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14. ABSTRACT
High carrier mobility organic materials for future application in high-speed photorefractive materials have been synthesized and characterized. These materials are discotic columnar liquid crystals and crystals composed of self-assembling functionalized dendron molecules. Examples consisting of monomeric and polymeric materials functionalized with carbazole and trinitrofluorinone charge-transport moieties have been investigated. Stable homeotropically aligned columnar liquid crystal samples have been produced. A characterization facility including three photoconductivity and two photorefraction measurements has been assembled. Initial measurements on carbazole-containing materials confirm a high hole mobility of the magnitude 10^{-3}-10^{-2} $cm^2/Vsec$. These mobility values confirm that this approach to high mobility materials hold considerable promise. Our results indicate that a new family of self-assembling, electronically and optically functional materials can be tailored from this class of materials.

15. SUBJECT TERMS
Polymers, Liquid Crystals, Photorefractive

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Objective of Program:

The program objective was to develop new classes of high carrier mobility photorefractive organic materials in order to improve the photorefractive properties of existing materials by 1) providing a faster response, and by 2) providing for operation at near-infrared communications wavelengths.

Approach:

Photoconducting polymers have been the subject of considerable research due to their application as photoreceptors in photocopying technology. More recently, interest has developed photoconducting materials applications in electroluminescent, photorefractive, photovoltaic, and transistor devices.(1) There has been intense research recently into photorefractive polymers based on photoconducting polymers(2,3,4,5,6,7) and liquid crystals(8,9). In addition, photoconducting materials have potential applications of relevance to the Air Force in producing flexible platform signatures and reconfigurable antennae. Each application has its unique requirements for such materials relating to the transport process. Thus the functions of photocarrier generation, transport and trapping will vary depending on application. Polymers are an ideal material in this regard, as different functionalities can be blended according to need. Since the physical mechanisms giving rise to these properties can vary, considerable variation in properties among polymers and other organic materials have been observed.

We have been pursuing research into photorefractive applications of photoconducting organic materials over the past two years. Our focus has been on increasing speed and long-wavelength sensitivity. We have made considerable progress in identifying candidate materials, as we will describe below. In particular, we have identified an exciting new class of materials possessing hole mobilities several orders of magnitude larger than polyvinyl carbazole composites (PVK).

Figure 1 outlines the dependence of charge carrier mobility, μ, [in cm^2/Vs] in conventional photoconducting materials versus supramolecular order (10,11). As expected, the increase of order from that of an amorphous material like poly(9-vinylcarbazole) to an aromatic single crystal like anthracene induces and increases the

mobility of up to seven orders of magnitude.

Both amorphous polymers and aromatic single crystals have advantages and disadvantages. The advantages of an amorphous polymer are: its excellent film forming properties, good mechanical properties, functional tailorability, and various processing capabilities. Its drawback consists mainly of its limited range of mobility. The advantage of a single crystal is its excellent mobility. However, the disadvantages of single crystals are: the high price of zone refined methodology for their preparation, lack of film forming properties and poor mechanical properties. An optimum technological compromise was accomplished with a solid solution of an amorphous polymer bisphenol-A polycarbonate) containing a low molar mass photoconducting material (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) (12).

As shown in Figure 1, the only other materials that can combine photoconductivity, order, processibility and therefore are expected to provide very high mobility are liquid crystals.

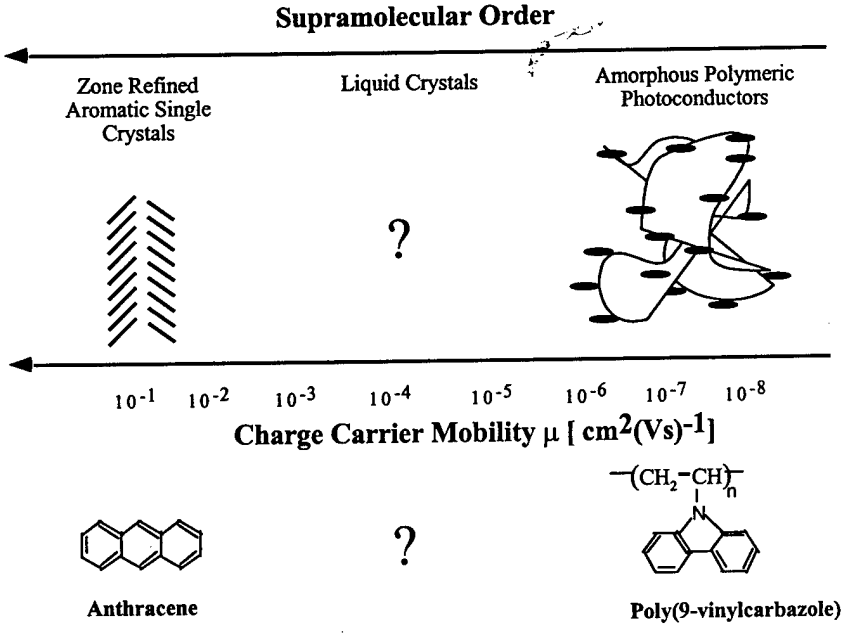


Figure 1. Impact of supramolecular order on carrier mobility.

Recently Ringsdoff *et al.* have demonstrated that discotic molecules like hexaalkyloxytriphenylene and hexaalkylthiotriphenylene exhibit a high mobility for photoconductivity ($\mu = 10^{-4}$ cm^2/Vs) in a discotic hexagonal disordered liquid crystalline (D_{hd}) phase ([13],[14],[15]). The mobility of hexahexylthiotriphenylene increases to 9×10^{-2} cm^2/Vs in a more ordered H phase. Most recently, Müllen *et al.* have demonstrated a mobility of 10^{-1} cm^2/Vs in the discotic hexagonal ordered liquid crystalline phase of hexatetradecyl hexa-peri-hexabenzocoronene(16). Figure 2 highlights these results. It is interesting to observe that the mobility in the H and D_{ho} phases (Figure 2) is approaching the values of aromatic single crystals (Figure 1). In our opinion this is not unexpected since the H and D_{ho} phases are not liquid crystalline but crystalline (Figure 1). These excellent results were however obtained on discotic molecules that are not easily synthesized and have limited synthetic capabilities concerning their insertion in polymeric structures, photosensitization in different wavelength range by complexation or by blending and blending with various additives in order to induce photorefractivity

