

Theory-guided nano-engineering of organic electro-optic materials for hybrid silicon photonic, plasmonic, and metamaterial devices

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ABSTRACT

Coarse-grained Monte Carlo/molecular dynamic calculations are employed to explore the effect of various of intermolecular electrostatic interactions upon chromophore order, lattice dimensionality, and viscoelasticity in electrically-poled organic second order nonlinear optical materials. The following classes of organic macromolecular materials are considered: (1) Chromophore-polymer composites, (2) chromophores covalently incorporated into polymers and dendrimers, (3) chromophores incorporating additional dipolar or quadrupolar interactions that enhance poling efficiency, and (4) binary chromophore materials. For chromophore-polymer composites, the competition of chromophore-chromophore dipolar interactions and nuclear repulsive (steric) interactions define poling-induced acentric order. For covalently incorporated chromophores, covalent bond potentials also influence poling-induced order. These first two classes of materials basically behave as Langevin (3-D) lattice materials. Dipolar (e.g., coumarin) and quadrupolar (arene-perfluoroarene) interactions act to influence lattice dimensionality and thus enhance poling efficiency (the ratio of electro-optic activity to electric poling field strength). The long-range molecular cooperativity associated with these interactions influences viscoelastic properties critical to material processing and integration into silicon photonic, plasmonic, and metamaterial devices. The interaction between different chromophore species in binary chromophore materials also enhances poling efficiency. Polarized laser radiation applied to certain binary chromophore materials can also be used to enhance poling efficiency through control of lattice dimensionality. Poling efficiency approaching 5 (nm/V)^2 has been achieved for these latter two classes of materials. Improvement in poling efficiency and control of material viscosity is particular important for integration of organic materials into complex device structures.

Keywords: Organic electro-optic materials and devices, intermolecular electrostatic interactions, order parameters and lattice dimensionality, Monte Carlo and molecular dynamics simulation, sub-wavelength photonic circuitry

1. INTRODUCTION

Because of the low dielectric breakdown threshold of silicon and relative conductivity issues of various materials, poling efficiency is a critical issue for the integration of organic electro-optic (OEO) materials into sub-wavelength devices. Frequently, poling voltages for organic OEO materials integrated into silicon photonics are limited to 60 volts/micron or less. Thus, although sub-1 volt operation has been demonstrated for a number of hybrid devices, the electro-optic activity in such devices is often less than 50 picometers/volt (pm/V) even though the same OEO materials yield electro-optic (EO) coefficients of several hundred pm/V when poled as thin films [1-26]. Low drive voltages can largely be attributed to reduced electrode spacings and/or morphological resonance effects associated with ring microresonator architectures [1-21]. Slow wave structures based on photonic crystal architectures have yielded effective electro-optic coefficients of 735 pm/V [9,10] and more recently in unpublished work to values as high 1000 pm/V [20]. The performance of hybrid OEO/silicon photonic (including photonic crystal waveguide) devices has clearly been impressive in terms of low drive voltage (power consumption), bandwidth, and reduced device size providing real impetus for pursuing chipscale integration of electronics and photonics [1-21]. The limitation on the voltage that can be used for introduction of acentric chromophore order and EO activity by electric field poling places increased emphasis on development of materials exhibiting improved poling efficiency (the ratio of electro-optic activity to poling field strength). For example, a materials exhibiting a poling efficiency of 5.0 (nm/V)^2 would permit an EO activity of 250 pm/V to be realized. Such a value is particularly important for highly

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compact device structures with effective electric field/photon interaction lengths of less than 1 cm (to device lengths as short as 0.3 mm [1-21]). Of course, other properties such as optical loss and processability are important considerations and these will also be influenced by intermolecular interactions.

2. CHROMOPHORE-POLYMER COMPOSITES

Chromophore-polymer composite OEO materials continue to be popular for prototype device demonstrations because of the ready availability of commercial host polymers (polymethylmethacrylate, polycarbonate, polyimide, etc.) and the obvious potential for low cost final materials [22-26]. Chromophores in such materials exhibit very little interactions with the host polymer and behave as if they are diffusing in a 3-D lattice at the poling (glass transition) temperature [22-26]. This observation is consistent with fully-atomistic statistical mechanical calculations [27-30]. Chromophore-chromophore dipolar interactions are problematic for composite materials leading to a maximum in the plot of electro-optic activity versus chromophore number density. Fortunately, there are two components to the chromophore-chromophore dipolar interaction potential—one which favors centrosymmetric (centric) organization and one which favors noncentrosymmetric (acentric) assembly. The relative contributions of these two components will depend on chromophore shape (nuclear repulsive interactions that define chromophore close approach) [31-38].

Chromophore-polymer composite materials are also attractive from a theoretical standpoint. Conjugated π -electron interactions of second order nonlinear optical chromophores inhibit internal flexibility facilitating the treatment of chromophores by coarse-grained (United Atom Approximation) methods [33]. Only sigma-bonded segments of the materials need to be treated by fully atomistic methods. General van der Waals interactions act to collapse component materials into a close packed lattice but poling-induced acentric order will be defined by the competition of chromophore-chromophore dipolar interactions and nuclear repulsive (steric) interactions. Thus, chromophore shape will be the critical design parameter [34]. Chromophores of spherical shape will yield optimum electro-optic activity [35,36]. Chromophore dipole moment and molecular hyperpolarizability are determined by the conjugated π -electron core of the chromophore while nuclear repulsive interactions will be defined by all components of the chromophore, i.e., by chromophore shape. There are four logical chromophore attachment points to which moieties can be added to influence effective chromophore shape and organization under the action of a poling field: The donor and acceptor ends of the chromophore and the front and back positions of the π -electron bridge. An example of donor and bridge attachment points is given in Fig. 1.

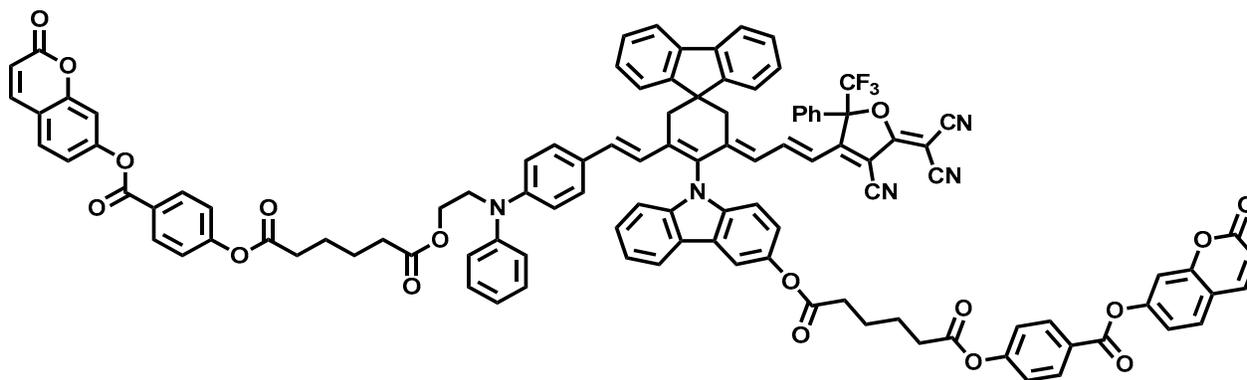


Figure 1. Modification of an isophorone-protected polyene bridge with moieties to inhibit chromophore-chromophore side-by-side close approach is shown. The donor end and bridge are also modified with coumarins to influence long-range cooperativity and lattice dimensionality. Other modifications will be discussed later.

