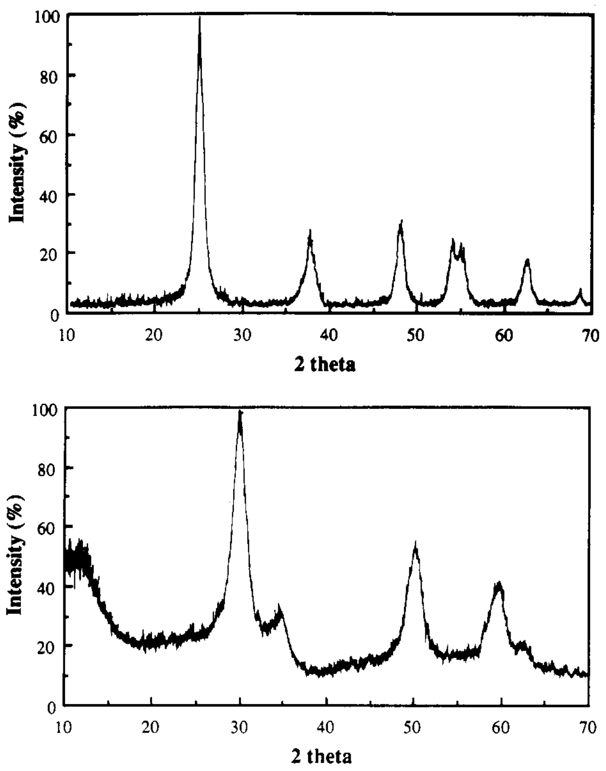

Figure 1. X-ray diffraction patterns for calcined NHG: (a, top) anatase (NHG prepared from $SiCl_4$–$Ti(OiPr)_4$ system then calcined at 500 °C for 5 h in air); (b, bottom) tetragonal zirconia (NHG prepared from $SiCl_4$–$Zr(OnPr)_4$ system then calcined at 1000 °C for 5 h in air).

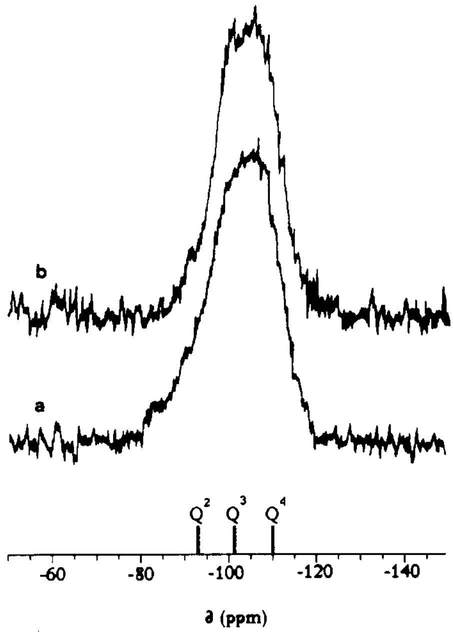

Figure 2. ^{29}Si solid-state MAS NMR spectra (on a BRUKER AM 300 apparatus, 30° flip angle, 20-s recycle delay time, chemical shifts referenced to TMS) for calcined NHG: (a) SiO_2–ZrO_2 (NHG prepared from $SiCl_4$–$Zr(OnPr)_4$ system then calcined at 600 °C); (b) SiO_2–TiO_2 (NHG prepared from $SiCl_4$–$Ti(OiPr)_4$ system then calcined at 500 °C).

olithic gels either in silica-based or in mixed-metal oxides; it allows controlling the composition of binary oxides. Further investigations are in progress to improve the comparison of NHG with conventional hydrolytic gels.

Registry No. Al-Si oxide, 1335-30-4; Si-Ti oxide, 52337-09-4; Si-Zr oxide, 110771-71-6; Al-Ti oxide, 37220-25-0.