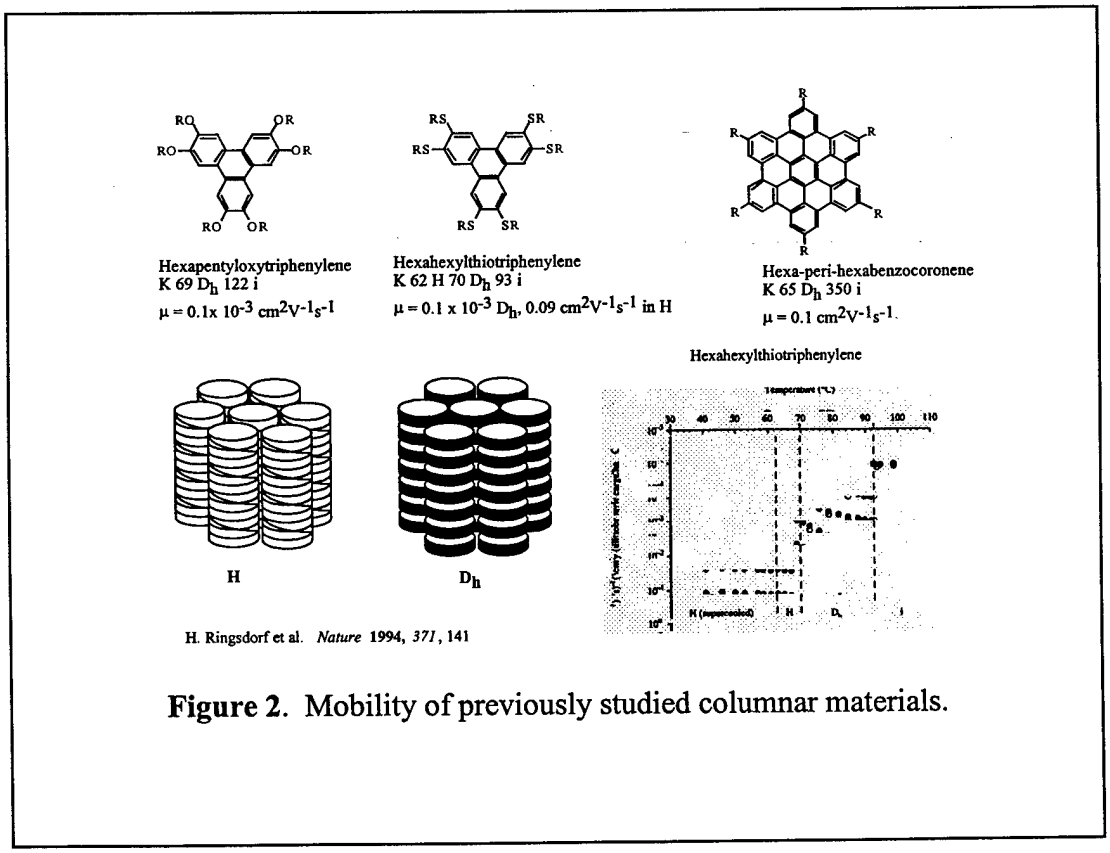


Figure 2. Mobility of previously studied columnar materials.

and other properties.

We have been investigating another approach to columnar liquid crystal structures which is decidedly more flexible in adjusting and adding functionality than the triphenylene systems. In the proposed work described here, we plan to 1) synthesize improved materials to further enhance the carrier mobility and sensitivity spectrum based on our concept of self-assembling columnar liquid crystal/polymer materials 2) characterize the basic photoconductive properties, such as mobility and charge generation toward an understanding of the physical mechanisms leading to the enhanced properties observed to find new ways to improve materials and 3) introduce trapping and nonlinear optical moieties for improved photorefractive properties. We now describe some exciting first results, and the extensions of present work being proposed here.

Results:

Materials and Characterization

We have recently elaborated a novel strategy for the self-assembly and co-assembly of functional supramolecular columns that self-organize in a hexagonal columnar liquid crystalline phase (17,18,19). The application of this concept to the induction of fast photoconductivity in conventional low molar mass and polymeric photoconducting materials is illustrated in Figure 3. Briefly, a suitable shaped (taper shaped i.e., pizza slice like) monodendron can be functionalized with a suitable donor (D) or acceptor (A) molecule in its core. The D or A containing monodendrons will self-assemble into supramolecular columns containing the D or A molecules in their center (see second and fourth verticals in Figure 3). Subsequently these supramolecular columns will self-organize in a hexagonal columnar liquid crystalline phase. The third vertical (i.e., middle one) in Figure 3 shows the co-assembly of D with A containing monodendrons in a supramolecular column containing donor-acceptor complexes in its core followed by its self-organization in the hexagonal columnar liquid crystalline phase. The first vertical on the left of Figure 3 illustrates the co-assembly of an amorphous polymer containing donor side groups with a monodendron containing acceptor groups. This co-assembly process produces a supramolecular column containing the polymer with donor groups as a donor-acceptor complex in its core. This process, by analogy with

other related examples reported from our laboratory (19,20) induces a helical chain conformation in the backbone of the donor groups containing homopolymer. The resulted supramolecular column self-organizes in a hexagonal columnar liquid crystalline phase (bottom of the first column in Figure 3). A similar process is illustrated in the fifth vertical of Figure 3 for the co-assembly of an amorphous polymer containing acceptor groups with a tapered monodendron containing a donor group.

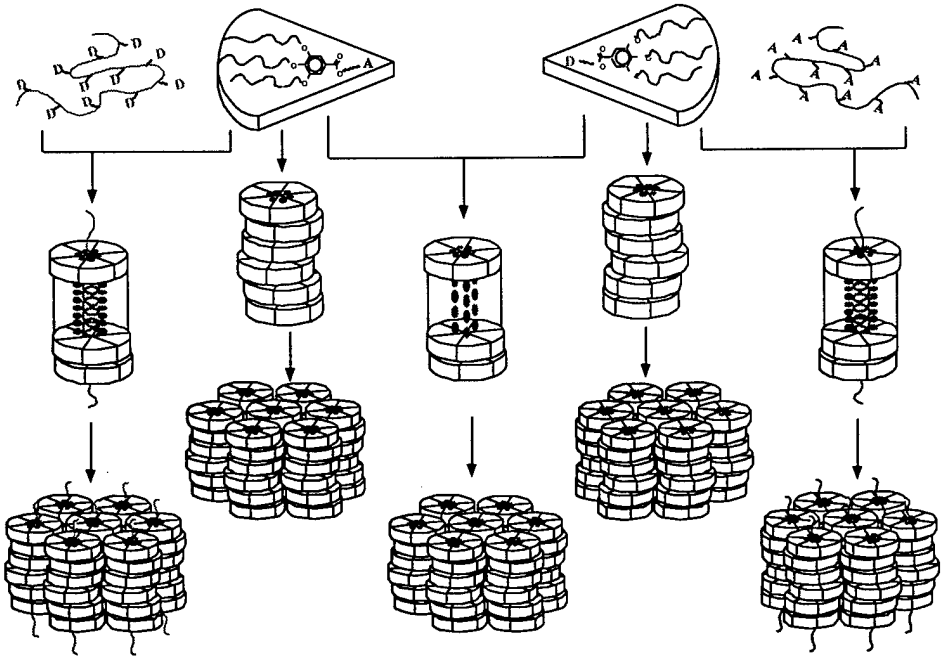


Figure 3. Schemes for self-assembly, co-assembly, and self-organization of dendrons containing donor (D) and acceptor (A) groups.

All five possibilities from Figure 3 have been demonstrated in our laboratory with the two most frequently used donor and acceptor groups employed in the production of conventional photoconductive materials, i.e., carbazole, carbazole containing polymers as donors and 2,4,7-trinitrofluorenone as acceptor. A sixth concept is illustrated in Figure 4. It shows an acetylenic monomer containing both carbazole and a tapered monodendron. Stereospecific polymerization of this acetylenic monomer produces a helical polymeric configuration (most probably a mixture of cis-cisoidal and cis-transoidal) which creates a

supramolecular column containing the polymeric chain to which the carbazole groups are attached, in its core. These supramolecular cylinders self-organize in a hexagonal columnar liquid crystalline phase.

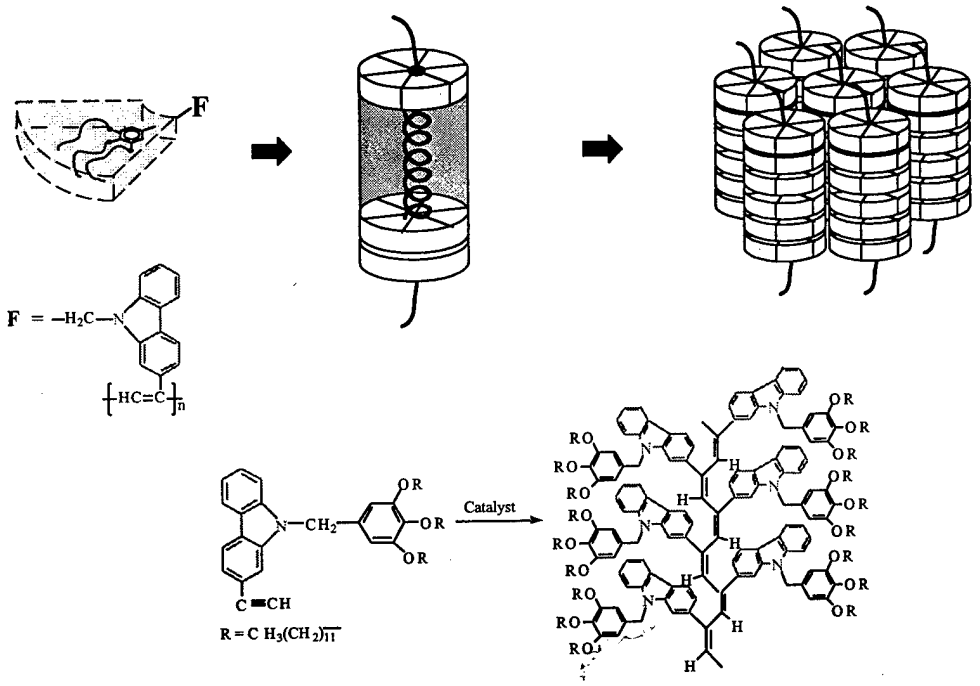


Figure 4. Self-organization of poly[9-{3,4,5-tris(n-dodecan-1-yloxy)benzyl}-2-carbazolylacetylene] into a columnar hexagonal LC lattice