Modification of chromophore bridges with aromatic moieties (such as shown in Fig. 1) is more effective than modification with flexible chain moieties because the rigid aromatic moieties are oriented orthogonal with respect to each other and the flexible chain moieties can wrap along the chromophore providing less effective inhibition of chromophore close approach. The best outcome that can be anticipated for chromophore shape modification of simple chromophore-polymer composite materials is that independent-particle-like behavior can be extended to

higher chromophore concentrations. Without chromophore modification, chromophore number density must be limited to approximately 20% loading (number densities on the order of 2×10^{20} chromophores/cm³). With modification, chromophore number densities can be increased significantly, e.g., to values greater than 50% loading. In addition to improving the maximum electro-optic activity (through achieving the maximum product of chromophore number density and acentric order parameter) such chromophore modification is useful for inhibiting chromophore-chromophore excitonic interactions. Such excitonic interactions are frequently problematic for their contribution to optical loss.

While chromophore-polymer composite materials represent the materials that can be most simply and quantitatively simulated by coarse-grained statistical mechanical methods and although they are attractive from the standpoint of ready availability and low cost, there are some disadvantages associated with such materials. These include phase separation of chromophore and host polymer during various stages of processing and with increasing chromophore concentration. The latter problem is manifest in spectral line broadening and solvatochromic shifts with increasing chromophore concentration.

2. CHROMOPHORES COVALENTLY INCORPORATED INTO POLYMERS AND DENDRIMERS

The initial motivation for covalently incorporating chromophores into polymers and dendrimers was to avoid phase separation associated with composite materials. Covalent coupling permits chromophore loading to be increased significantly while avoiding phase separation. For such materials, chromophore-chromophore dipolar interactions and nuclear repulsive interactions continue to be important considerations. To these must be added a consideration of the impact of covalent bond potentials upon poling-induced order [37,38]. Normally, somewhat flexible linkers are used to connect second order nonlinear optical chromophores to polymer and dendrimer macromolecular materials [38]. These must be treated by atomistic Monte Carlo or molecular dynamics approaches while aromatic and polyene moieties can be treated in the United Atom Approximation (by coarse-graining) [38]. If flexible chains coupling chromophores to polymers are too long, then results approach those observed for chromophore-polymer composite materials. Covalent bond potentials can contribute to the inhibition centrosymmetric organization and lead to poling efficiencies in the range of 1-2 (nm/V)² [38] while chromophore-polymer composite materials typically are limited to values of 1 (nm/V)² or less. As with chromophore-polymer composite materials, quantitative simulation of electro-optic activity (poling efficiency and the variation of poling efficiency with chromophore number density) is achieved for chromophores covalently incorporated into dendrimers and polymers [38,39]. This is not surprising as these are very strong interactions and best quantitative simulation is obtained for systems characterized by the competition of a small number of strong interactions. As the complexity of material systems increases not only does realization of quantitative simulation become more elusive but also the cost of simulation increases.

As with chromophore-polymer composite materials, materials containing covalently incorporated chromophores behave as Langevin (3-D) lattice materials, i.e., there is no dimensional restriction of chromophore reorientation associated with intermolecular electrostatic interactions.

4. MATRIX INTERACTIONS THAT ENHANCE POLING EFFICIENCY

Statistical mechanical calculations demonstrate that as the rotational freedom (dimensionality) of chromophores is reduced, electric field poling-induced acentric order is enhanced for a given poling field strength [40-43]. This is illustrated in Fig. 2. Such an improvement in acentric order by simply reducing the dimensionality of the lattice surrounding chromophores is very attractive because it does not involve any change in chromophore electronic (photonic) properties or in chromophore number density. Thus, optical loss is typically not impacted. In order to reduce lattice dimensionality, spatially-anisotropic interactions that produce long range cooperativity must be introduced into materials. Lattice dimensionality reduction has been demonstrated by the introduction of dipolar (e.g., coumarin moieties—see Fig. 1) or quadrupolar interactions (e.g., arene-perfluoroarene moieties) [41]. These interactions also influence molecular dynamics, e.g., viscoelasticity [41-49].