Poled, Chromophore-Functionalized Polymeric Nonlinear Optical Materials. Probing Second Harmonic Generation Temporal Characteristics via Site-Selective Cross-Linking/Hydrogen Bonding

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Appending high-β chromophores to glassy macromolecules represents an advance in NLO materials[1] design in that chromophore number densities are greatly enhanced and structural disorientation/physical aging processes subsequent to cessation of electric field poling are impeded.[2,3] Further enhancements in the SHG (second harmonic generation) temporal stability of such materials can be achieved by effecting thermal cross-linking/vitrification of the matrix in concert with the poling process.[2a,4,5] Nevertheless, optimum architectural strategies for such cross-linking processes, either chemical or hydrogen hydrogen-bonding, have not been systematically addressed. We report here modifications of our previously investigated

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(1) (a) *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. E., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (b) *Nonlinear Optical Properties of Organic Materials IV*, Singer, K. D., Ed.; *SPIE Proc.*, 1991, *1560*. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) *Nonlinear Optical Properties of Organic Materials III*; Khanarian, G., Ed.; *SPIE Proc.* 1991, 1337. (e) *Nonlinear Optical Properties of Organic Materials II*, Khanarian, G., Ed.; *SPIE Proc.* 1991, *1147*. (f) *Nonlinear Optical Effects in Organic Polymers*; Messier, J., Kajar, F., Prasad, P. N., Ulrich, D., Eds.; Kluwer Academic Publishers: Dordrecht, 1989. (g) *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1988.

(2) (a) Dai, D.-R.; Hubbard, M. A.; Li, D.; Park, J.; Ratner, J. A.; Marks, T. J.; Yang, J.; Wong, G. K. In ref 1a, pp 226–249 and references therein. (b) Dai, D.-R.; Marks, T. J.; Yang, J.; Lundquist, P. M.; Wong, G. K. *Macromolecules* **1990**, *23*, 1894–1896. (c) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Lundquist, P. M.; Wong, G. K. In ref 1f, pp 263–269. (d) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1988**, *21*, 2901–2904. (e) Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1987**, *20*, 2322–2324.

(3) (a) Köhler, W.; Robello, D. R.; Willand, C. S.; Williams, D. J. In *Macromolecules* **1991**, *24*, 4689–4599 and references therein. (b) Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y.; Steier, W. H. *SPIE Proc.* **1991**, *1409*, 202–213. (c) Eich, M.; Sen, A.; Looser, H.; Bjorklund, G. C.; Swalen, J. D.; Twieg, R.; Yoon, D. Y. *J. Appl. Phys.* **1989**, *66*, 2559–2567. (d) Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Sohn, J. E.; Lalama, S. J.; Commizzoli, R. B.; Katz, H. E.; Schilling, M. L. *Appl. Phys. Lett.* **1988**, *53*, 1800–1802.

(4) (a) Dai, D.-R.; Hubbard, M. A.; Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 93–106. (b) Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1990**, *2*, 229–231. (c) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167–169. (d) Hubbard, M. A.; Marks, T. J.; Lin, W.; Wong, G. K., *Chem. Mater.*, following paper in this issue.

(5) For alternative thermal cross-linking approaches, see: (a) Hubbard, M. A.; Minami, N.; Ye, C.; Marks, T. J.; Wong, G. K., *SPIE Proc.* **1988**, *971*, 136–143. (b) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167–169. (c) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys. Lett.* **1989**, *66*, 3241–3247. (d) Jungbauer, D.; Rich, B.; Twieg, R.; Yoon, D. Y.; Willson, C. G.; Swalen, J. D. *Appl. Phys. Lett.* **1990**, *56*, 2610–2612. (e) Chen, M.; Yu, L.; Dalton, L.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421–5428.

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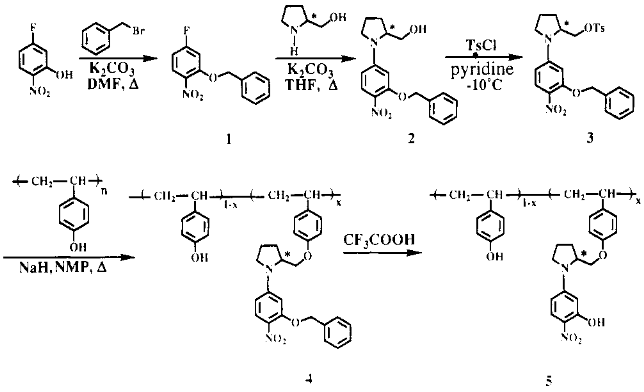
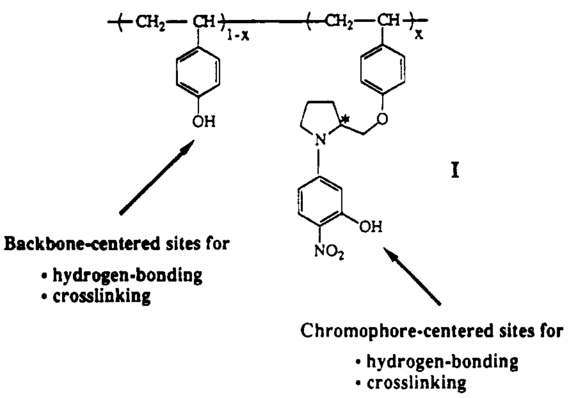
Scheme I



