

# Multi-scale theory-assisted, nano-engineering of plasmonic-organic hybrid electro-optic device performance

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## ABSTRACT

Multi-scale (correlated quantum and statistical mechanics) modeling methods have been advanced and employed to guide the improvement of organic electro-optic (OEO) materials, including by analyzing electric field poling induced electro-optic activity in nanoscopic plasmonic-organic hybrid (POH) waveguide devices. The analysis of in-device electro-optic activity emphasizes the importance of considering both the details of intermolecular interactions within organic electro-optic materials and interactions at interfaces between OEO materials and device architectures. Dramatic improvement in electro-optic device performance—including voltage-length performance, bandwidth, energy efficiency, and lower optical losses have been realized. These improvements are critical to applications in telecommunications, computing, sensor technology, and metrology. Multi-scale modeling methods illustrate the complexity of improving the electro-optic activity of organic materials, including the necessity of considering the trade-off between improving poling-induced acentric order through chromophore modification and the reduction of chromophore number density associated with such modification. Computational simulations also emphasize the importance of developing chromophore modifications that serve multiple purposes including matrix hardening for enhanced thermal and photochemical stability, control of matrix dimensionality, influence on material viscoelasticity, improvement of chromophore molecular hyperpolarizability, control of material dielectric permittivity and index of refraction properties, and control of material conductance. Consideration of new device architectures is critical to the implementation of chip-scale integration of electronics and photonics and achieving the high bandwidths for applications such as next generation (e.g., 5G) telecommunications.

**Keywords:** Multi-scale computational methods, coarse-grained Monte Carlo simulations, organic electro-optic materials, plasmonic-organic hybrid (POH) technology, Mach Zehnder modulators, ring resonators, chip-scale integration

## 1. INTRODUCTION

Plasmonic-organic hybrid (POH) technology affords a unique opportunity with respect to achieving high bandwidth electro-optic performance, e.g., single channel bandwidths on the order, of or even exceeding, 1 THz. Such high bandwidths are possible due to the femtosecond response times of organic electro-optic (OEO) materials coupled with the short (femtosecond) RC time constants associated with plasmonic devices. OEO materials permit electro-optic (EO) modulation via the Pockels effect and thus the response time to time varying electric fields is the phase relaxation time of the conjugated  $\pi$ -electron system. Exploiting this fast response in THz generation and detection, all-optical

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modulation, and time-resolved femtosecond pulse experiments have established that bandwidths of at least 15 THz are possible with OEO materials<sup>1</sup>. The bandwidths of EO modulators incorporating OEO materials have been limited by the RC time constants of traveling wave (stripline) device electrodes (devices) or by the quality (Q) factor of resonant devices.<sup>1-4</sup> Other important performance parameters include device footprint, energy efficiency, drive voltage, and insertion loss. These are all strongly influenced by in-device electro-optic activity. In plasmonic devices, electro-optic performance is determined by the fundamental EO activity of the material, by the electric field enhancement and confinement associated with the nanoscopic electrode separations, and by the “slow light” effect associated with the propagation of surface plasmon polaritons.<sup>5,6</sup> A convenient figure of merit is the voltage-length ( $U_{\pi}L$ ) parameter, which relates directly to electro-optic activity,  $r_{33}$ , and device length,  $L$ , and inversely to electrode separation,  $d$ . Increasing electro-optic activity permits the use of smaller drive voltages or shorter device lengths. Realization of device footprints approaching  $1 \mu\text{m}^2$  together with digital level drive voltages requires  $U_{\pi}L$  of  $< 40 \text{ V}\cdot\mu\text{m}$ . Such footprints are likely required for effective chipscale integration of electronics and photonics for a number of applications. Shorter device lengths are also important for reducing optical propagation loss, which has been a critical issue impacting the utilization of plasmonic devices. Low  $U_{\pi}L$  is also important to optimizing energy efficiency, e.g., reducing energy consumption to values to on the order of 1 femtojoule/bit or even lower. Values on this order have already been achieved for silicon-organic hybrid (SOH) devices<sup>6,7</sup> and plasmonic-organic hybrid (POH) devices<sup>8</sup>.

Given the importance of electro-optic activity for optimizing various device performance parameters, a determined effort has been, and is being made, to improve  $r_{33}$  values in nanoscopic waveguide devices. The complexity of OEO materials (number of atoms involved in chromophores and the multiplicity of inter and intramolecular interactions that must be explicitly considered) has required the use of advanced statistical mechanical simulations and quantum mechanical calculations to understand poling-induced electro-optic activity in organic materials. Coarse-grained statistical mechanical calculations have been required to deal with the complexity and limits of current computational resources.

