

Theoretically-Guided Optimization of the Electro-Optic Activity of Organic Materials: 300 pm/V and Beyond

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Introduction

Quantum and statistical mechanical methods have been employed to optimize the electro-optic activity of organic materials. Since the year 2000, electro-optic activity has been improved by nearly an order of magnitude to values greater than 300 pm/V. This improvement has been accomplished while keeping optical loss values to less than 2 dB/cm and keeping material glass transition temperatures to values on the order of 200°C. Although the molecular first hyperpolarizability of chromophores has been improved significantly through guidance provided by quantum mechanics, the greatest improvement in macroscopic electro-optic activity has been achieved by optimizing the product of chromophore number density, N , and acentric order parameter, $\langle \cos^3\theta \rangle$ through use of guidance from statistical mechanical calculations. The essential issue to be addressed is that of overcoming unwanted intermolecular electrostatic interactions driving centrosymmetric ordering of chromophores.

Three general approaches have been pursued in optimizing acentric order for high chromophore concentrations. The first involves modification of chromophore shape making chromophores more spherical [1]. This concept is derivative from the realization that there are two components to the intermolecular chromophore dipole-dipole interaction potential; namely, one that favors acentric order while the other favors centric (centrosymmetric) order. Making chromophores more spherical shifts the relative importance of these two contributions to yield a better electric field poling induced order. The second approach involves using covalent bond potentials to inhibit centrosymmetric ordering. This approach has been typically applied to multi-chromophore-containing dendrimers (as will be illustrated in this communication) but recently it has also been applied to the investigation of multi-chromophore-containing bundles [2,3]. A third approach has involved doping a second chromophore into a lattice comprised of single-chromophore-containing dendrimers, multi-chromophore-containing dendrimers, or chromophore-containing dendronized polymers. The enhanced order observed for this third case appears to arise from an "Ising-lattice-like" effect where one type of chromophore affects the order of the other (and vice versa) in the electric poling experiment. In this communication, examples of the second and third effect are given.

Intermolecular electrostatic interactions also play a significant role in defining optical loss (as well as electro-optic activity, mechanical properties, and thermal stability). Researchers at Lockheed Martin Corporation [4] have demonstrated that doping chromophores into polymer materials such as amorphous polycarbonate (Aldrich Chemical) leads to increased optical loss measured at telecommunication wavelengths. This is attributed to two effects: (1) Broadening of the interband absorption transition from increased inhomogeneous broadening arising from poorer chromophore/polymer solubility at increased chromophore concentrations and (2) red-shifting of the interband transition with increasing chromophore concentrations associated with the corresponding increase of the dielectric constant of the composite material with higher chromophore loading. Doping of dendrimer materials can lead to much lower optical loss due to dramatic attenuation of these effects.

In like manner, material glass transition temperature and the thermal stability of electro-optic activity (after the poling field is turned off) can be affected by intermolecular electrostatic interactions.

Material glass transition temperature can also be controlled by material crosslinking and a breakthrough in this regard has been the utilization of two types of cycloaddition crosslinking interactions, based either on the Diels-Alder/Retro-Diels-Alder reaction [5] for on the irreversible crosslinking of the fluorovinyl ether functionality [6]. These reactions have facilitated the realization of electro-optic materials with glass transition temperatures on the order of 200°C. The Diels-Alder/Retro-Diels-Alder reaction is also useful in turning

the processing temperature of electro-optic materials relevant to soft and nanoimprint lithography [7,8] and to controlling the temperature at which electric field poling is carried out.

A notable advantage of organic electro-optic materials in addition to a fast response, large electro-optic activity, which facilitates the production of high bandwidth, low drive voltage devices, is their processability. In addition to permitting the fabrication of three dimensional photonic circuits and a variety of device structures ranging from stripline, to cascaded prism, to ring microresonator (and other resonant devices including etalons and photonic bandgap devices), organic electro-optic materials can be straightforwardly incorporated into silicon photonic circuitry leading to high bandwidth electro-optic modulation and switching and to optical rectification (photodetection) [9].

Experimental

The materials to be discussed in this communication are illustrated in Figure 1. Their synthesis has been and will be described elsewhere [10].

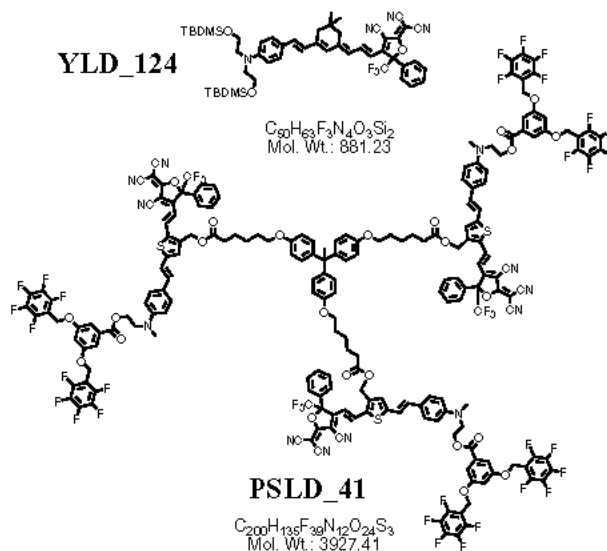


Figure 1. The structure of the dopant chromophore YLD_124 and the guest dendritic lattice PSLD_41 are shown.