Figure 5 presents selected examples that demonstrate the universality of this concept for the induction of fast photoconductivity in conventional materials via a combination of self-assembly, co-assembly and self-organization. Before going into the discussion of Figure 5, we should mention that the concept to be described was structurally demonstrated by a combination of analysis by X-ray diffraction, differential scanning calorimetry, thermal optical polarized microscopy, scanning force microscopy, and transmission electron microscopy.

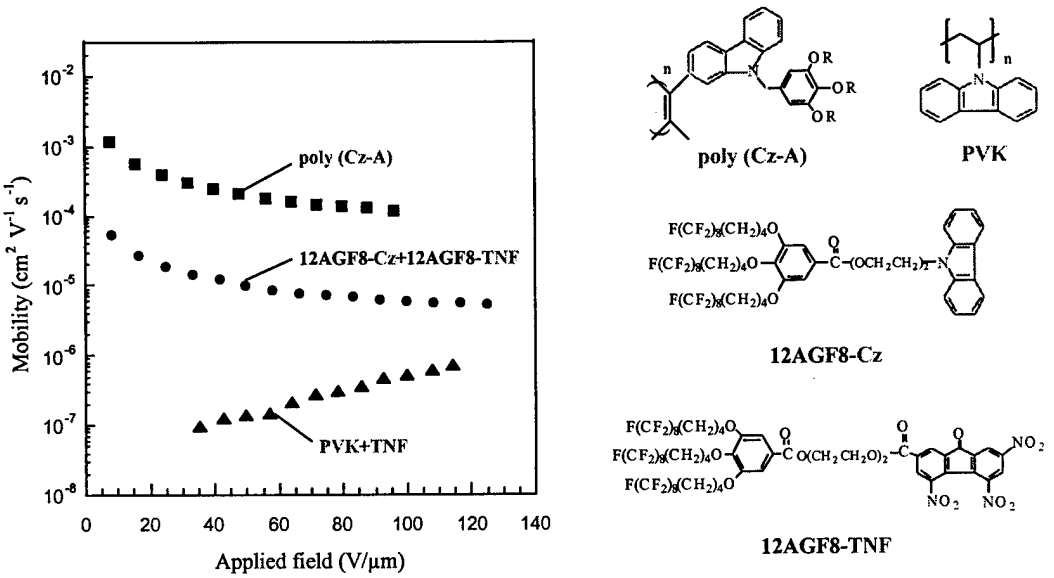


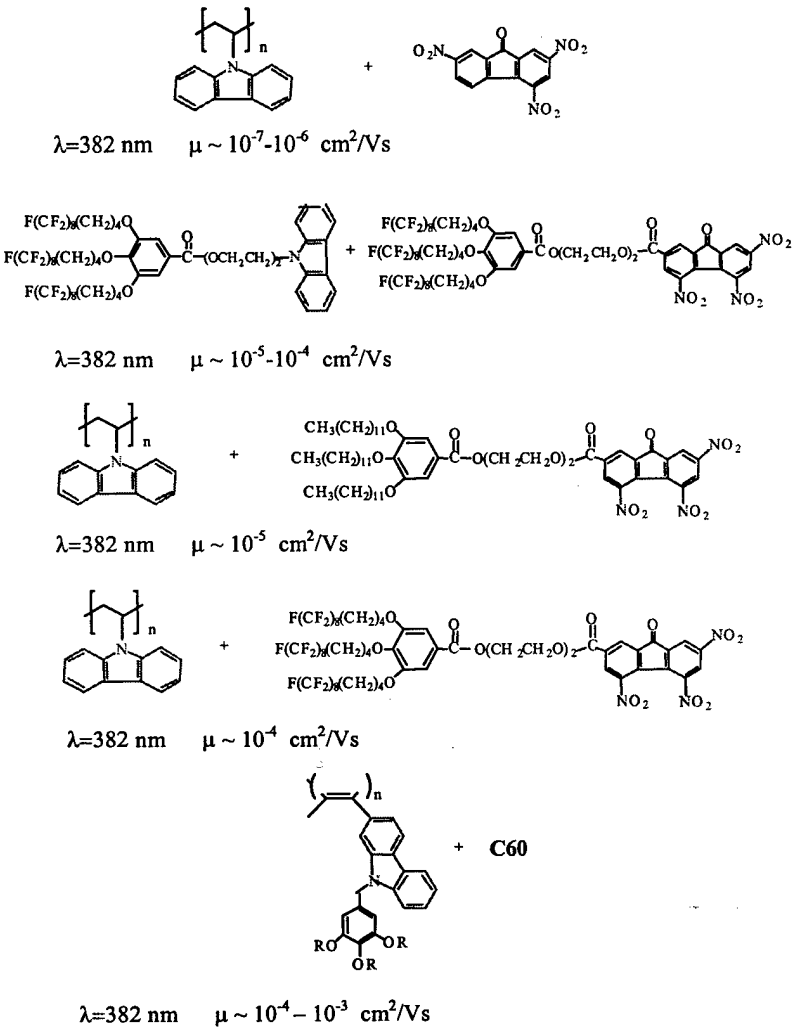
Figure 5. Results of time-of-flight mobility measurements for three materials.

The plots on the left side of Figure 5 are showing the dependence of mobility, determined by time of flight method, of an amorphous photoconducting material [i.e., poly(9-vinylcarbazole), PVK, complexed with 2,4,7-trinitro-9-fluorenone (TNF)] (bottom left side), followed by the same measurement for the supramolecular assembly obtained from the carbazole containing the 12AGF8 tapered group (12AGF8-Cz) co-assembled by complexation with a trinitrofluorenone containing a tapered group (12AGF8-TNF), in the hexagonal columnar liquid crystalline phase(21). The mobility was measured using a 382 nm laser pulse of approximately 5 ns duration. The resultant charge pulses showed considerable dispersion, and time-of-flights were extracted using a log-log plot(22). An increase in mobility at low applied field from 10^{-7} to 10^{-4} is observed. The top plot shows the mobility for the -1polycarbazolyl acetylene containing the tapered group [poly(Cz-A)] in its hexagonal columnar mesophase. At low applied field, a mobility of 10^{-3} $cm^2v^{-1}s^{-1}$ is

observed. This value is higher than those reported by Ringsdoff *et al.* for discotic photoconductors in their liquid crystalline phase and is therefore the highest mobility observed to date in liquid crystalline state. The values reported in Scheme 5 are also the highest for any carbazole based photoconducting material known to date.