A critical issue for such calculations is to identify the appropriate trade-off with respect to chromophore structural detail in coarse-grained simulations versus minimizing computational time that is possible with such approximations. This has been addressed by development of the level of detail (LOD) method.<sup>6,9-11</sup> In the LOD method, ellipsoids are used to represent conjugated  $\pi$ -electron moieties. In the lowest level of detail, a single ellipsoid is used to represent the chromophore core. To represent chromophore curvature, a LOD = 2 (2 ellipsoids) is required as is illustrated in Fig. 1.

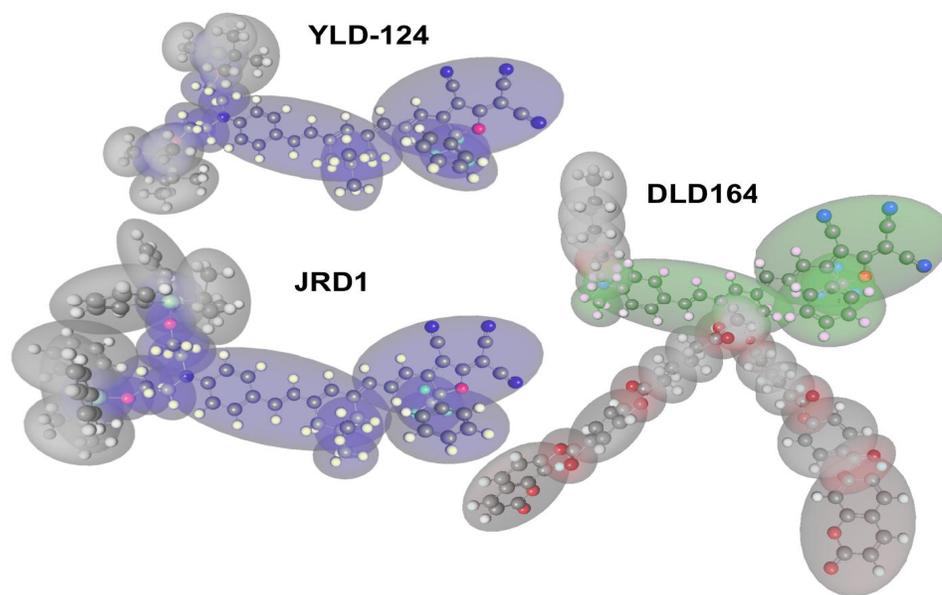


Fig. 1. The coarse-grained Monte Carlo simulation representations of three common electro-optic chromophores are shown. The chromophore cores are represented by two ellipsoids (LOD = 2). Note that LOD refers to the chromophore core; ellipsoids are also used to represent moieties beyond the chromophore cores (e.g., phenyl rings).

Another problem encountered in experimental studies and computer simulation of OEO materials is the kinetic trapping of chromophores in local (non-global) energetic minima during electric field poling. These higher-energy configurations

tend to have higher centrosymmetric order and lower acentric order than the thermodynamic minimum and thus lower electro-optic activity is observed than for case where a global energy minimum is reached in the poling experiment. The adiabatic volume adjustment (AVA) method for accelerating simulation convergence has been developed to solve this problem.<sup>9-11</sup> During the initial steps of implementation of the AVA method, the simulation is run at low chromophore number density and constant volume with only repulsive Lennard-Jones interactions (this can be considered to mimic chromophores in a solvent). During the transition phase, the volume is gradually reduced and attractive Lennard-Jones interactions are slowly phased in and full electrostatics and poling interactions are turned on (this mimics solvent evaporation). Once interactions are fully transitioned on, the simulation proceeds in a conventional thermodynamic ensemble (typically NPT, isothermal-isobaric ensemble). AVA calculations provide faster convergence and better agreement with experiments for cases where the global minimum can be realized. Comparison of AVA simulation results with conventional NPT simulation results can provide insight into kinetic trapping effects. For the chromophores shown in Fig. 1, the YLD-124 chromophore shows a propensity for kinetic trapping in poorly ordered states. AVA simulations illustrate the importance of the modifications at the donor end of the chromophore, leading to JRD1, which reduces the propensity for trapping.

Coarse-grained Monte Carlo simulations have led to a number of important observations including the subtle nature of the trade-off between improving poling-induced acentric order ( $\langle \cos^3\theta \rangle$ ) and decreasing chromophore number density ( $\rho_N$ ) that is associated with such chromophore modifications. Indeed, a number of properties must be considered in the modification of chromophores including material matrix hardening (chemical crosslinking) protocols that must be implemented in the latter stages of poling to elevate material glass transition temperatures to values on the order of 200°C. Such high glass transition temperatures are necessary to assure adequate thermal and photochemical stability that exceed Telcordia standards.<sup>1</sup> Chromophore modification can also be used to influence the matrix dimensionality that impacts chromophore rotational freedom during poling. Reduced matrix dimensionality (e.g., from 3-D to 2-D or even lower) can lead to improved acentric order and thus improved electro-optic activity.<sup>12-15</sup> As already noted from a comparison of YLD-124 and JRD1, modification can also influence viscoelastic properties and trapping in higher energy, poorly-ordered states. Fig. 2 shows the influence of additional modifications on the glass transition of neat, amorphous uncrosslinked chromophores.