Electro-optic activity was measured by modified simple reflection or attenuated total reflection methods as described elsewhere [9,10]. To improve the reliability of measurements, electro-optic activity is reported as the principle electro-optic coefficient, r_{33} , divided by the poling voltage, E_p . Thus each r_{33}/E_p data point for a given N is obtained by performing a linear least squares fit of electro-optic activity over a range of poling voltages. *In situ* monitoring of poling was carried out as described elsewhere [10,11] and included monitoring of current flow during poling.

Results and Discussion

Figure 2 illustrates a critical summary of data that includes data for the basic chromophore of PSLD_124 (an "FTC" type chromophore [10, 11] denoted CF3-FTC) dissolved in amorphous polycarbonate (APC) and a variant of PSLD_124 that does not contain the Frechet dendrons (a lower generation dendrimer relative to PSLD_124). This second multi-chromophore-containing dendrimer, of course, has a higher chromophore number density.

The data for the CF3-FTC/APC composite material (denoted by triangles) exhibits a maximum r_{33}/E_p value of less than 1 while the same chromophore in the two dendrimer materials exhibit values of greater than 1. Robinson and coworkers [12] have employed pseudo-atomistic Monte Carlo calculations (that permit entanglement of dendrimers) to simulate the new results reported here for the multi-chromophore-containing dendrimers. They show that the intermolecular chromophore dipolar electrostatic interactions experienced by the chromophores in the dendrimer materials is analogous to the chromophore dipole-dipole interactions that would be experienced by the same chromophore embedded in a sphere with a

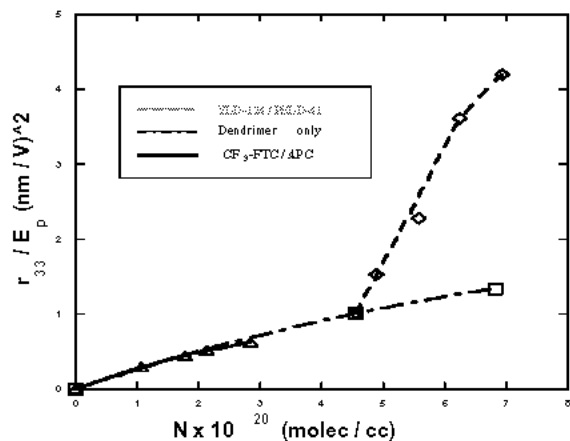


Figure 2. Normalized electro-optic activity (r_{33} divided by poling field strength, E_p) is plotted versus chromophore number density for three types of materials. The triangles correspond to a CF₃-FTC type chromophore dissolved in amorphous polycarbonate (APC). The squares correspond to two different dendrimers containing the CF₃-FTC chromophore. The diamonds correspond to doping the YLD₁₂₄ chromophore into the PSLD-41 dendrimer (see Figure 1). To provide a better calibration of the meaning of r_{33}/E_p values, the reader should note that an r_{33}/E_p value of 3 corresponds to an electro-optic coefficient of 300 pm/V for a 100 volt/micron poling field.

a diameter corresponding to the long axis of the CF₃-FTC chromophore. In Figure 3, we compare data for the YLD₁₂₄

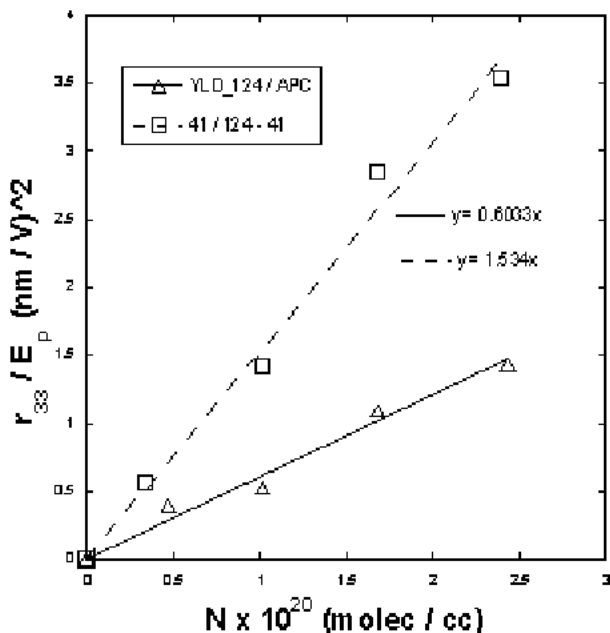


Figure 3. Normalized electro-optic activity (r_{33} divided by poling field strength E_p) is plotted against chromophore number density, N , for the YLD₁₂₄ chromophore in APC (data denoted by triangles) and for the same YLD-124 chromophore doped into the PSLD-41 dendrimer (data denoted by squares).