poly(*p*-hydroxystyrene)-*N*-(4-nitrophenyl)-(*S*)-prolinol (NPP-PHS) chromophore-functionalized polymer system,[2c,d] which afford the first opportunity to probe SHG temporal stability as a function of cross-link/hydrogen-bond location (I).



I

A high-β_{vec} hydroxyl-functionalized analogue of NPP (HNPP),[6] protected with a benzyl group (BNPP, 2), was synthesized as shown in Scheme I. Subsequent tosylation and reaction with deprotonated poly(*p*-hydroxystyrene) ($\bar{M}_w \approx 6000$) yielded BNPP-PHS (4). Deprotection was readily accomplished with trifluoroacetic acid to yield NHPP-PHS (5). Polymers 4 and 5 were purified by repeated hexane precipitation from the THF solution and drying under high vacuum at elevated temperatures. Purity was verified by 400-MHz ^{1}H NMR, elemental analysis and UV-visible spectroscopy.

Films of 4 and 5 (1-2-μm thickness) were cast from triply filtered (5-μm syringe filter) THF (distilled from Na/K) solutions onto ITO-coated glass in a Class 100 laminar flow hood. Films were dried for 24 h at 25 °C, 1 h at 100 °C under flowing N_2, and for 24 h at 100 °C under high vacuum (to remove adventitious solvent and effect partial cross-linking—vide infra). Cross-linking experiments were carried out by introducing an equimolar (1:1 epoxy unit/OH group) quantity of 1,2,7,8-diepoxyoctane (DEO) into the polymer/THF solutions. Optimum cross-linking conditions were established through independent experiments monitored by FT-IR spectroscopy (diminution of epoxy-centered modes)[4b,7] on films cast upon KBr plates. All films were then corona-poled at 140 °C for 1 h in a field of +5 kV using a 1.0-cm needle-to-film distance. The instrumentation and calibration procedures for SHG measurements at 1.064 μm have been described elsewhere.[2,4] Films were stored in a desiccator at 25 °C between SHG measurements.

Table I. Second Harmonic Generation Frequency Doubling Efficiency and Temporal Stability Parameters for Corona-Poled HNPP-Functionalized Poly(*p*-hydroxystyrene) Films

material	T_g (°C)[a]	d_{33}[b] (10^{-9} esu)	τ_1 (days)[c]	τ_2 (days)[c]	A[c]
1,2,7,8-Diepoxyoctane Cross-Linked Systems					
35% HNPP-PHS	144	14	35	>1 year	0.48
35% BNPP-PHS[d]	108	24	30	>1 year	0.57
Hydrogen-Bonded Systems					
35% HNPP-PHS	137	22	4	120	0.30
35% BNPP-PHS[c]	97	23	4	80	0.20
88% HNPP-PHS	114	34	4	110	0.50

[a] For materials cross-linked as described in the text. Measured at a heating rate of 10 °C/min. [b] At $\hbar\omega$ = 1.17 eV. [c] See eq 1 in text. [d] Benzyl-protected HNPP.

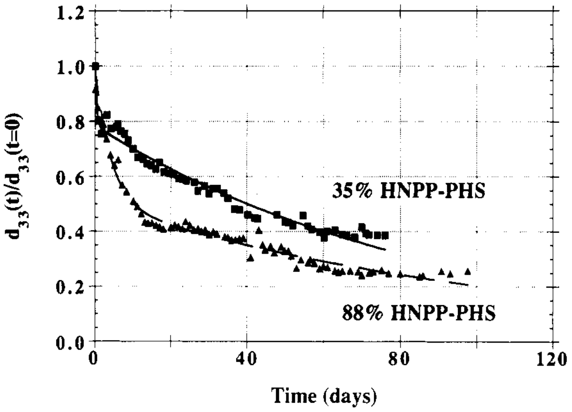


Figure 1. Temporal characteristics at 25 °C of the second harmonic coefficient, d_{33}, for two poled HNPP-PHS films having differing HNPP functionalization levels (percent phenol rings functionalized). The solid lines represent fits to eq 1.