The electric field dependence of the PVK-TNF material is consistent with previously reported results(23). The decrease in mobility with electric field for our new materials suggests that positional (off-diagonal) disorder dominates the field dependence and that the energetic disorder is small. This implies a paucity of traps, which certainly will enhance mobility. It also suggests that traps will need to be introduced in order to be optimized for photorefraction. Approaches to doing this will be presented in the next section. We have doped poly-(Cz-A) with 5CB and C_{60} and have observed weak photorefraction by four-wave mixing.(24) Introduction of appropriate traps and covalently functionalized chromophores will lead to enhanced high-speed photorefraction.(25,26)

Figure 6 summarizes the mobilities (μ) of selected examples of amorphous and hexagonal columnar liquid crystalline carbazole based materials. In most cases, μ values are presented as a range that is dependent on the applied field. Let us discuss these data starting from the top of Figure 6. PVK complexed with TNF is the classic amorphous photoconducting material. It has the lowest mobility from the entire Figure 6. The supramolecular system 12AGF8-Cz + 12AGF8-TNF shows an increase of 2 to 3 orders of magnitude of the photoconductivity in the hexagonal columnar LC phase. The amorphous complex PVK + 12AG-TNF shows a mobility $\mu = 10^{-5}$ $cm^2v^{-1}s^{-1}$. This enhancement over PVK-TNF may be due to the enhanced proximity between the donors and acceptors arising from the repulsion of the polar and nonpolar moieties. The same complex based on the semifluorinated 12AGF8-TNF + PVK becomes hexagonal columnar. Its $\mu = 10^{-4}$ $cm^2v^{-1}s^{-1}$. Finally poly (Cz-A) shows, depending on the applied field, has $\mu = 10^{-4} - 10^{-3}$ $cm^2v^{-1}s^{-1}$ in its hexagonal columnar LC phase. The conjugated backbone plays a role in enhancing mobility. It is not clear how the hopping transport models are applicable in these cases, especially in the polyacetylene system. This will be a subject of proposed work



* Mobility, μ, is determined by the time of flight method

Figure 6. Mobilities of selected materials.

These results have demonstrated the universality of the concept illustrated in Figures 1 and 2. Fast photoconductivity can be induced in conventional photoconducting materials via self-assembly, co- assembly and self-organization in supramolecular columnar liquid crystalline dendrimers. These results also demonstrate that the photoconducting element does not have to have a planar discotic shape as reported in the experiments of Ringsdorf et al. (13,14) (Figure 2). We expect that the mobility of these materials can be increased to values that will reach those reported by Ringsdorf et al. (14)

and Müllen et al. (16) in their more ordered crystalline states (Scheme 2). The ordered hexagonal columnar crystalline phase can be induced by increasing the alkyl tail length of the monodendritic building blocks (20). In addition we believe that more efficient photoconducting groups than carbazole (i.e., triarylamine based groups (12) as well as other photosensitive functionalities such as photorefractive and NLO functionalities, etc.) can be incorporated in these supramolecular systems.

Characterization Facility

A characterization facility for evaluation of photoconductive and photorefractive properties was assembled. Five experimental setups are presented in Appendix A. Three involve photoconductivity measurements, and two are photorefractivity setups. In the photoconductivity setup, the dc photoconductivity is measured, in the time-of-flight setup, the carrier mobility is measured. Additionally, photogeneration is measured by the xerographic discharge method. Photorefractive experiments include two-beam coupling and four-wave mixing.

In the photoconductivity setup, the dynamics of the dc photoconductivity is measured. The detection circuit shown in the figure is used for all of the photoconductivity measurements. The input has protection diodes in advance of the current to voltage converter. This is followed by a preamplifier. For the dc-photoconductivity, a lock-in amplifier is used for data acquisition. The dc-photoconductivity is used to study the dynamics of the space-charge buildup as an important component of the photorefractive speed.(27) It also can be used in conjunction with the time-of-flight mobility and charge generation efficiency measurements to determine the carrier lifetime (carrier range) using $\sigma_{ph} = (\Phi \alpha I \tau / h\nu) e\mu$ where Φ is the charge generation efficiency, α the absorption coefficient, I the light intensity, τ the carrier lifetime, e the electronic charge, and μ the carrier mobility.

The experimental setup for time of flight is shown in the appendix. Here the sample has aluminum electrodes. A weak pulse (well below the space charge limit CV) of ultraviolet light produced by third harmonic (355nm) of a nanosecond Nd:YAG laser illuminates one electrode. We also use anti-Stokes stimulated Raman scattering of the Nd:YAG second harmonic to produce pulses at 320nm. The light is completely absorbed

near the surface and the generated charge drifts across the sample. Assuming that the carrier range exceeds the sample thickness, the carrier mobility is given by,(1)

$\mu = L^2 / t_T V$

where L is the sample thickness, V the applied voltage, and t_T the transit time. The transit time is determined using the technique of Scher and Montroll.(28)

The photogeneration efficiency setup uses the xerographic discharge technique. In this technique the sample is first charged and the surface charge is measured and monitored with an electrostatic voltmeter. Following charging in the dark, a He-Ne laser is applied leading to photoinduced decay of the surface charge. The initial slope of the light-induced decay determines the charge generation efficiency. The cross-section of photogeneration s was calculated from the slope of the dependence of the rate of discharge on the intensity of illumination: $\left|\frac{dV}{dt}\right|_{light} = \frac{sL^2 eN_A}{\varepsilon_0 \varepsilon} I$, where I is the intensity of light, L is a thickness of the sample, ε is a dielectric constant and N_A is a concentration of acceptors.

The photorefractive properties of polymers were determined using four-wave mixing techniques as shown in the appendix and described in reference(26). Here, a photorefractive grating is written by crossing two incident laser beams (at the same wavelength), and read by the diffraction of a counterpropagating beam. Due to the geometry of the samples, measurements are carried out at an oblique angle. The diffracted beam is monitored as a function of time to determine the diffraction efficiency, and from the initial derivative, the photorefractive sensitivity can be determined.

Two-beam coupling can be measured by eliminating the counterpropagating beam and measuring the output intensity of one beam as a function of the intensity of the other beam and measuring asymmetric beam coupling. The setup is shown in the appendix. Two-beam coupling is used to determine the density of traps and the relative contribution of the electronic electro-optic effect and the orientation enhancement effect.(26) The phase of the photoinduced grating can be determined by translating the grating.(29)

Photorefractive properties of PVK/5CB composites

This new characterization facility was used to measure the photorefractive properties of a nematogen-polymer composite. Two-beam coupling measurements were carried out to characterize the photorefractive properties and mechanism of composites of 5CB/PVK/C_{60}.(24) Films of composition 40wt. % 5CB, 0.2 wt. % C_{60} PVK were prepared. Measurements of the photorefractive gain and space charge field phase shift were carried out as a function of the applied electric field for both p-and s-polarized light. The photorefractive gain coefficient is shown in Figure 1, which demonstrates the large gain coefficient observed and suggests the presence of a sizable orientational enhancement. The curves shown are fits of the data to Kukhtarev's theory for space-charge field formation. The results of the fit are analyzed according to the model for orientational enhancement. The data indicate that the ratio of the orientation to electronic Pockel's contribution is C_{BR}/C_{EO}~2.9. We compared this to the expected ratio based on