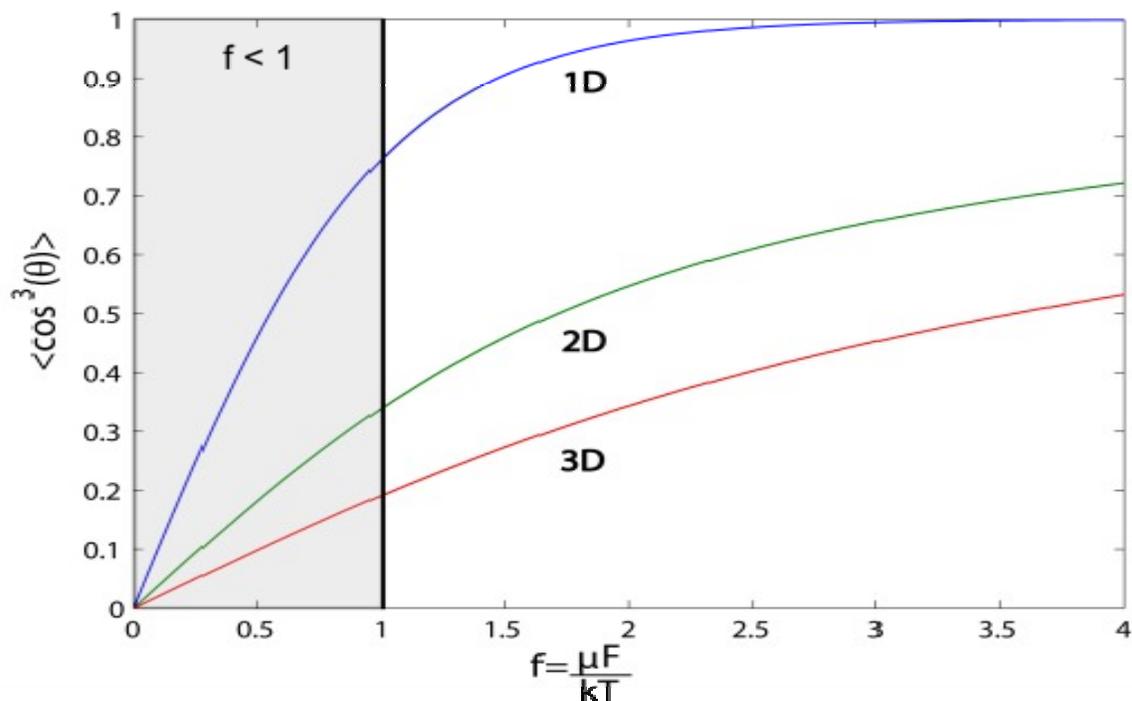


Figure 2. The dependence on lattice dimensionality of the plot of poling-induced acentric order, $\langle \cos^3\theta \rangle$, versus normalized poling energy, f , is shown. μ is the chromophore dipole moment, F is the poling field felt by the chromophore, k is the Boltzmann constant, and T is the Kelvin poling temperature. The shaded region illustrates the most commonly utilized poling field strengths. Reproduced from reference [42] with permission.

Organic electro-optic materials are ideal for investigating the effect of lattice dimensionality on poling-induced acentric order in that lattice dimensionality can be experimentally defined by measuring the ratio of acentric to centric order parameters [42]. Centric order parameters can be measured by variable angle polarization reference absorption spectroscopy (VAPRAS) [50] and by variable angle spectroscopic ellipsometry (VASE) [51,52]. VASE has the additional advantage of permitting (in some cases) of defining the relative orientation of chromophores and lattice defining moieties such as coumarins [41-43]. Acentric order parameters can be determined from measurements of electro-optic activity by techniques such as attenuated total reflection (ATR) [22]. Statistical mechanical calculations yield all order parameters and thus theoretical and experimental data can be compared with confidence.

The effect of introduced dipolar and quadrupolar interactions on lattice dynamics can be measured by techniques such as shear modulation force microscopy (SM-FM) [53], intrinsic friction analysis (IFA) [54], and dielectric relaxation spectroscopy (DRS) [45]. These measurements permit definition of the thermodynamic parameters (free energy, enthalpy, and entropy) associated with various phases of matter including phases characterized by reduced lattice dimensionality. The combination of IFA and DRS data permits definition of the length scale of molecular cooperativity [45]. Theoretical simulation of molecular dynamics is more challenging than the simulation of equilibrium properties but phase transitions can be predicted in some cases.

Moieties that impact molecular cooperativity and lattice dimensionality can be positioned at the donor and acceptor ends of chromophores and at the front and back positions of chromophores—the same positions at which modification is carried out for steric control. Exploiting selectively incorporated dipolar and quadrupolar interactions for control of lattice dimensionality as a design paradigm for improving poling efficiency and auxiliary properties is challenging. Active moieties, such as coumarins and arenes, can interact with chromophores as well as with each other and the results will depend upon the positioning and the length of flexible chain connectors.

Computational difficulty increases substantially and modification of traditional Monte Carlo/molecular dynamics methods is required to prevent calculations from failing to converge to equilibrium lattices [40]. The potential for moieties to interact with chromophores emphasizes the need to effectively utilize control of chromophore shape to influence chromophore organization under the action of an electric poling field. While statistical mechanical computations have reproduced the critical observations of the coumarin-modified materials, computational costs have prevented extensive exploration of structures that would lead to improved poling efficiency.

To the present, coumarin modification of chromophores (C1 and C1-CLD [41-43,55]) has led to lattices characterized by dimensionalities ranging from 1.8 to 2.5 with corresponding molecular cooperativity lengths ranging from tens to hundreds of nanometers. Poling efficiencies have been increased by factors of 2-3 leading to electro-optic activity in thin films of several hundred pm/V.

5. BINARY CHROMOPHORE MATERIALS AND LASER-ASSISTED POLING

A material consisting of a guest chromophore incorporated into a chromophore-containing host is also an example of a material where lattice dimensionality can be exploited to improve poling efficiency [22,37,55-57]. Both guest and host chromophores interact with the poling field reducing their order from 3-D to a lower dimensionality. Both guest and host chromophores interact through their dipole moments and experience an overall reduction in dimensionality [22,37,55,57]. This effect leads to improvement in poling efficiency as illustrated in Fig. 3.