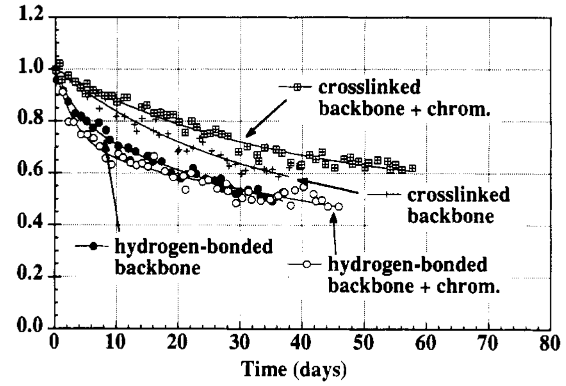


Figure 2. Temporal characteristics at 25 °C of the second harmonic coefficient, d_{33}, for four poled HNPP-PHS-based films (35% HNPP functionalization level) having differing degrees of HNPP/PHS protection and/or 1,2,7,8-diepoxyoctane cross-linking. The solid lines represent fits to eq 1.

In Table I are compiled glass transition temperature (T_g) data and initial SHG coefficients, d_{33}, for the films processed as described above. The T_g data reflect the con-

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[6] (a) Calculated via the ZINDO/SOS formalism:[6b,c] NPP: μ = 7.6 D, $\beta_{vec}(\hbar\omega$ = 1.17 eV) = 30.5 × 10^{-30} cm^5 esu^{-1}; HNPP: μ = 9.5 D, $\beta_{vec}(\hbar\omega$ = 1.17 eV) = 25.7 × 10^{-30} cm^5 esu^{-1}. We thank Dr. D. A. Kanis for these calculations. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Mater.* **1991**, *3*, 19–22. (c) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Int. J. Quantum. Chem.* **1992**, *43*, 61–82.

[7] (a) McAdams, L. V.; Gannon, J. A. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 6, pp 322–382 and references therein. (b) Mertzel, E.; Koenig, J. L. *Adv. Polym. Sci.* **1985**, *75*, 74–112. (c) Cross-linking/poling conditions were those which gave large diminutions (≥90% versus an internal standard) of the epoxide 920-cm^{-1} vibrational bands.[4b] Longer heating times led to insignificant changes (plateauing) in the spectra (or in T_g), while higher temperatures led to frequent dielectric breakdown.

sequences of benzylation, which blocks matrix-immobilizing hydrogen-bonding groups,[8] increasing backbone functionalization, which not unexpectedly enhances chain mobility,[9] and thermal epoxide cross-linking, which clearly has the greatest inhibitory effect on chain mobility. The second harmonic coefficients, measured at 25 °C within 10 min of cessation of poling, are relatively large, reflecting both the sizable chromophore number densities[2,4] as well as the anticipated $\mu\beta_{\text{vec}}$ value of HNPP.[6]

The temporal characteristics of d_{33} ($d_{33}(t)$) for the films prepared in this study are shown in Figures 1 and 2. The data in Figure 1 clearly indicate the diminution in SHG efficiency temporal stability incurred at very large chromophore functionalization levels. The data in Figure 2 compare $d_{33}(t)$ behavior for four HNPP-PHS-based systems, having (i) no protection or cross-linking, (ii) HNPP protection (BNPP) but no cross-linking, (iii) HNPP protection (BNPP) and cross-linking at the PHS backbone hydroxyl residues only, and (iv) cross-linking at both HNPP and PHS backbone positions. Several trends are evident. First, while T_g values afford a gross index of matrix mobility, they provide only a qualitative guide to the temporal stability of SHG efficiency (cf. i versus ii). The data show that any hydroxyl–hydroxyl hydrogen-bonding interactions involving the chromophore moieties have little if any effect on $d_{33}(t)$ over and above those provided by the polymer backbone hydroxyl moieties. Although cross-linking at the PHS functionalities alone (iii) affords a significantly lower T_g material than HNP-P-PHS (i), the effect on $d_{33}(t)$ is clearly the opposite and large (Figure 2). Finally, cross-linking that *directly involves* the chromophore substituent affords the greatest stabilization of SHG efficiency (and correspondingly, the highest T_g).