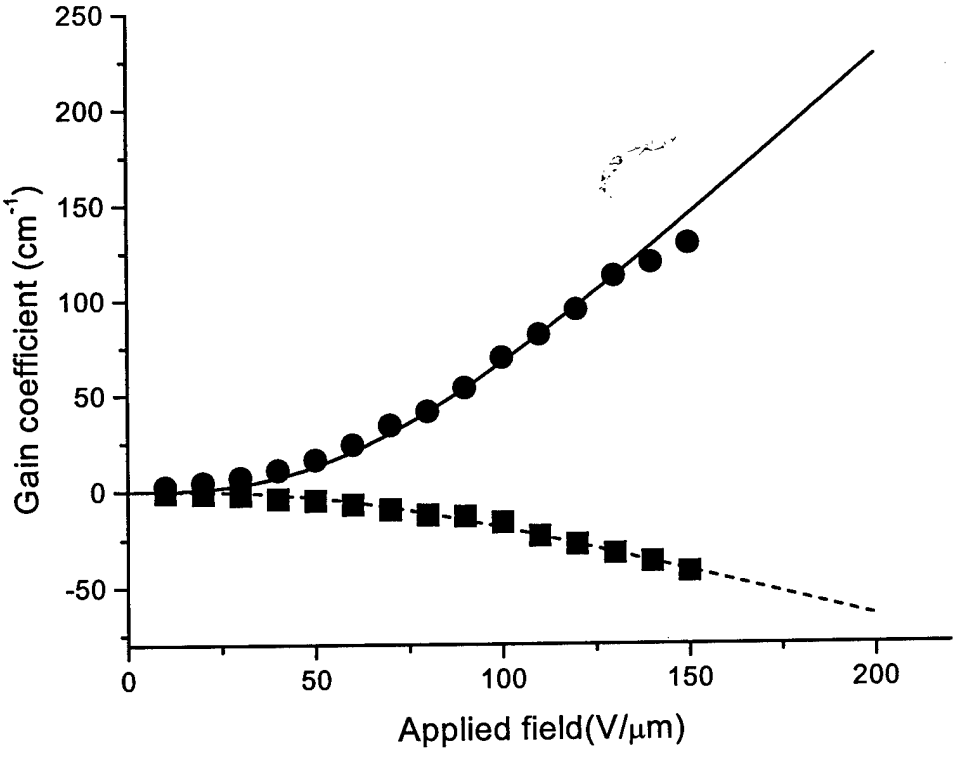


Figure 1. Photorefractive gain versus applied field for 5CB/PVK/C_{60} composite. Lines are fits to Kukhtarev's theory. Circles are p- and squares s-polarized light (He-Ne).

molecular optical parameters and a free rotation oriented gas model which predicts C_{BR}/C_{EO}~40.

The glass transition temperature of this composite is approximately 40C so that our room temperature measurements were carried out in the glassy state. We believe that further enhancement of the photorefractive gain will result in composites of higher concentration possessing lower glass transition. In this case, the orientational mobility will be enhanced as measurements are carried out near or above the glass transition temperature. The density of transport traps was deduced from these measurements using Kukhtarev's theory and found to be $N_{eff}=3.5\times10^{22}m^{-3}$.

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Marcel van der Sluis, Post-doctoral researcher (1 mo. with V. Percec)
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Publications

1. J. Zhang and K.D. Singer, "Homogeneous Photorefractive Polymer/Nematogen Composite", *Appl. Phys. Lett.* **72,** 2948 (1998).

2. J. Zhang and K.D. Singer, "Novel photorefractive liquid crystal polymer composites", *Proc. SPIE* **3471**, 110 (1998).

3. 5 manuscripts in preparation

Interactions/Transitions

1. "Design of Complex Supramolecular Architectures with Well Defined Shapes with the Aid of Liquid Crystallinity, by V. Percec, Invited Lecture, NATO Advanced Workshop: Self-Assembly in Synthetic Chemistry, Val Morin, Quebec, May 16-21, 1996. Abstracts p. 8.

2. Liquid Crystals 100 Years Later. What are the New Concepts Used in the Design of Molecular, Macromolecular and Supramolecular LC?", by V. Percec, Invited Lecture, NATO Advanced Research Workshop: Manipulation of Organization in Polymers Using Tandem Molecular Interactions, Il Chiocca, Italy, May 29 - June 1, 1996. Abstracts, p. 38.

3. "Living Radical Polymerization Initiated with Substituted Arylsulfonyl Halides", by V. Percec, DuPont Marshall Research Laboratory, Philadelphia, PA, June 18, 1996.

4. "Design of New Macromolecular Architectures by Using Quasi-Equivalent Monodendrons as Building Blocks" by V. Percec, Invited Lecture, 36th IUPAC International Symposium on Macromolecules, Macro Seoul '96, Seoul , Korea, August 4-9, 1996. Abstracts, p. 25.

5. "Extremely Narrow Polydispersity Poly(methyl methacrylate) via "Living Radical Polymerization", by V. Percec, B.Barboiu and D.H. Hill International Symposium on

Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1196. Abstracts, p. 68.

6. "Self-Assembly of Supramolecular Tubular Architectures from Taper Shaped Polystyrenes", by C.H. Ahn and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 547.

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9. "Aryl Mesylates in Ni(0)-Catalyzed Homocoupling and Cross-Coupling Reactions", by V. Percec, D.H. Hill, J.-Y. Bae, and M. Zhao, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul Korea, August 4-9, 1996. Abstracts, p.673.

10. Synthesis of Functional Poly(p-phenylene)s via Ni(0)-Catalyzed Homocoupling of Arylene Bismesylates", by V. Percec, Dale H. Hill, Mingyang Zhao and Jin-Young Bae, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul Korea, August 4-9, 1996. Abstracts, p. 674.

11. "Side Chain and Main Chain Liquid Crystalline Polymers Containing Supramolecular Rodlike Mesogens Obtained from Collapsed Main Chain Macrocyclics", by A.D. Asandei, P. Chu and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 675.

12. "Rational Design of the Fist Noshperical Dendrimer which Displays Calamitic Nematic and Semectic Thermotropic Liquid Crystalline Phases", by P. Chu, V. Percec, Goran Ungar and Jianping Zhou, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 676

13. "Design of the First Self-Assembling Spherical Dendrimers", by W.D. Cho, V. Percec, G. Johansson, G. Ungar and V.S.K. Balagurusamy, 36th International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 677.

14. "Supramolecular Tubular Architectures via Ruthenium Carbene Initiated Living Ring Opening Metathesis Polymerization of Taper-Shaped 7-Oxanorbornene Monomers",

by D. Schlueter and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 1145.

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16. "Construction of Well-Defined Nanoscale Supramolecular Tubular Architectures from Taper-Shaped Molecules", by D. Schlueter, G. Johansson, C.-H. Ahn, J.C. Ronda, J. Heck, G. Ungar and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 1147.

17. "Columnar Hexagonal Liquid Crystalline Networks Self-Assembled via Hydrogen Bonding", by C.-H. Ahn and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 1148.

18. "Ordered Supramolecular Structures Formed by Poly(methacrylate)s with Highly Tapered Side Groups and by Their Monomer Precursors" Invited Lecture by J. Blackwell, Y.K. Kwon S.N. Cjavlun and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 538.

19. "Viscoelastic Studies of Liquid Crystals Polymers Dissolved in Nematic Solvents" Invited Lecture by A. M. Jamieson, D. Gu, F.-L. Chen, S.R. Hudson, and V. Percec, International Symposium on Macromolecules, IUPAC Macro Seoul '96, Seoul, Korea, August 4-9, 1996. Abstracts, p. 271.

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21. "New Strategies for the Design of Chiral Polymers by Learning from the Self-Assembly of Viruses", by Virgil Percec, Invited Lecture, Mario Farina Memorial Symposium on Materials Chirality, Orlando, FL August 25-30, 1996. Polymer Preprints, p. 477.

22. S.F. Hubbard, R.G. Petschek, and K.D. Singer, ``Dispersion and Spectral Content Studies of Nonlinear Light Scattering from Organic Materials", OSA/ACS Symposium: Optical Properties of Polymers, ACS Meeting, Orlando, FL, August 27-29, 1996.
23. K.D. Singer, "Photorefractive Nonlinear Optics: Holograms, Optical Computers, and Polymers", Bowling Green University, December, 1998.

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26. K.D. Singer and J.H. Andrews, "Contribution of Two-Photon States to the Third-Order Optical Nonlinearity in Squaraine Compounds", *Proc. SPIE* (1998).

27. K.D. Singer, "Nonlinear Light Scattering from Chiral Molecules", University of Pennsylvania, Department of Physics, February, 1998.

28. K.D. Singer, R.G. Petschek, S.F. Hubbard, O. Ostroverkhova, N. D'Sidocky, C. Hudson, L.C. Chien, P.A. Cahill, and C.C. Henderson, "Chiral Molecules for Second-Order Nonlinear Optics: Measurements and Exploitation", 8th Iketani Conference, Hokkaido, Japan, October, 1998.