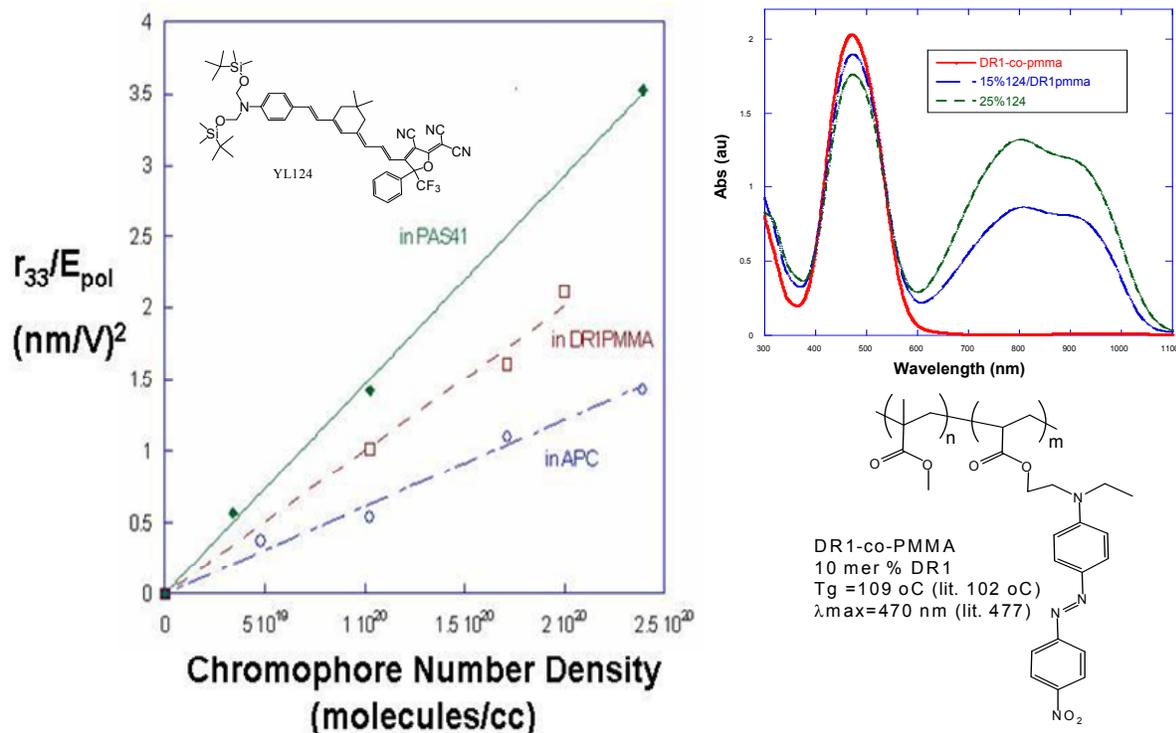


Figure 3. (Left) The variation of poling efficiency versus guest chromophore number density is shown for a CLD-type chromophore (YLD-124) dissolved in amorphous polycarbonate (APC) to form a composite and incorporated into two binary chromophore materials (into a chromophore-containing dendrimer, PAS41, and into the disperse red chromophore covalently incorporated into polymethylmethacrylate, PMMA). (Right) The variation of optical spectra with guest chromophore concentration and the structure of the DR1-co-PMMA chromophore host are shown.

Binary chromophore intermolecular electrostatic interactions lead to factors of 2-3 improvements in poling efficiency and to poling efficiencies approaching 4 (or even larger at the highest chromophore number densities). This improvement in poling efficiency reflects an increase in chromophore number density that can be effectively

exploited (see Fig. 3 left) as well as an increase in acentric order. The right hand side of Fig. 3 illustrates another interesting feature of binary chromophore composites. Unlike conventional chromophore-polymer composite materials, no solvatochromic shifts or spectral line broadening are observed in the linear optical spectra as a function of increasing guest chromophore concentration. This is not surprising because of the favorable enthalpy and entropy of mixing associated with dissolving a polar guest chromophore into a dipolar host in contrast to dissolving the guest chromophore into a non-polar host as is the case with conventional composites. The high concentration of chromophores in binary chromophore glasses can contribute to optical loss through absorption loss unless care is exercised. It is, in general, important to keep total (absorption + scattering) propagation loss to values of less than 2 dB/cm. Of course, the maximum propagation loss that can be tolerated will depend on device length and application. It should also be kept in mind that hybrid device technologies involving silicon photonics, plasmonics (metal optics), and metamaterial architectures have loss issues that are as important as chromophore absorption and scattering loss issues.

Chromophore materials discussed in the preceding section (those incorporating non-chromophore dipolar and quadrupolar interactions) can also be used as hosts for development of binary chromophore materials. In general, an improvement in poling efficiency is observed but the results can vary widely in terms of the magnitude. Poling efficiencies of 5 have been observed.

Binary chromophore materials are also of interest from the standpoint that, in some cases, lattice dimensionality can also be influenced by laser-assisted electric field poling, i.e., irradiating the material with polarized laser radiation while applying an electric poling field [57,58]. DR1-co-PMMA is known to respond to polarized radiation with the DR1 chromophore undergoing rapid trans-cis-trans isomerization leading to rotation of the chromophores into a plane (i.e., to an orientation where the transition moment is zero). Use of 532 nm polarized laser radiation leads to factors of 2-4 improvement in poling efficiency. Unfortunately, due to photo-generation of charge carriers, the maximum electric poling field strength that can be utilized is reduced so that the full impact of lattice dimensionality control cannot be exploited. Polarized laser radiation can also be used to effect spatially-selective melting of materials where the material glass transition temperature is lower than the material decomposition temperature [59]. In some cases, acentric order can be improved to unity by this approach.

6. AUXILIARY PROPERTIES

Auxiliary properties such as processability, stability (thermal and photochemical), and optical loss are important and are strongly influenced by intermolecular electrostatic interactions. As already noted introduction of dipolar and quadrupolar interactions can be used to tune viscoelasticity and phase transition temperatures. These properties are obviously critical to processability, including for the integration of OEO materials with disparate materials and incorporation into waveguide architectures characterized by nanometer dimensions. The material glass transition temperature will influence the thermal and photochemical stability of poling-induced acentric order (and electro-optic activity). Thermal and photochemical stability can also be significantly improved by post-poling crosslinking (lattice hardening). Lattice hardening is currently most frequently effected exploiting Diels-Alder/Retro-Diels-Alder chemistry [22,60-63]. Final glass transition temperatures of 200°C or greater are routinely achieved with this approach. Coumarin moieties introduced to influence lattice dimensionality can also be photo-crosslinked to increase lattice hardness.

Tailoring of the lattices that surround chromophores can also be used to influence material index of refraction and dielectric properties as well as the above-mentioned properties. Control of dielectric properties can be extremely important for sensor applications and for realization of ultrahigh bandwidth operation. Dielectric permittivity also affects molecular first hyperpolarizability [64]. Index of refraction control can be important for optical confinement in waveguides. For example, integration with silicon nitride waveguide structures may require OEO materials with lower index of refraction than for integration with silicon waveguides. Typically, the acentric order of electrically-poled OEO materials is low, so little birefringence exists. Low acentric order is also evident from the fact that the ratio of electro-optic coefficients (r_{33}/r_{13}) is often close to 3. As order is increased birefringence will correspondingly increase and the r_{33}/r_{13} ratio will increase in a nonlinear manner.

For chromophores such as shown in Fig. 1, the most serious contribution to optical loss typically arises from interband electronic absorption. It is important to keep the absorption maximum of this transition significantly below 1 micron. The interband charge-transfer transition will be influenced by the dielectric environment that surrounds the chromophore. It is important to keep that environment as homogeneous as possible and in particular to avoid excitonic contributions to absorption loss. In this regard, modification of chromophores to inhibit close approach leading to orbital-orbital interactions is important. Modification of the donor and acceptor ends of the chromophores and of the 2 and 5 positions of the isophorone-protected bridge (see Fig. 1) with bulky substituents is frequently necessary to achieve this. Ideally, it is desirable to have the absorption spectrum of the thin film chromophore-containing material to approach that of the chromophore solved in a solvent of comparable dielectric constant. This observation also holds for third order nonlinear optical materials used for all-optical signal processing and indeed chromophore modification similar to that described here is now being pursued in the development of optimized third order materials. If optical loss at 1.55 microns associated with electronic transitions is reduced to insignificant contributions (e.g., as observed for materials based on the DR1 chromophore), then absorption loss will be defined by overtone vibrations associated with hydrogen. Such contributions are most problematic for chromophore-polymer composite materials since proton densities are typically higher in traditional commercial polymers than for chromophores. Proton densities can be reduced by replacement of protons with fluorine or by carbon-carbon bonds as in dendrimer structures. Proton densities are also lower in aromatic than in aliphatic organic moieties. In some cases, optical loss can be reduced to values as low as 0.2 dB/cm comparable to the loss observed for lithium niobate. Scattering losses are typically low when phase separation and material damage is avoided in processing. If material homogeneity and processability together with poling efficiency is effectively controlled through control of intermolecular electrostatic interactions, then modifications of structure can be effected to reduce and control optical loss.