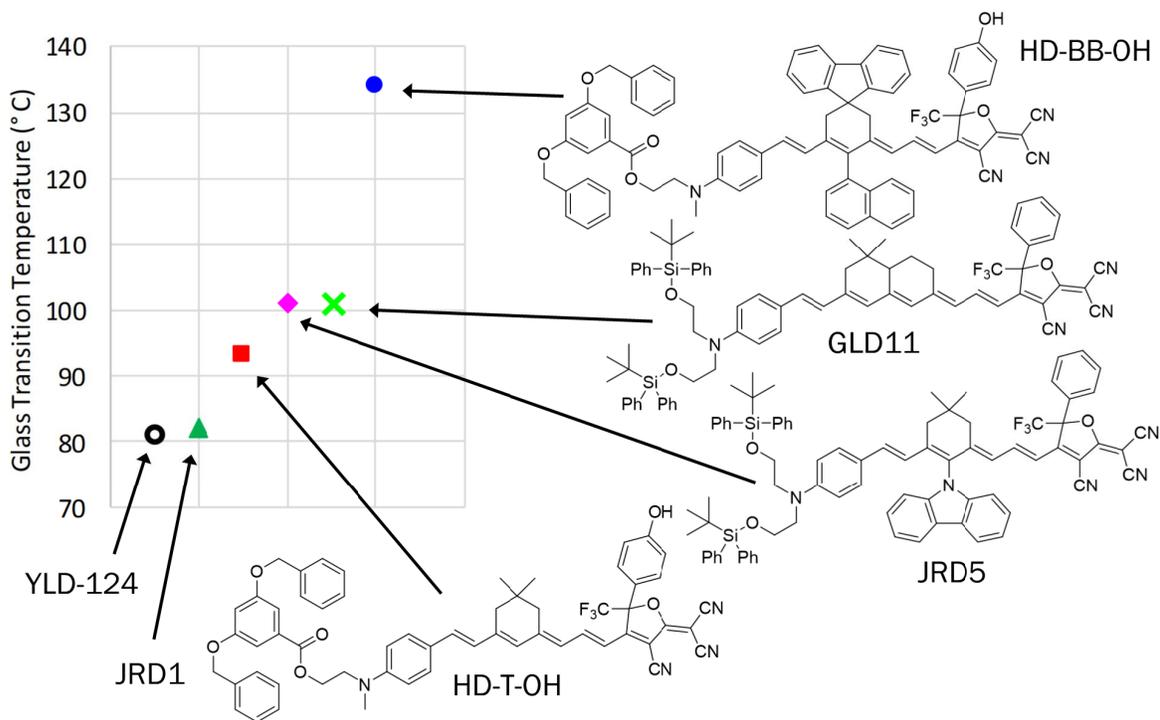


Fig. 2. The structures and glass transitions of representative chromophores are shown illustrating the tuning of glass transition with structural modification.

Control of the glass transition temperature is important for optimizing poling efficiency and lattice hardening when using thermally-activated crosslinking reactions.<sup>1</sup> Ideally, chromophore modification should serve multiple purposes including disrupting formation of centrosymmetric structures via steric hindrance, control of matrix dimensionality, improvement of viscoelastic properties, and facilitation of lattice hardening. Coarse-grained simulations have illustrated the importance of chromophore symmetry with respect to optimizing poling efficiency; straight chromophore cores are predicted to yield better electro-optic activity than bent (nonlinear) chromophore cores with similar amounts of functionalization. Of course, not all theoretically considered chromophore structures can be synthesized so synthetic expertise is a critical component in contemplating putative structures. Also, factors other than intermolecular electrostatics can impact poling efficiency. For example, the conductance of OEO materials, if too high, can reduce the effective poling field felt by the chromophores during poling and conductance can depend on chromophore modification in ways that are not easily simulated.