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30. "Designing a Polymer Science Made of Visualizable Chains," by V. Percec, Invited Lecture, DuPont Experimental Station, Wilmington, DE, January 12, 1998.

31. "Designing a Polymer Science Made of Visualizable Chains," by V. Percec, Invited Lecture, Exxon, Baytown, TX, February 13, 1998.

32. "Constructing a Polymer Science Made of Visible Chains Acting as Individual Complex Functional Systems" by V. Percec, Invited Lecture, Massachusetts Institute of Technology, February 18, 1998.

33. "Controlling Polymerization Mechanism, Chain Conformation and Polymer Shape via Self-Encapsulation and Jacketing with Dendritic Coats" by V. Percec, Invited Lecture, Makromolekulares Kolloquium, Freiburg, Germany, February 26-28, 1998, *Makromolekulares Kolloquium*, p. 85.

34. "Spontaneous and Simultaneous Self-Assembly and Self-Organization of Giant Functional Supramolecular Systems on Surfaces" by V. Percec, Invited Lecture, Regio-Surface Conference, Freiburg, Germany, March 2-4, 1998.

35. "Designing a Polymer Science Made of Visualizable Chains Activity as Individual Complex Systems," by V. Percec, Invited Lecture, Ulm University, Ulm, Germany, March 9, 1998.

36. "State of the Art and Future Trends in Polymer Synthesis," by V. Percec, Invited Lecture, Symyx Company, Santa Clara, CA, March 14, 1998.

37. "Designing a Polymer Science Based on Visible Macromolecular Chains" by V. Percec, Invited Lecture, The American Physical Society March 1998 Meeting, Los Angeles, CA, March 16-20, 1998. *Bulletin of the American Physical Society*, 43(1), 141.

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41. "Constructing Giant Macromolecular Supramolecular Systems: Using Nature as a Model and Liquid Crystallinity as a Synthetic Tool" by V. Percec, Invited Lecture, 1998 Conference on Pharmaceutical Science and Technology and the 28th Annual Meeting of the Fine Particle Society, Dallas, TX, April 1-3, 1998.

42. "Living Radical Polymerization," by V. Percec, Invited Lecture, Ulm University, Ulm, Germany, April 15, 1998.

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44. "Design and Construction of a Polymer Science Made of Giant Visualizable Spherical and Cylindrical Macromolecules Produced from Backbones Coated with Libraries of Self-Assembling Monodendrons," by V. Percec, Invited Lecture, Taniguchi Conference, Kyoto, Japan, May 9-13, 1998. *Abstracts*, p. 113-119.

45. "Arenesulfonyl Halides: A Universal Class of Functional Initiators for Metal-Catalyzed Living Radical Polymerization" by V. Percec, B. Barboiu, and H.-J. Kim, Invited Lecture, "Polymer Chemistry," Central Regional Meeting of the American Chemical Society, Cleveland, OH, May 27 - 29, 1998. *Abstracts*, p. 405.

46. "Constructing a Polymer Science Made of Visualizable Chains with the Aid of Supramolecular Chemistry" by V. Percec, Invited Lecture, "Polymers - The Way Forward," Central Regional Meeting of the American Chemical Society, Cleveland, OH, May 27 - 29, 1998. *Abstracts*, p. 254.

47. "Metal Catalyzed Living Radical Polymerization of Methacrylates Initiated with Alkyl and Aryl Sulfonyl Chlorides" by V. Percec, B. Barboiu, and M. van der Sluis, Invited Lecture, "Polymers - The Way Forward," Central Regional Meeting of the American Chemical Society, Cleveland, OH, May 27 - 29, 1998. *Abstracts*, p. 253.

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49. "Self-Assembly of the First Library of Functional Monodendrons" by V. Percec, W.-D. Cho, and N. Pesa, Invited Lecture, "Polymers - The Way Forward," Central Regional Meeting of the American Chemical Society, Cleveland, OH, May 27 - 29, 1998. *Abstracts*, p. 264.

50. "Synthesis of Multi-Arm Stars by Metal Catalyzed Living Radical Polymerization Initiated with Sulfonyl Halides" by V. Percec, M. van der Sluis, B. Barboiu, B. De, and J. D. Smith, Invited Lecture, "Polymers - The Way Forward," Central Regional Meeting of the American Chemical Society, Cleveland, OH, May 27 - 29, 1998. *Abstracts*, p. 404.

51. "Using Supramolecular Chemistry to Construct a Polymer Science Made of Visualizable Chains," by V. Percec, Invited Lecture, Xerox Research Centre of Canada, May 29, 1998.

52. "Supramolecular Membranes" by V. Percec, Invited Lecture, Office of Naval Research, Jacksonsville, FL, May 31 - June 3, 1998.

53. "From Metal Catalysis to Self-Catalysis in Polymer Synthesis" by V. Percec, Invited Lecture, MRSEC & CUMIRP Spring Meeting, Amherst, MA, June 8 - 10, 1998.

54. "Acceleration via Self-Encapsulation in the Radical Polymerization of Monodendritic Monomers" by V. Percec, B. Barboiu, C.-H. Ahn and A. Kasko, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

55. "Kinetic Mismatch in Metal Catalyzed 'Living' Radical Polymerization Initiated with Sulfonyl Chlorides" by V. Percec, B. Barboiu and H.-J. Kim, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

56. "Rate Enhancement by Benzoates of the CuCl Catatlyzed 'Living' Radical Polymerization" by M. van der Sluis, B. Barboiu and V. Percec, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

57. "Retrosynthetic Structural Analysis of the First Library of Cylindrical and Spherical Supramolecular Dendrimers" by V. Percec, W.-D. Cho, C.-H. Ahn, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar and D. J. P. Yeardley, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

58. "Self-Regulated Phase Transfer Cu(0)/BPy and Cu_2O/BPy Catalyzed 'Living' Radical Polymerization" by V. Percec, B. Barboiu and M. van der Sluis, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

59. "Star Polymers by Metal Catalyzed 'Living' Radical Polymerization" by V. Percec, M. van der Sluis, B. De, J. Smith, J. M. J. Fréchet and R. Grubbs, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

60. "Visualization of Cylindrical Macromolecules Generated from Backbones Coated with Libraries of Self-Assembling Monodendrons" by V. Percec, W. -D. Cho, G. Ungar and D. J. P. Yeardley, Gordon Research Conference, New England College, Henniker, NH, June 14-19, 1998.

61. "New Synthetic Concepts for Decontamination" by V. Percec, Army Research Office, Edgewood, Baltimore, June 23, 1998.

62. "Controlling Shape of Supramolecular Dendrimers via the Architecture of Dendritic Synthons" by V. Percec, University of Ulm, Ulm, Germany, July 31, 1998.

63. "Constructing a Polymer Science Made of Visualizable Chains with the Aid of Supramolecular Chemistry" by V. Percec, Technical University Munchen, Munchen, Germany, August 5, 1998.

64. "A Universal Method for the Preparation of Dendrimers and Hyperbranched Polymers from Conventional Commerical Monomers" by V. Percec and B. Barboiu, Dendrimer MURI Symposium, Natick, MA, Army Labs, August 21, 1998.

65. "Shape Control in Libraries of Functional Dendrimers Provides a New Concept for DECON" by V. Percec, Dendrimer MURI Symposium, Natick, MA, Army Labs, August 21, 1998.

66. "Functionalized Epoxies: From Adhesion to Decontamination" by V. Percec and J. M. J. Frechet, Dendrimer MURI Symposium, Natick, MA, Army Labs, August 21, 1998.

67. "Surface Patterning by 'Fat' Macromolecules with a Well Defined Cylindrical Shape" by S. S. Sheiko, S. A. Prokhorova, M. Möller, C.-H. Ahn, and V. Percec, ACS Fall Meeting, Boston, MA, August 23-27, 1998, *Polymer Preprint,* 39(2), 1157-1158.