7. MATERIAL PROCESSING

Organic electro-optic materials have been prepared by (1) crystal growth, (2) sequential synthesis-self assembly multi-step methods, and (3) electric field poling [55]. Intermolecular electrostatic interactions are critical for each of these approaches. Strong intermolecular interactions (ionic or strong dipolar interactions such as hydrogen bonding) are typically required for crystal growth. These interactions frequently elevate material glass transition temperatures above material decomposition temperatures resulting in the loss of melt processability. Strong interactions (ionic, hydrogen bonding, or even covalent coupling) are typically used to promote acentric order in materials prepared by sequential synthesis-self assembly (Langmuir-Blodgett and Merrifield) methods. Again, material glass transition temperatures are typically elevated above material decomposition temperatures. OEO materials prepared by crystal growth and sequential synthesis-self assembly methods exhibit excellent thermal and photochemical stability due to dense, hard lattices resulting from strong intermolecular interactions.

With incorporation of dipolar and quadrupolar interactions that promote acentric self-assembly (i.e., that assist the electric poling field), electric field poling methods are approaching those of crystal growth and sequential synthesis-self assembly. This is very important for circumventing the inherent limit on poling-induced acentric order that applies for Langevin (3-D) independent particle lattices. Use of interactions that promote self-assembly has the potential of permitting the realization of electro-optic coefficients exceeding 1000 pm/V. Current efforts have focused on the utilization of coumarin and arene-perfluoroarene interactions but stronger interactions (e.g., hydrogen bonding and even ionic interactions) may be appropriate. Ideally, the interaction should be as strong as possible while avoiding elevation of material glass transitions above material decomposition temperatures. Melt processability is a significant processing advantage and can be used to anneal out micordomain structures that may form with spin casting and rapid self-assembly.

The direction of the principle axis of the electro-optic tensor in OEO materials prepared by electric field poling is influenced by the direction of the applied poling field as well as the details of self-assembly and surface forces while only these latter two effects define tensor orientation for materials prepared by crystal growth and by sequential synthesis. The control afforded by the poling field can be important for utilization of the principle element (r_{33}) in various device architectures.

Whatever the processing option pursued, it is clear that greater use of theory needs to be exercised. Chromophore shape and covalent bond potentials, as well as strong intermolecular electrostatic interactions that drive acentric

assembly, are important for crystal growth and sequential synthesis methods as well as for electric field poling. Recent advantages in statistical mechanical methods that speed up simulations and avoid materials locking up in configurations far from equilibrium are important for increased utilization of theoretical modeling.

7. CHROMOPHORE HYPERPOLARIZABILITY

A significant advance in development of improved OEO materials occurred with the introduction of the tricyanovinylfuran (TCVF) acceptor of Fig. 1 [22]. This acceptor permitted important increases in both molecular first hyperpolarizability and stability. Chromophores with even greater molecular first hyperpolarizability than the CLD-type chromophore of Fig. 1 have been suggested and indeed even some experimental evidence has been presented to support this contention [65]. Unfortunately, these materials have yet to be translated to prototype device demonstrations. Nevertheless, there are a number of simple modifications to chromophore structures that are likely to lead to improved molecular first hyperpolarizability and ultimately to improved electro-optic activity. For example, simple replacement of cyano (-CN) groups with $-S(=O)_2R$ groups is theoretically predicted to lead to improvement in molecular hyperpolarizability. This type of modification also facilitates modification of the chromophore with additional moieties at the acceptor end (i.e., modification of the R group).

Chromophores are normally designed for a given optical nonlinear-optical transparency tradeoff. Chromophores such as illustrated in Fig. 1 are designed for operational wavelengths near 1.55 microns. Interest occasionally arises for applications at shorter wavelengths. Chromophores appropriate for such applications typically require chromophores with short π -electron bridges. Note that different classes of chromophores can exhibit quite different behavior for the optical nonlinearity-optical transparency tradeoff as a function of wavelength so that a class of chromophores that is optimum for longer wavelength applications may very well not be optimum for shorter wavelengths. Note also that optical loss issues change significantly with wavelength, e.g., loss from vibrational overtone absorption becomes insignificant at wavelengths less than 1 micron and scattering loss exhibits a well-known dependence on wavelength. It is, in general, important to prevent excitonic absorption associated with π - π orbital interactions between chromophores at close approach. Modification of chromophore shape is important for sterically-controlling chromophore close approach and such orbital-orbital interactions. In most cases, control of chromophore shape can be achieved with little influence on chromophore hyperpolarizability.

8. CONCLUSIONS

Incorporation of dipolar and quadrupolar moieties to control self assembly and lattice dimensionality has become an important route to improving the performance of organic electro-optic materials. Theoretical consideration of such interactions is computationally challenging but when coupled with consideration of chromophore-chromophore dipolar interactions and steric (nuclear repulsive) interactions, leads to improved understanding of the design criteria needed to optimize poling efficiency and electro-optic activity. Specifically-incorporated intermolecular electrostatic interactions also influence material processability, stability, and optical loss.

Integration of organic electro-optic materials into silicon photonic, plasmonic, and metamaterial device architectures affords many advantages including exploitation of sub-wavelength photonics and dramatic reduction in the dimensions of active photonic devices. However, maximum poling voltages that can be employed with such device structures are often less than those used with simple thin film devices. Thus, improvement in poling efficiency and auxiliary properties by control of intermolecular electrostatic interactions is very important for OEO hybrid device technology development.

Further optimization in the electro-optic activity of organic materials is likely to be realized. Indeed, factors of 5-8 improvement are not out of the question. Such improvements may be used to effect reduction in drive voltages and power consumption but they may also be used to facilitate shorter device lengths. Device lengths of some active devices are already on the order of 1 mm or even less. Spatial light modulation and terahertz generation and detection applications may also benefit from improved poling efficiencies associated with control of intermolecular electrostatic interactions.