The details of device architectures can influence poling efficiency. The most dramatic (recently observed and simulated) effect is the dependence of electro-optic activity on the width of plasmonic-organic hybrid and silicon-organic hybrid waveguides.<sup>6,16</sup> If material conductance varies with waveguide width, changing conductance could also contribute to the experimentally observed behavior; however, simulations executed to the present suggest that the observed behavior is strongly influenced by electrostatic interactions at the interface between OEO materials and device electrodes. Indeed, the attraction to the electrodes by OEO chromophores may produce increased centrosymmetric ordering of chromophores near the electrode surfaces. This interaction appears to cause chromophores to orient along the electrode surfaces and normal to the poling field direction. Preliminary simulations of chromophores in nanoscale waveguides also appear to suggest that the transition from such chromophore orientation to bulk orientation behavior as a function of distance from the waveguide walls occurs abruptly rather than uniformly as distance from the electrode surface is increased. Obviously, more careful examination of the waveguide width dependence is required, as is further theoretical examination of chromophore cooperativity; however, the current studies already emphasize the importance of considering interfacial interactions in optimizing the performance of devices with nanoscopic waveguide widths. The results also suggest the possibility of reconsidering the utility of sequential synthesis processing protocols<sup>1</sup> as covalent modification of surfaces and use of covalent bonds to influence chromophore assembly clearly has potential for improving chromophore order in very thin films. It should also be kept in mind that it is already clear that the details of chromophore structure can influence interfacial interactions; for example, while JRD1 affords the lowest  $U_{\pi L}$  values in films with widths greater than 150 nm, DLD164 yields the smallest values for the narrowest waveguide widths.<sup>16</sup> This is, of course, not unexpected from a consideration of their structures shown in Fig. 1; however, there may be even more effective modified chromophore structures than DLD164.

A variety of device structures have been examined recently.<sup>6,17-28</sup> These range from phase, Mach Zehnder amplitude, and In-Phase Quadrature (IQ) modulators to various resonant antenna and ring resonator structures. 100 Gbd operation of a plasmonic intensity modulator has been demonstrated with a bandwidth of  $> 170$  GHz.<sup>22</sup> Plasmonic photonic modulators (PPM) have been integrated into resonant antenna structures (e.g., a four-clover leaf shaped antenna), where the antenna arms are directly connected to the plasmonic slot of the PPM.<sup>23</sup> The resonance enhances the voltage drop across the plasmonic slot resulting in a field strength increase on the order of 92,000. Direct conversion of free-space wireless radio signals to the optical domain is accomplished without the use of electronics. Integration of multiple PPMs on a chip permitted fabrication of a plasmonic beam forming array for 60 GHz beamforming. Higher resonant frequencies can be accessed by downscaling resonator dimensions.

An important research objective in plasmonics is reduction of insertion loss for plasmonic devices. Plasmonic waveguide propagation loss necessitates the use of short devices, specifically, lengths,  $L$ , under  $20 \mu\text{m}$ . Two recent publications represent different approaches to minimizing insertion loss associated with utilization of plasmonic modulators. In a recent *Science* article, propagation loss is minimized by directly integrating an all metal Mach Zehnder plasmonic modulator to a multi-core silica fiber using a vertical grating coupler and a polarization rotator (see Fig. 3),<sup>25</sup> thus eliminating loss associated with silicon photonic waveguides frequently used with plasmonic devices.<sup>6</sup> Four-level pulse-amplitude modulation (PAM4) operation at 116 Gbit/s was demonstrated with a modulator with overall dimensions of  $36 \mu\text{m}$  by  $6 \mu\text{m}$ . A bit error ratio (BER) of  $1.7 \times 10^{-3}$  was reported, which is below the hard-decision forward error correction (HD-FEC) limit. The BER improved to  $5.6 \times 10^{-6}$  for 72 Gbit/s (PAM2) operation. An energy efficiency of 30 fJ/bit was reported for 116 Gbit/s operation. This approach minimized optical loss by eliminating the need for a silicon photonic waveguide to transition between silica fiber and the plasmonic modulator. In a second approach, it has been demonstrated that insertion loss can be reduced below 3 dB without suffering an unacceptable reduction in bandwidth or thermal stability by resorting to resonant structures.<sup>4</sup>

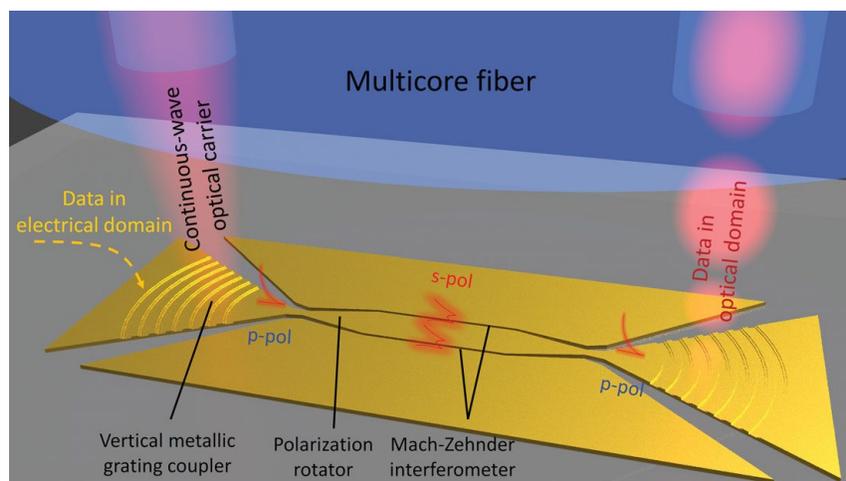


Fig. 3. A schematic illustration of an all-metal plasmonic Mach Zehnder modulator integrated with an organic electro-optic material is shown. Reproduced with permission from reference 25.