68. "Polymer Chemistry: From Metal Catalysis to Autocatalysis" by V. Percec, Toray Research Laboratories, Nagoya, Japan, September 4, 1998.

69. "Supramolecular Systems" by V. Percec, Toyota Central Research and Development, Nagoya, Japan, September 5, 1998.

70. "Triggering Reversible and Irreversible Shape Changes in Libraries of Supramolecular and Macromolecular Dendritic Systems" by V. Percec, Invited Lecture, Gordon Research Conference on Organic Structures, Fukuoka, Japan, September 6-11, 1998.

71. "Constructing a Polymer Science Made of Visualizable Single Chain Polymer Systems" by V. Percec, Nagoya University, Department of Chemistry, Nagoya, Japan, September 8, 1998.

72. "A Retrosynthetic Supramolecular Approach to Monodendritic Synthons for the Construction of Giant Supermolecules and Macromolecules with Controlled Shape, Functionality and Stiffness" by V. Percec, Plenary Lecture, European Research Conference: Supramolecular Chemistry. Advanced Materials, Rolduc, The Netherlands, September 10-15, 1998.

73. "Imagination of Biomimetic Materials and Engineering" by Virgil Percec, Plenary Lecture, Kimberly-Clark 12th Technical Conference: "Imagination", Grand Geneva Resort, Lake Geneva, WI, September 13-16, 1998.

74. "Nature as a Model for the Design of Complex Molecular, Supramolecular and Macromolecular Nanosystems," by V. Percec, University of Pennsylvania, Philadelphia, PA, September 24, 1998.

75. "Liquid Crystals. From Synthetic Goal to Synthetic Tool" by Virgil Percec, Invited Lecture, Erigen Medal Symposium (in honor of Nobel Laureate Professor Pierre-Gilles de Gennes), Washington State University, Pullman, WA, September 27–30, 1998. *Soc. Eng. Sci.,* H. M. Zbib Ed., **98**, p. 33-34.

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77. "Construction of Giant Super- and Macromolecules with Controlled Shape and Functionality," by V. Percec, Plenary Lecture, International Symposium:

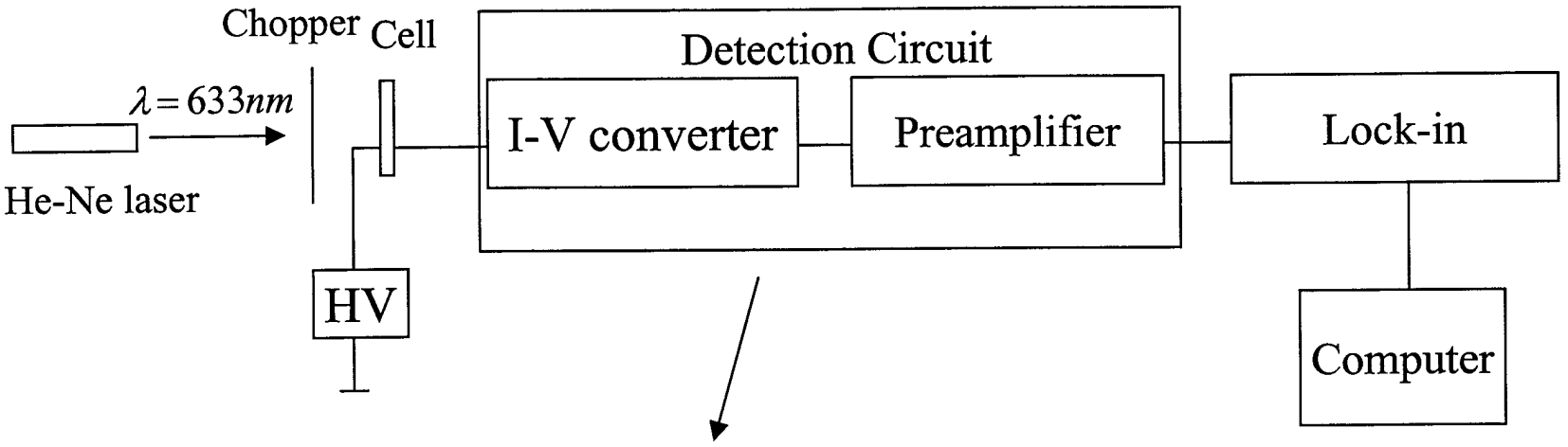
"Mesoscopic Materials. Preparation, Function and Application," University Ulm, Ulm, Germany, October 7-9, 1998.

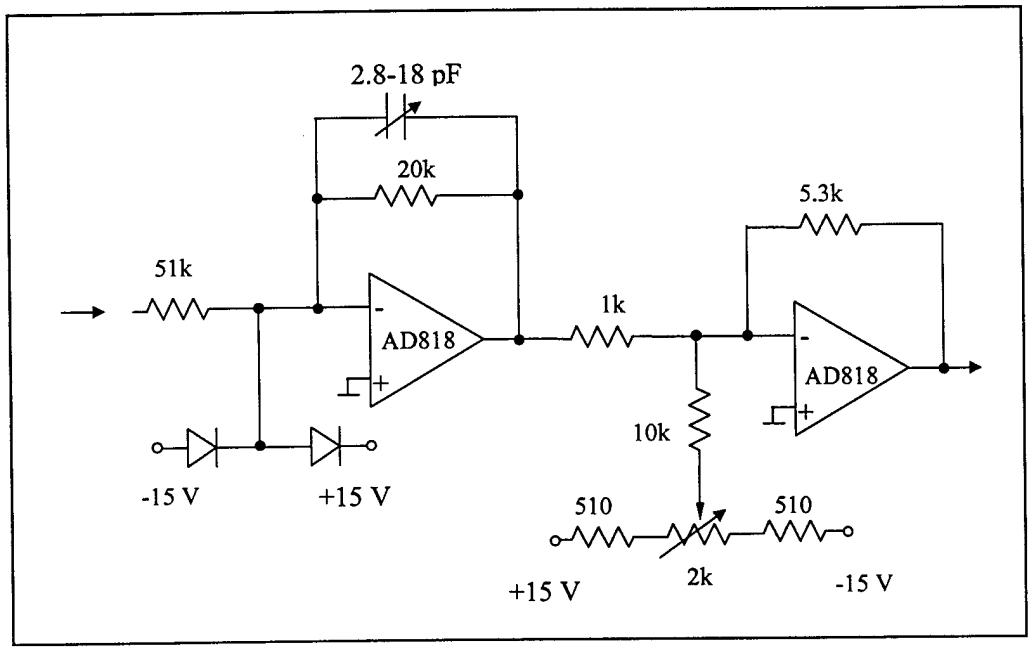
78. "Rational Design with Synthetic Building Blocks" by V. Percec, Army Research Laboratory, Aberdeen, MD, October 23, 1998.

79. "Functional Supramolecular and Macromolecular Dendrimers on a Lattice," by V. Percec, Invited Lecture, International Symposium: "Organic and Supramolecular Structure and Function," Materials Research Society Fall 1998 Meeting, Boston, MA, November 30 – December 4, 1998. *Abstracts*, p.125, U.2.2.