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REFERENCES

- [1] Baehr-Jones, T., Hochberg, M., Wang, G., Lawson, R., Liao, Y., Sullivan, P.A., Dalton, L.R., Jen, A.K.-Y., and Scherer, A., "Optical modulation and detection in slotted silicon waveguides," *Opt. Express*, 13, 5216-5226 (2005).
- [2] Baehr-Jones, T., Penkov, B., Huang, J., Sullivan, P.A., Davies, J., Takayesu, J., Luo, J., Kim, T.-D., Dalton, L.R., Jen, A.K.-Y., Hochberg, M., and Scherer, A., "Nonlinear polymer-clad silicon slot waveguide modulator with a half wave voltage of 0.25 V," *Appl. Phys. Lett.*, 92, 163303-1-3 (2008).
- [3] Takayesu, J., Hochberg, M., Baehr-Jones, T., Chan, E., Wang, G., Sullivan, P.A., Liao, Y., Davies, J., Dalton, L.R., Scherer, A., and Krug, W., "A hybrid electro-optic microring resonator-based $1 \times 4 \times 1$ ROADM for wafer scale optical interconnects." *IEEE J. Lightwave Technol.*, 27, 440-448 (2008).
- [4] Ding, R., Baehr-Jones, T., Kim, W.-J., Spott, A., Fournier, M., Fedeli, J.-M., Huang, S., Luo, J., Jen, A.K.-Y., Dalton, L.R., and Hochberg, M., "Sub-volt silicon-organic electrooptic modulator with 500 MHz bandwidth," *IEEE/OSA J. Lightwave Technol.*, 29, 1112-117 (2011).
- [5] Figi, H., Bale, D. H., Szep, A., Dalton, L. R., and Chen, A., "Electro-optic modulation in horizontally slotted silicon/organic crystal hybrid devices," *J. Opt. Soc. Amer. B*, 28, 2291-2300 (2011).
- [6] Block, B.A., Younkin, T.R., Reshotko, R., Chang, P., Luo, L.D., and Jen, A.K.-Y., "Electro-optic polymer cladding ring resonator modulators." *Opt. Express*, 16, 18326-18333 (2008).
- [7] Ding, R., Baehr-Jones, T., Liu, Y., Bojko, R., Witzens, J., Huang, S., Luo, J., Benight, S., Sullivan, P., Fedeli, J.-M., Fournier, M., Dalton, L. R., Jen, A., and Hochberg, M., "Demonstration of a low π L modulator with GHz bandwidth based on an electro-optic polymer-clad silicon slot waveguide," *Opt. Express*, 18, 15618-15623 (2010).
- [8] Gould, M., Baehr-Jones, T., Ding, R., Huang, S., Luo, J., Jen, A.K.-Y., Fedeli, J.-M., Fournier, M., and Hochberg, M., "Silicon-polymer hybrid slot waveguide ring-resonator modulator," *Opt. Express*, 19, 3952-3961 (2011).
- [9] Lin, C.-Y., Wang, X., Chakravarty, S., Lee, B.S., Lai, W., Luo, J., Jen, A.K.-Y., and Chen, R.T., "Electro-optic polymer infiltrated silicon photonic crystal slot waveguide modulator with 23 dB slow light enhancement," *Appl. Phys. Lett.*, 97, 093304-1-3 (2010).
- [10] Wang, X., Lin, C.-Y., Chakravarty, S., Luo, J., Jen, A.K.-Y., and Chen, R.T., "Effective in-device r_{33} of 735 pm/V on electro-optic polymer infiltrated silicon photonic crystal slot waveguides," *Opt. Lett.*, 36, 882-884 (2011).
- [11] Wulbern, J.H., Hampe, J., Petrov, A., Eich, M., Luo, J.D., Jen, A.K.-Y., Falco, A.D., Krauss, T.F., Bruns, J., and Ptermann, K., "Electro-optic modulation in slotted resonant photonic crystal heterostructures," *Appl. Phys. Lett.*, 94, 241107-1-3 (2009).
- [12] Wulbern, J.H., Prorok, S., Hampe, J., Petrov, A., Eich, M., Luo, J., Jen, A.K.-Y., Jenett, M., and Jacob, A., "40 GHz electro-optic modulation in hybrid silicon-organic slotted photonic crystal waveguides," *Opt. Lett.*, 35, 2753-2755 (2010).
- [13] Wulbern, J.H., Petrov, A., and Eich, M., "Electro-optic modulator in a polymer infiltrated silicon slotted photonic crystal waveguide heterostructure resonator," *Opt. Express*, 17, 304-313 (2009).
- [14] Leuthold, J., Freude, W., Brosi, J.-M., Baets, R., Dumon, P., Biaggio, I., Scimeca, M.L., Diederich, F., Frank, B., and Koos, C., "Silicon organic hybrid technology—A platform for practical nonlinear optics," *Proc. IEEE*, 97, 1304-1316 (2009).
- [15] Koos, C., Vorreau, P., Vallaitis, T., Dumon, P., Bogaerts, W., Baets, R., Esembeson, B., Biaggio, I., Michinobu, T., Diederich, F., Freude, W., and Leuthold, J., "All-optical high-speed signal processing with silicon-organic hybrid slot waveguides," *Nat. Photonics*, 3, 216-219 (2009).
- [16] Shi, S. and Prather, D.W., "Ultrabroadband electro-optic modulator based on hybrid silicon-polymer dual vertical slot waveguide," *Adv. Optoelectron.*, 2011, 714895-1-6 (2011).