## 2. RESULTS AND DISCUSSION

Electro-optic coefficients in the range 400-550 pm/V are observed for  $\mu\text{m}$  thick films of OEO materials such as shown in Fig. 1, while values in the range 90-390 pm/V are observed in ultra-thin films with thicknesses (electrode separations) of less than 150 nm. As noted in the previous section, JRD1 exhibits larger electro-optic activity than DLD164 in thicker films but the reverse is true for the narrowest waveguide widths (electrode separations). These results are reasonably well understood and will not be discussed further here. Rather, we now turn attention to the further improvement of OEO materials and the performance of devices incorporating new materials. The objective of the following report and discussion is to illustrate lessons learned from past studies and to discuss the process being followed to produce next generation materials and devices. In particular, a brief overview of promising work in progress is given.

Multi-scale simulation starts with quantum mechanical calculations, most commonly involving hybrid density functional theory (DFT) methods. These calculations are used to provide electronic structural information that is fed into coarse-grained statistical mechanical methods such as Monte Carlo simulations. Quantum calculations are also used to identify promising chromophore structures. Considerable effort has been expended comparing various computational alternatives and identifying the amount of exact Hartree-Fock exchange that leads to the best calculation of relative molecular first hyperpolarizability,  $\beta$ .<sup>1,29-34</sup> It is relative, rather than absolute,  $\beta$  values that are particularly useful in down-selecting putative chromophores for synthesis and further investigation.<sup>1,29-34</sup> Dielectric and frequency effects are now routinely simulated in the initial identification of relative  $\beta$  values of chromophores considered for synthesis and modification for integration into devices.<sup>34</sup> Quantum mechanical considerations come full circle in the feedback loop involving quantum/statistical/quantum mechanics when chromophore distributions from coarse-grained statistical mechanical calculations are used to execute quantum mechanical calculations on strongly interacting chromophores in condensed phase organic electro-optic materials.<sup>31</sup>

There exists a virtually endless array of potential chromophore structures to choose from as a starting point for the development of a new OEO material. Prior theoretical and experimental work has identified chromophores based on a polyene bridge as commonly exhibiting the largest  $\beta$  values and thus representing the most promising class of chromophores for further and more detailed exploration. Isophorone group protection of the polyene bridge has been shown to significantly enhance photochemical stability and provide a convenient site for chemical derivatization/functionalization.<sup>1,35-38</sup> However, even restricting consideration to chromophores based on polyene bridges leaves an enormous number of candidates for consideration as illustrated in Fig. 4. In this figure, basic chromophore structures CLD-1, GLD-1, and ZLD are shown to illustrate how electro-optic activity can increase as the length of the polyene bridge is extended. Basic chemical reactions related to chromophore synthesis are also illustrated, as is the

modular nature of organic electro-optic chromophores. It is at this point in the consideration that lessons learned from previous coarse-grained statistical mechanical calculations and experimental measurements come into play.