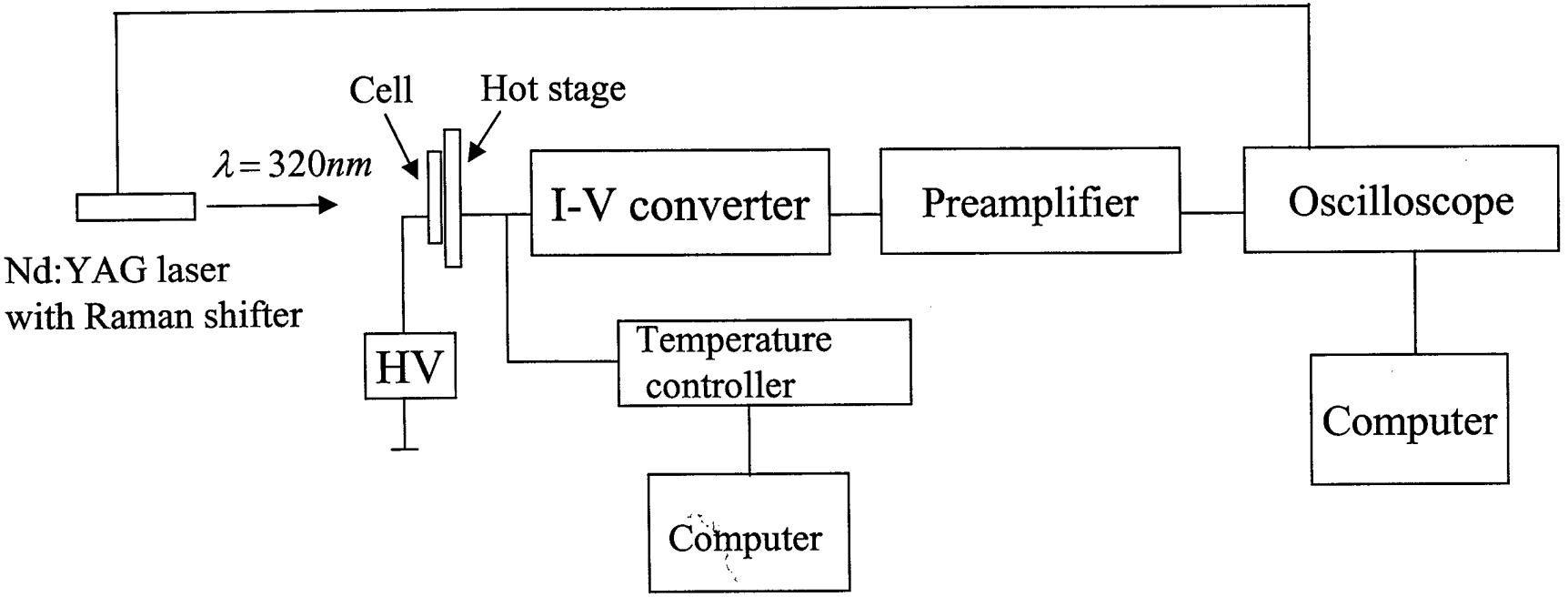
Appendix

Photoconductivity set-up

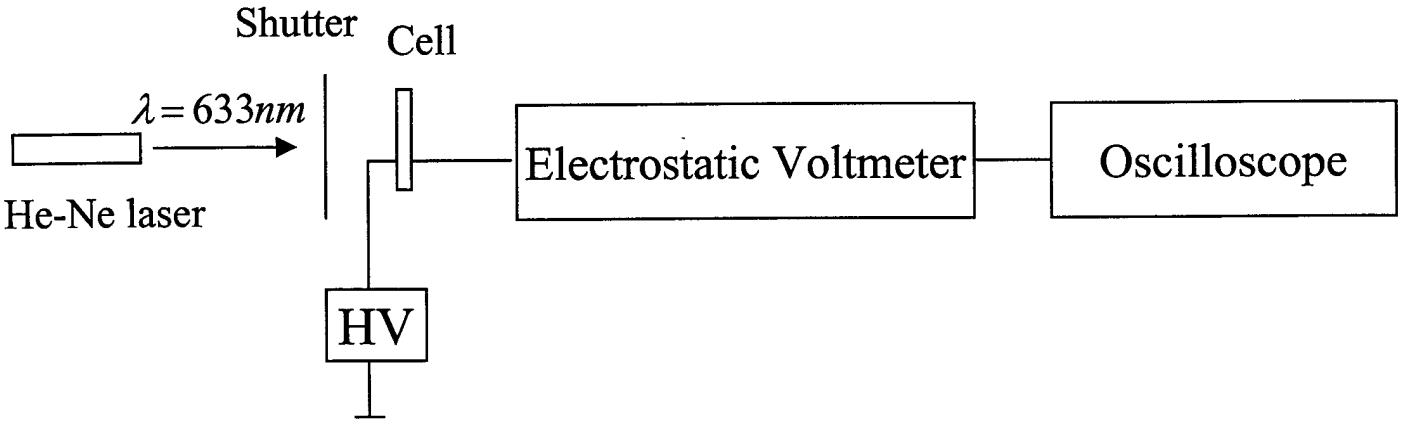




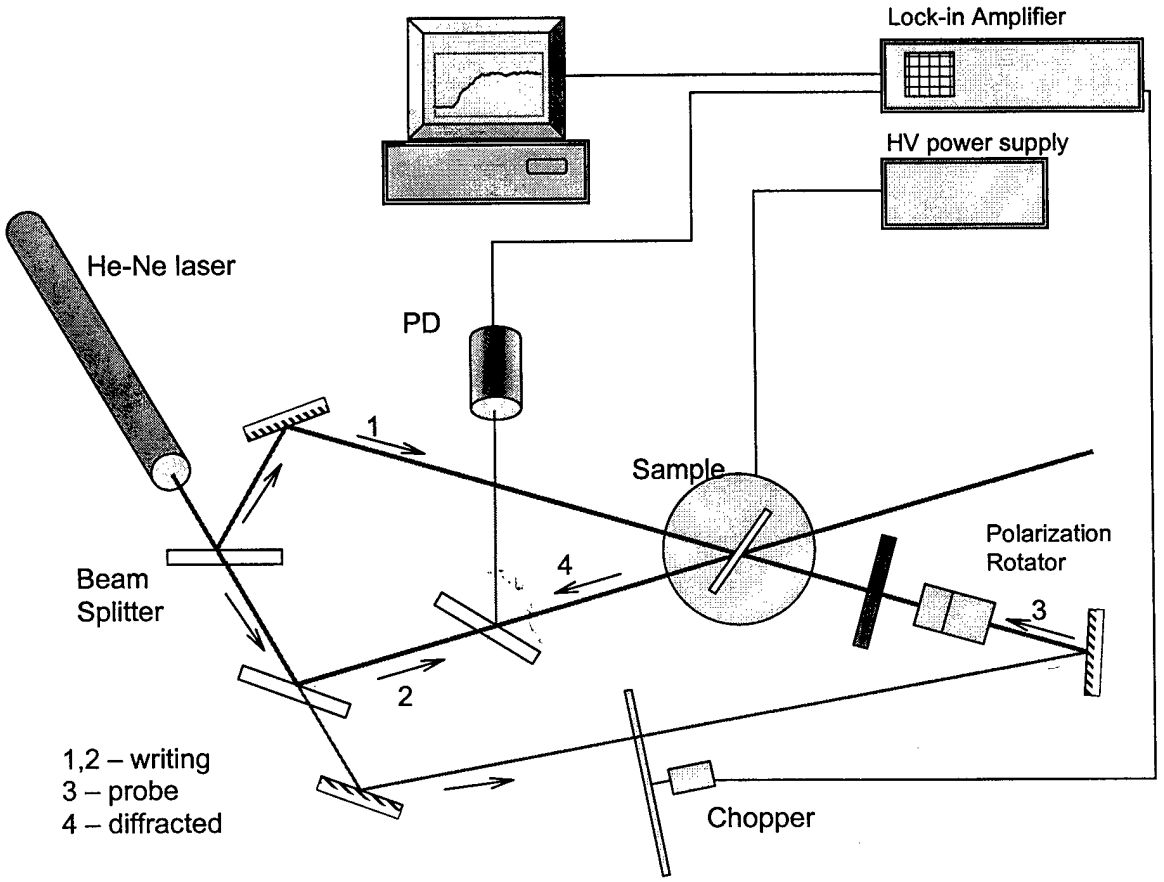
Time-of-flight set-up



Photogeneration efficiency set-up



Four-wave mixing set-up



Two-beam coupling setup