- [17] Shi, S. and Prather, D.W., "Dual rf-optical slot waveguide for ultrabroadband modulation with a subvolt $V\pi$," *Appl. Phys. Lett.*, 96, 201107-1-3 (2010).
- [18] Kim, S.-K., Park, J., Fetterman, H.R., Sylvain, N., Benight, S. J., Kosilkin, I., Bale, D. H., Robinson, B. H., Jen, A. K.-Y., Dalton, L. R., Geary, K., Steier, W. H., and Perini, P., "Active plasmonic and metamaterial devices," *Proc. SPIE*, 7754, 775403-1-10 (2010).
- [19] Dalton, L.R., Jen, A.K.-Y., Robinson, B.H., Overney, R., Benight, S.J., Knorr, D.B., Jr., Kim, S.-K., Fetterman, H.R., and Zhang, C., "Optimization of organic NLO materials for integration with silicon photonic, plasmonic (metal optics), and metamaterial devices," *Proc. SPIE*, 7935, 793502-1-15 (2011).
- [20] Chen, R. T., private communication.
- [21] Norwood, R. A., private communication.
- [22] Dalton, L. R., Sullivan, P. A., and Bale, D. H., "Electric field poled organic electro-optic materials: State of the art and future prospects. *Chem. Rev.*, 110, 25-55 (2010).
- [23] Sullivan, P. and Dalton, L. R., "Theory-inspired development of organic electro-optic materials," *Acc. Chem. Res.*, 43, 10-18 (2010).
- [24] Burland, D. M., Miller, R. D., and Walsh, C. A., "Second-order nonlinearity in poled polymer systems," *Chem. Rev.*, 94, 31-75 (1994).
- [25] Cho, M. J., Choi, D. H., Sullivan, P. A., Akelaitis, A. J. P., and Dalton, L. R., "Recent progress in second-order nonlinear optical polymers and dendrimers," *Prog. Poly. Sci.*, 33, 1013-1058 (2008).
- [26] Dalton, L.R., Harper, A.W., Ren, A.S., Wang, F., Todorova, G., Chen, J., Zhang, C., and Lee, M., "Polymeric electro-optic modulators: From chromophore design to integration with semiconductor VLSI electronics and silica fiber optics," *Ind. Eng. Chem. Res.*, 38, 8-33 (1999).
- [27] Kim, W.-K. and Hayden, L.M., "Fully atomistic modeling of an electric field poled guest-host nonlinear optical polymer," *J. Chem. Phys.*, 111, 5212-5222 (1999).
- [28] Leahy-Hoppa, M.R., French, J., Cunningham, P.D., and Hayden, L.M., "Atomistic molecular modeling of electric field poling of nonlinear optical polymers," in *Nonlinear Optical Properties of Matter: From Molecules to Condensed Phases*, Papadopoulos, M.G., Leszczynski, and J., Sadlej, A.J., Eds.; Kluwer Press: New York, NY, USA, 2006; pp. 337-357.
- [29] Leahy-Hoppa, M.R., Cunningham, P.D., French, J.A., and Hayden, L.M., "Atomistic molecular modeling of the effect of chromophore concentration on the electro-optic coefficient in nonlinear optical polymers," *J. Phys. Chem. A*, 110, 5792-5797 (2006).
- [30] Makowska-Janusik, M., Reis, H., and Papadopoulos, M.G., "Molecular dynamics simulation of electric field poled nonlinear optical chromophores incorporated in a polymer matrix," *J. Phys. Chem. B*, 108, 588-596 (2004).
- [31] Dalton, L.R., Harper, A.W., and Robinson, B.H., "The role of London forces in defining noncentrosymmetric order of high dipole moment-high hyperpolarizability chromophores in electrically poled polymeric thin films," *Proc. Natl. Acad. Sci. USA*, 94, 4842-4847 (1997).
- [32] Dalton, L.R., Robinson, B.H., Jen, A.K.-Y., Steier, W.H., and Neilsen, R., "Systematic development of high bandwidth, low drive voltage organic electro-optic devices and their applications," *Opt. Mater.*, 21, 19-28 (2003).
- [33] Robinson, B.H. and Dalton, L.R., "Monte Carlo statistical mechanical simulations of the competition of intermolecular electrostatic and poling field interactions in defining macroscopic electro-optic activity for organic chromophore/polymer materials," *J. Phys. Chem. A*, 104, 4785-4795 (2000).
- [34] Shi, Y., Zhang, C., Zhang, H., Bechtel, J.H., Dalton, L.R., Robinson, B.H., and Steier, W.H., "Low (sub-1 volt) halfwave voltage polymeric electrooptic modulators achieved by control of chromophore shape," *Science*, 288, 119-122 (2000).
- [35] Neilsen, R., Rommel, H., and Robinson, B., "Simulation of the loading parameter in organic nonlinear optical materials," *J. Phys. Chem.*, 108, 8659-8667 (2004).
- [36] Rommel, H.L. and Robinson, B.H., "Orientation of electro-optic chromophores under poling conditions: A spheroidal model," *J. Phys. Chem. C*, 111, 18765-18777 (2007).
- [37] Pereverzev, Y.V., Gunnerson, K.N., Prezhdo, O.V., Sullivan, P.A., Liao, Y., Olbricht, B.C., Akelaitis, A.J.P., Jen, A.K.-Y., and Dalton, L.R., "Guest-host cooperativity in organic materials greatly enhances the nonlinear optical response," *J. Phys. Chem. C*, 112, 4355-4363 (2008).