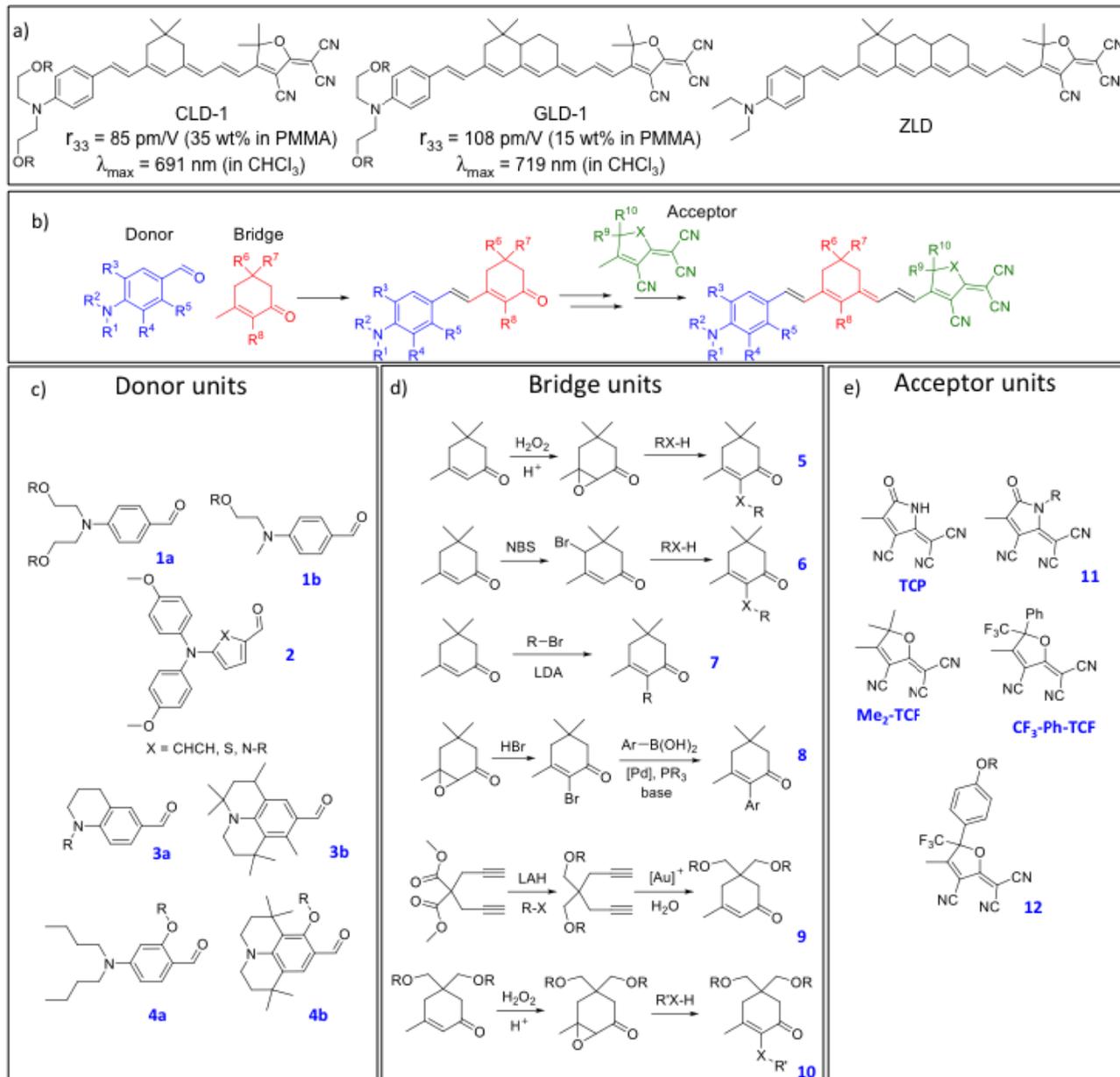


Fig. 4. a) Improvement of electro-optic activity with chromophore length is illustrated for isophorone-protected, polyene bridge chromophores CLD-1, GLD-1, and ZLD. b) through e) The modular nature of OEO chromophores is shown together with illustration of synthesis schemes for assembling donor, bridge, and acceptor building blocks into CLD-type chromophores.

Before the introduction of POH devices, an effort was made to keep optical propagation loss associated with OEO materials to 1-2 dB/cm at telecommunication wavelengths. Thus, chromophores with lengths longer than CLD-1 were not pursued. However, recently it has been shown<sup>39</sup> that the optical propagation loss associated with OEO materials is typically smaller than corresponding plasmonic losses so that shorter operational optical wavelengths or longer chromophore core lengths can usefully be considered to enhance both  $r_{33}$  and index of refraction,  $n$ , without unwanted

impact on propagation loss. Figs. 5 and 6 illustrates how index of refraction values (for unpoled samples of JRD1 and GLD11) vary with chromophore length (Fig. 5) and with wavelength and chromophore concentration (JLD1, Fig. 6).