chromophore doped into APC with the YLD₁₂₄ chromophore doped into the PSLD-41 dendrimer. The dramatically enhanced slope suggests that the acentric order parameter is significantly enhanced for the doped dendrimer system. Indeed, in the low concentration regime shown, the YLD-124 chromophore in APC should correspond to the independent particle limit (where the chromophore experiences no interaction with surrounding chromophores). The greater slope

observed for the YLD₁₂₄/PSLD-41 material suggests that intermolecular electrostatic interactions operational in this material act to enhance poling-induced order. Of course, it still remains to prove that this increased slope is not due to some other factor such as a different effective dielectric constant. It should also be noted that by Ising-lattice-like environment we simply mean that the chromophores sense a more restrictive environment than the three-dimensional environment of a conventional polymer such as APC.

Conclusions

Incorporation of chromophores into multi-chromophore-containing dendrimers is shown to lead to a significant enhancement in electro-optic activity. These results are reasonably well simulated by pseudo-atomistic Monte Carlo calculations that permit dendrimers to interpenetrate (entangle). Calculations also lead to the correct prediction of material densities. An even greater enhancement in electro-optic activity is observed when such dendrimer materials are doped with a second chromophore. This latter effect may reflect an Ising-lattice-type phenomenon where one chromophore impacts the ordering of the other and vice versa.

These two approaches strongly suggest that chromophore number density and acentric order parameter can be dramatically improved using dendrimer and doped dendrimer materials relative to what can be obtained for conventional undoped polymer composite materials. Preliminary data also suggested that improved optical loss may also apply.

Acknowledgements

Support of the National Science Foundation under grant DMR-0037986000 is gratefully acknowledged as are discussions with Professors Bruce H. Robinson, Alex Jen, D. H. Choi, and members of their research groups.

References

- [1] Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; and Steier, W. H. *Science* **2000**, *288*, 119.
- [2] Liao, Y.; Bhattacharjee, S.; Firestone, K. A.; Eichinger, B. E.; Paranj, R.; Anderson, C. A.; Robinson, B. H.; Reid, P. J.; and Dalton, L. R. *J. Am. Chem. Soc.* **2006**, *128*, 6847.
- [3] Liao, Y.; Firestone, K. A.; Bhattacharjee, S.; Luo, J.; Haller, M.; Hau, S.; Anderson, C. A.; Lao, D.; Eichinger, B. E.; Robinson, B. H.; Reid, P. J.; Jen, A. K. Y.; and Dalton, L. R. *J. Phys. Chem.* **2006**, *110*, 5434.
- [4] Barto, R., Jr.; Bedworth, P.; Frank, C.; Ermer, S.; and Taylor, R. **2005** *J. Chem. Phys.* *122*, 234907.
- [5] Haller, M.; Luo, J.; Li, H.; Kim, T. D.; Liao, Y.; Robinson, B. H.; Dalton, L. R.; and Jen, A. K. Y. *Macromolecules* **2004**, *37*, 688.
- [6] Suresh, S.; Chen, S.; Topping, C.; Ballato, J.; and Smith, D., Jr., *Proc. SPIE* **2003**, *4991*, 530.
- [7] Palocz, G.; Huang, Y.; Yariv, A.; Luo, J.; Jen, A. *Appl. Phys. Lett.*, **2004**, *85*, 1662.
- [8] Yariv, A.; Zhang, C.; Dalton, L. R.; Huang, Y.; and Palocz, G. T. *J. Phys. Chem. B* **2004**, *108*, 8006.
- [9] Baehr-Jones, T.; Hochberg, M.; Wang, G.; Lawson, R.; Liao, Y.; Sullivan, P. A.; Dalton, L. R.; Jen, A. K. Y.; and Scherer, A. *Optics Express* **2005**, *13*, 5216.
- [10] Sullivan, P. A.; Akelaitis, A. J. P.; Lee, S. K.; McGrew, G.; Lee, S. K.; and Choi, D. H. *Chem. Mater.* **2006**, *18*, 344.
- [11] Sullivan, P. A., Ph.D. Thesis, 2006, University of Washington, Seattle.
- [12] Robinson, B. H. unpublished results to be published.

- [1] Denton, F. R., III. and Lahti, P. M. in *Electrical and Optical Polymer Systems - Fundamentals, Methods, and Applications*; Wise, D. L., et al., Eds.; Marcel Dekker: New York, **1998**; Chapter 3.
- [2] Ahn, K.-D.; Chung, C.-M.; Koo, D.-I. *Chem. Mater.* **1994**, *6*, 1452.
- [3] R. A. Wessling, and R. G. Zimmerman, U.S. Patent **1968**, 3401, 152.