The $d_{33}(t)$ data were fit by nonlinear regression methods[10] to a biexponential expression (eq 1)[2,4] that can be

$$d_{33} = Ae^{-t/\tau_1} + (1 - A)e^{-t/\tau_2} \qquad (1)$$

viewed as a "two-state" description of chromophore reorientation rates, e.g., in "liquidlike" and "glasslike" regions of the matrix.[11-14] Derived short-term and long-term decay time constants as well as A values are set out in Table I. These quantitatively amplify the above discussion, with the τ_2 values/SHG temporal stability parameters rivalling those of any other known NLO chromophore-functionalized glassy polymer system.

These results provide the first information for a chromophore-functionalized glassy NLO polymer on the sensitivity of SHG temporal stability to the exact nature and position of hydrogen-bond/thermal cross-link points. It can be seen that these structural features can considerably modify, and can be employed to enhance, $d_{33}(t)$ characteristics, and in ways that are not necessarily obvious from T_g data alone.

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Registry No. 1,2:7,8-Diepoxyoctane, 2426-07-5.

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[8] For discussions of the importance of hydrogen bonding in poly(*p*-hydroxystyrene) structure and chain dynamics, see: (a) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228–234. (b) Nakamura, A.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1981**, *22*, 473–476. (c) Hatakeyama, T.; Nakamura, A.; Hatakeyama, H. *Polymer* **1978**, *19*, 593–594.

[9] (a) Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, 1982; Chapter 11. (b) Rabek, J. T. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980; Chapter 32.

[10] Typical r values for the fits were in the range 0.98–0.99. Nevertheless, the accuracies of quantities representing extremely large τ_2 values are adversely affected by the necessarily limited duration of the data collection.

[11] Torkelson, J. M., private communication.

[12] Yu, W.-C., Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355–364 and references therein.

[13] (a) The $d_{33}(t)$ data could be fit at a similar level of confidence (r = 0.98–0.99) to the more phenomenological Kohlrausch–Williams–Watts stretched exponential expression:[13b-e]

$$d_{33} = e^{-(t/\tau)^{\beta}} \quad (0 < \beta \leq 1) \qquad (2)$$

Derived β values for the cross-linked materials (0.78–0.85) at 25 °C suggest some degree of three-dimensional character.[14] (b) Frederickson, G. H.; Brawer, S. A. *J. Chem. Phys.* **1968**, *84*, 3351–3366. (c) Shlesinger, M. F.; Montroll, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 1280–1283. (d) Montroll, E. W.; Bendler, J. T. *J. Statist. Phys.* **1984**, *34*, 129–162. (e) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80–87.

[14] Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1988**, *39*, 149–180.

Poled Polymeric Nonlinear Optical Materials. Enhanced Second Harmonic Generation Temporal Stability of Epoxy-Based Matrices Containing a Difunctional Chromophoric Co-Monomer

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The long-term orientational stabilization of nonlinear optical (NLO) chromophores which have been preferentially aligned within a polymeric medium by electric field poling represents a crucial test of the extent to which polymer relaxation/physical aging can be controlled chemically and is of paramount importance to the development of efficient polymer-based second-order NLO materials.[1] We recently reported[2] an effective approach to chromophore immobilization which utilizes electric-field-induced alignment of high-β_{vec} chromophores dispersed within a two-component epoxy matrix[3] which is

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[1] (a) *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stucky, G. E., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (b) *Nonlinear Optical Properties of Organic Materials IV*; Singer, K. D., Ed.; *SPIE Proc.* **1991**, *1560*. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) *Nonlinear Optical Properties of Organic Materials III*; Khanarian, G., Ed.; *SPIE Proc.* **1991**, *1337*. (e) *Nonlinear Optical Properties of Organic Materials II*; Khanarian, G., Ed.; *SPIE Proc.* **1991**, *1147*. (f) *Nonlinear Optical Effects in Organic Polymers*; Messier, J., Kajar, F., Prasad, P. N., Ulrich, D., Eds.; Kluwer Academic Publishers: Dordrecht, 1989. (g) *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1988.

[2] (a) Dai, D.-R.; Hubbard, M. A.; Li, D.; Park, J.; Ratner, J. A.; Marks, T. J.; Yang, J.; Wong, G. K. In ref 1a, pp 226–249 and references therein. (b) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167–169. (c) Hubbard, M. A.; Minami, N.; Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *SPIE Proc.* **1988**, *971*, 136–143.

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