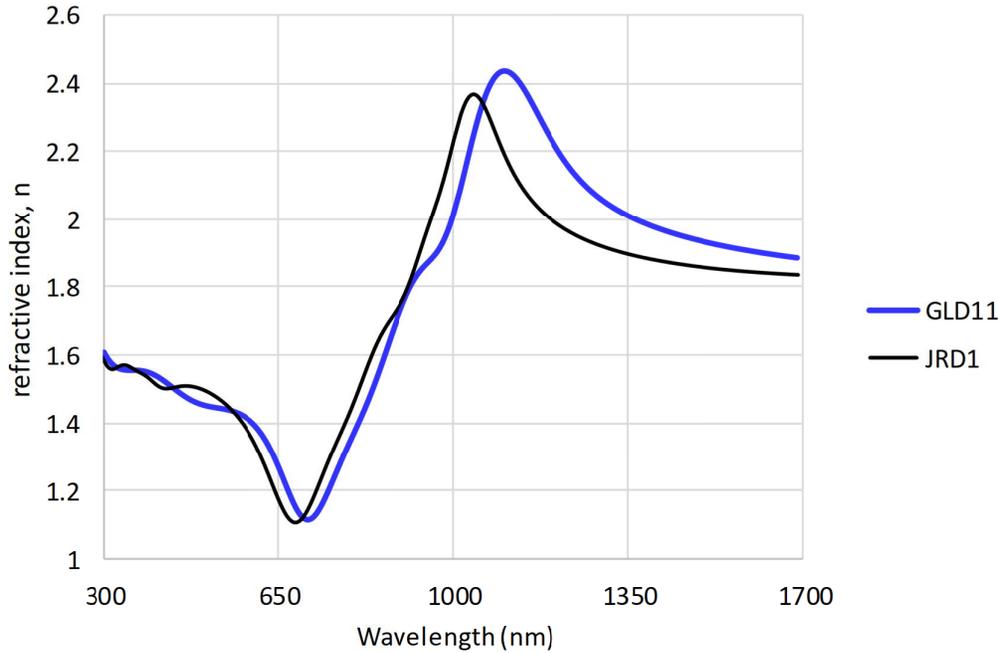


Fig. 5. VASE data illustrating the variation of isotropic refractive index with chromophore length. GLD11 (see Fig. 2) is the JRD1 analog of GLD1 (see Fig. 4). Data are shown for unpoled samples.

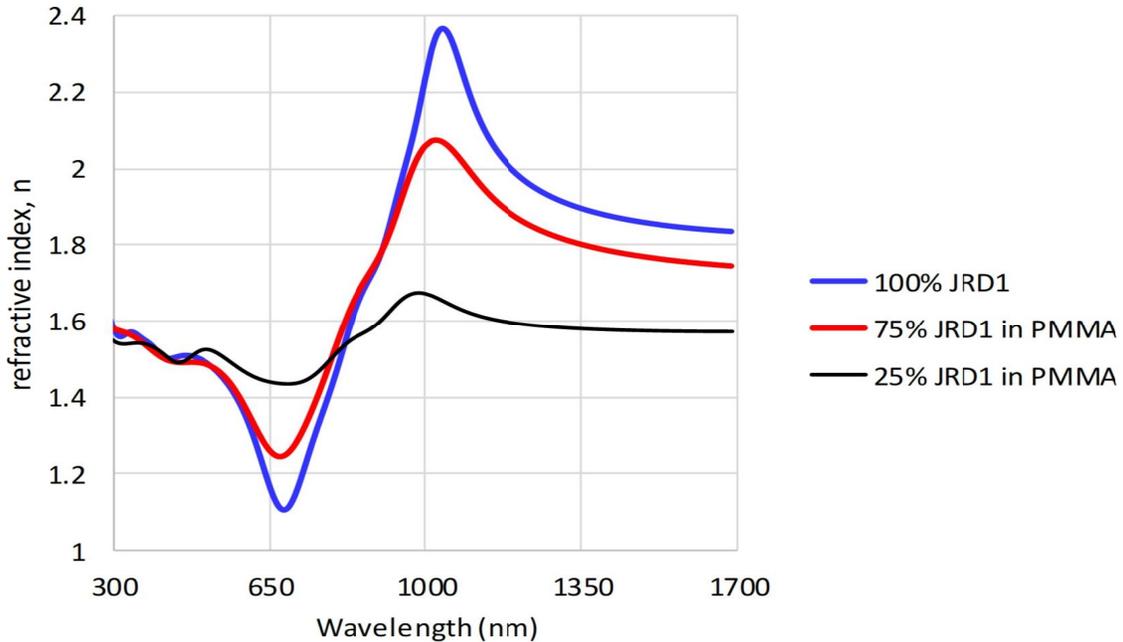


Fig. 6. VASE measurements of thin films of JRD1 on glass substrates are shown as functions of chromophore concentration (number density) and wavelength. PMMA is poly(methylmethacrylate). Data are shown for unpoled samples.

This is an important observation because it not only permits improvement of  $\beta$  and  $n$  (and thus  $n^3 r_{33}$ ) but also permits reduction of device insertion loss because shorter device lengths,  $L$ , can be utilized if larger electro-optic activity or lower  $U_{\pi}L$  are available. Another important observation deriving from coarse-grained Monte Carlo calculations is that chromophores with dipole moments on the order of that of YLD-124 yield optimum  $r_{33}$  (more precisely optimum  $\rho_N \langle \cos^3 \theta \rangle$ , where  $\rho_N$  is the chromophore number density in units of  $10^{20}$  molecules/cm<sup>3</sup> and  $\langle \cos^3 \theta \rangle$  is the poling-induced acentric order parameter, which varies between 0 and 1). As can be seen from Fig. 7 (showing calculated relative  $\beta$  values for current and putative chromophores), chromophores with this range of dipole moment values are also predicted to exhibit optimum  $\beta$  values. Fig. 7 illustrates that factors of 4-5 improvement in  $\beta$  may be expected with synthesis of new chromophores such as shown in Fig. 4 with dipole moments close to that of YLD-124. Improvement is derivative partially from a longer  $\pi$ -electron conjugation length and partially due to more effective donor and acceptor moieties and better control of chromophore conformation through utilization of steric interactions.

