S. K.; Flom, S. R. *Appl. Phys. Lett.* 1990, 57, 126.
- (7) (a) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* 1990, 2, 629-631. (b) Roberts, M. F.; Jenekhe, S. A., to be submitted.
- (8) (a) Vanherzeele, H.; Meth, J. S.; Jenekhe, S. A.; Roberts, M. F. *Appl. Phys. Lett.*, in press. (b) Jenekhe, S. A. *Extended Abstracts, Electrochemical Soc. Mtg.*, Seattle, WA, Oct 1990; Vol. 90-2, p. 966. (c) Lindle, L. R.; Bartoli, F. L.; Hoffman, C. A.; Kim, O. K.; Lee, Y. S.; Shirk, J. S.; Kafafi, Z. H. *Appl. Phys. Lett.* 1990, 55, 712.
- (9) (a) McDiarmid, A. G.; Chiang, J. C.; Hatpern, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* 1985, 121, 173. (b) Straftstrom, S.; Brédas, J. L.; Epstein, A. J.; Woo, H. S.; Tarner, D. B.; Huang, W. S.; McDiarmid, A. G. *Phys. Rev. Lett.* 1987, 59, 1464. (c) McDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* 1986, 18, 285. (d) Sun, Y.; McDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* 1990, 529.
- (10) (a) Epstein, A. J.; Ginder, J. M.; Roe, M. G.; Gustafson, J. L.; Angelopoulos, M.; McDiarmid, A. G. In ref 1a, pp 313-318. (b) McCall, R. P.; Ginder, J. M.; Leng, J. M.; Ye, H. J.; Manohar, S. K.; Masters, J. G.; Asturias, G. E.; McDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* 1990, 41, 5202.