- [38] Sullivan, P.A., Rommel, H.L., Takimoto, Y., Hammond, S.R., Bale, D.H., Olbricht, B.C., Liao, Y., Rehr, J.J., Eichinger, B.E., Jen, A.K.-Y., Reid, P. J., Dalton, L. R., and Robinson, B. H., "Modeling the optical behavior of complex organic media: From molecules to materials," *J. Phys. Chem. B*, 113, 15581-15588 (2009).
- [39] Sullivan, P.A., Rommel, H., Liao, Y., Olbricht, B.C., Akelaitis, A.J.P., Firestone, K.A., Kang, J.-W., Luo, J., Choi, D.H., Eichinger, B.E., Reid, P. J., Cehn, A., Jen, A. K.-Y., Robinson, B. H., and Dalton, L. R., "Theory-guided design and synthesis of multi-chromophore dendrimers: An analysis of the electro-optic effect," *J. Am. Chem. Soc.*, 129, 7523-7530 (2007).
- [40] Robinson, B. H., Johnson, L. E., Tillack, A., and Garrett, K., private communication.
- [41] Benight, S.J., Johnson, L.E., Barnes, R., Olbricht, B.C., Bale, D.H., Eichinger, B.E., Dalton, L.R., Sullivan, P.A., and Robinson, B.H., "Reduced dimensionality in organic electro-optic materials. *J. Phys. Chem. B*, 114, 11949-11956 (2010).
- [42] Dalton, L.R., Benight, S.J., Johnson, L.E., Knorr, D.B., Jr., Kosilkin, I., Eichinger, B.E., Robinson, B.H., Jen, A., and Overney, R., "Systematic nano-engineering of soft matter organic electro-optic materials," *Chem. Mater.*, 23, 430-445 (2011).
- [43] Benight, S. J., Knorr, D. B. Jr., Johnson, L. E., Sullivan, P. A., Lao, D., Sun, J., Kocherlakota, L. S., Elangovan, A., Robinson, B. H., Overney, R. M., and Dalton, L. R., "Nano-engineering lattice dimensionality for a soft matter organic functional material," *Adv. Mater.*, 24, 3263-3268 (2012).
- [44] Zhou, X. H., Luo, J., Kim, T. D., Jang, S. H., Overney, R. M., Dalton, L. R. and Jen, A. K. Y., "Molecular design and supramolecular organization of highly efficient nonlinear optical chromophores for exceptional electro-optic properties," in *Organic Thin Films for Photonics Applications*, eds. Herman, W., Flom, S. R., and Foulger S. (ACS Symposium Series, Washington DC, 2010) Chapter 4, pp. 51-66.
- [45] Knorr, D. B. Jr., Benight, S., Krajina, B., Zhang, C., Dalton, L. R., and Overney, R. M., "Thermorheological relaxation behavior in dendritic non-linear optical glasses," *J. Phys. Chem. B*, 116, 13793-13805 (2012).
- [46] Gray, T., Kilgore, J.P., Luo, J., Jen, A.K.-Y., and Overney, R.M., "Molecular mobility and transitions in complex organic systems studied by shear force microscopy," *Nanotechnology*, 18, 044009-1-9 (2007).
- [47] Gray, T., Kim, T.D., Knorr, D.B., Jr., Luo, J., Jen, A.K.-Y., and Overney, R.M., "Mesoscale dynamics and cooperativity of networking dendronized nonlinear optical molecular glasses," *Nano Lett.*, 8, 754-739 (2008).
- [48] Knorr, D.B., Jr., Zhou, X.-H., Shi, Z., Luo, J., Jang, S.-H., Jen, A.K.-Y., and Overney, R.M., "Molecular mobility in self-assembled dendritic chromophore glasses," *J. Phys. Chem. B*, 112, 14180-14188 (2009).
- [49] Zhou, X.-H., Luo, J., Huang, S., Kim, T.-D., Shi, Z., Cheng, Y.-J., Jang, S.-H., Knorr, D.B., Jr., Overney, R.M. and Jen, A.K.-Y., "Supramolecular self-assembled dendritic nonlinear optical chromophores: Fine-tuning of arene perfluoroarene interactions for ultralarge electro-optic activity and enhanced thermal stability," *Adv. Mater.*, 21, 1976-1981 (2009).
- [50] Olbricht, B.C., Sullivan, P.A., Davies, J.A., Dennis, P.C., Hurst, J.T., Johnson, L.E., Bale, D.H., Benight, S.J., Hilfiker, J.N., Chen, A., Eichinger, B. E., Reid, P. J., Dalton, L. R., and Robinson, B. H., "Measuring order in contact-poled organic electro-optic materials with variable angle polarization-referenced absorption spectroscopy (VAPRAS)," *J. Phys. Chem. B*, 115, 231-241 (2011).
- [51] Woollam, J.A., "Overview of variable angle spectroscopic ellipsometry (VASE), Part I: Basic theory and typical applications," In *Optical Metrology*; SPIE: Bellingham, WA, USA, 1999; Volume CR72, pp. 3-28.
- [52] Johs, B., "Overview of variable angle spectroscopic ellipsometry (VASE), Part II: Advanced applications," In *Optical Metrology*; SPIE: Bellingham, WA, USA, 1999; Volume CR72, pp. 29-58.
- [53] Gray, T., Kilgore, J.P., Luo, J., Jen, A.K.-Y., and Overney, R.M., "Molecular mobility and transitions in complex organic systems studied by shear force microscopy," *Nanotechnology*, 18, 044009-1-9 (2007).
- [54] Knorr, D.B., Jr., Gray, T.O., and Overney, R.M., "Intrinsic friction analysis—Novel nanoscopic access to molecular mobility in constrained organic systems," *Ultramicroscopy*, 109, 981-1000 (2009).
- [55] Dalton, L. R., Jazbinsek, M., Kwon, O. P., Gunter, P., and Sullivan P. A., *Organic Electro-Optic Materials*, Cambridge University Press, Cambridge, 2013.
- [56] Kim, T.-D., Luo, J., Cheng, Y.-J., Shi, Z., Hau, S., Jang, S.-H., Zhou, X.-H., Tian, Y., Polishak, B., Hunag, S., Ma, H., Dalton, L. R., and Jen, A. K.-Y., "Binary chromophore systems in nonlinear optical dendrimers and polymers for large electrooptic activities," *J. Phys. Chem. C*, 112, 8091-8098 (2008).
- [57] Olbricht, B.C., Sullivan, P.A., Wen, G.-A., Mistry, A., Davies, J.A., Ewy, T.R., Eichinger, B.E., Robinson, B.H., Reid, P.J., and Dalton, L.R., "Laser-assisted poling of binary chromophore materials," *J. Phys. Chem. C*, 112, 7983-7988 (2008).

- [58] Kim, S., Pei, Q., Fetterman, H.R., Olbricht, B.C., and Dalton, L.R., "Photo-assisted corona poled YLD 124/DR1-co-PMMA electro-optic device using photoisomerization," *IEEE Photonics Technol. Lett.*, 23, 845-847 (2011).
- [59] Wang, Z., Sun, W., Chen, A., Kosilkin, I., Bale, D., and Dalton, L.R., "Direct-laser assisted poling of vacuum deposited organic electro-optic thin films," *Opt. Lett.*, 36, 2853-2855 (2011).
- [60] Shi, Z., Liang, W., Luo, J.D., Huang, S., Polishak, B.M., Li, X., Younkin, T.R., Block, B.A., and Jen, A.K.-Y., "Tuning the kinetics and energetic of Diels-Alder cycloaddition reactions to improve poling efficiency and thermal stability of high temperature crosslinked electro-optic polymers," *Chem. Mater.*, 22, 5601-5608 (2010).
- [61] Shi, Z., Luo, J., Huang, S., Chen, Y.-J., Kim, T.-D., Polishak, B. M., Zhou, X.-H., Tian, Y., Jang, S.-H., Knorr, D. B. Jr., Overney, R. M., Youkin, T. R., and Jen, A. K.-Y., "Controlled Diels-Alder reactions used to incorporate highly efficient polymeric chromophores into maleimide-containing side-chain polymer for electro optics," *Macromolecules*, 42, 2438-2445 (2009).
- [62] Sullivan, P. A., Olbricht, B. C., Akelaitis, A. J. P., Mistry, A. A., Liao, Y., and Dalton, L. R., "Tri-component Diels-Alder polymerized dendrimer glass exhibiting large, thermally stable, electro-optic activity," *J. Mater. Chem.*, 17, 2899-2903 (2007).
- [63] Shi, Z., Hau, S., Luo, J., Kim, T.-D., Tucker, N. M., Ka, J.-W., Sun, H., Pyayt, A., Dalton, L. R., Chen, A., and Jen, A. K.-Y., "Highly efficient Diels-Alder crosslinkable electro-optic dendrimers for electric-field sensors," *Adv. Funct. Mater.*, 17, 2557-2563 (2007).
- [64] Bale, D., Liang, W., Dalton, L. R., Reid, P., Robinson, B. H., Eichinger, B. E., and Li, X., "Dielectric dependence of the first molecular hyperpolarizability for electro-optic chromophores," *J. Phys. Chem. B*, 115, 3505-3513 (2011).
- [65] Kang, H., Facchetti, A., Jiang, H., Carlati, E., Righetto, S., Ugo, R., Zuccaccia, C., Macchioni, A., Stern, C. L., Liu, Z., Ho, S.-T., Brown, E. C., Ratner, M. A., and Marks, T. J., "Ultralarge hyperpolarizability twisted π electron system electro-optic chromophores: Synthesis, solid-state and solution-phase structural characteristics, electronic structures, linear and nonlinear optical properties, and computational studies," *J. Am. Chem. Soc.*, 129, 3267-3286 (2007).