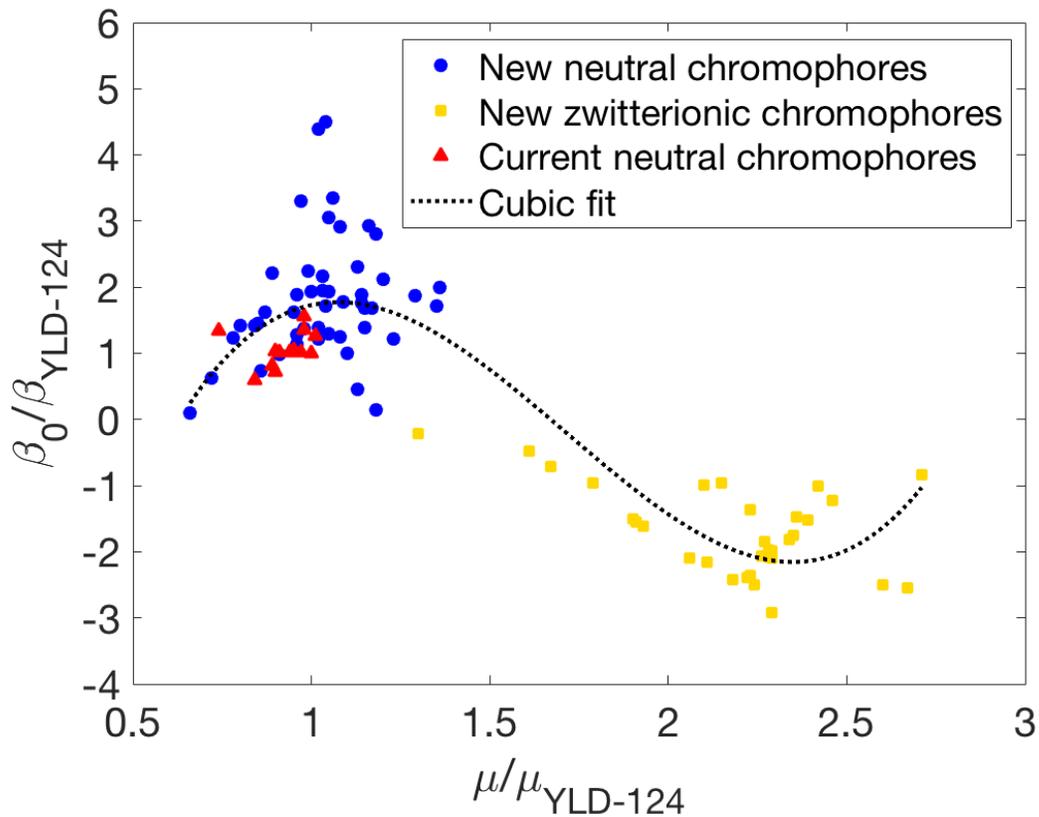


Fig.7. Relative (vs. benchmark chromophore YLD-124) molecular first hyperpolarizability and dipole moments of existing chromophores (shown in red) and new designs (shown in blue and yellow) calculated at the M062X/6-31+G(d) level of theory in PCM chloroform are shown and plotted against each other. Two maxima are observed, one at a similar dipole moment to YLD-124, and another for zwitterionic chromophores (negative hyperpolarizability, shown in yellow) with much large dipole moment. Because of exceptionally strong centrosymmetric aggregation, it has proven extremely difficult to pole zwitterionic chromophores. Some new chromophores (shown in blue) are predicted to exhibit 4.5 times larger  $\beta$  values.

The next stage of development of OEO materials is to modify the structure of promising chromophores to optimize poling efficiency, yield desired viscoelasticity, and facilitate lattice hardening. The importance of structure has already been illustrated in our discussion of YLD-124, JRD1 and DLD164. Other modifications have been discussed in the literature.<sup>33-38</sup> Some lessons learned regarding modification have been that chromophore symmetry (linear vs. nonlinear), site isolation, control of added intermolecular dipolar and quadrupolar interactions, and utilization of binary

chromophore materials are important considerations. As already noted, it is important to achieve multiple improvements with a single modification to avoid excessive reduction of chromophore number density (and corresponding impact on electro-optic coefficients and index of refraction values).

For example, preliminary modifications to facilitate crosslinking (lattice hardening) based on Diels-Alder cycloaddition have been carried out for recently developed chromophores. In most cases, this modification has been accomplished without attenuation of poling-induced electro-optic activity. This is because such modification often yields improved site isolation that permits  $\langle \cos^3\theta \rangle$  to be increased sufficiently to offset the effect of reduction of chromophore number density on electro-optic activity and index of refraction. Another route to keeping chromophore number densities high while exploiting an expanded range of intermolecular interactions and chromophore symmetries is to mix two chromophores to form binary chromophore organic glasses.<sup>1,38,40</sup> Both enthalpic and entropy interactions can be exploited and some of the largest poling efficiencies are observed for binary chromophore organic glasses. One of the binary chromophores can be used to influence matrix dimensionality and thus poling efficiency of both chromophores, permitting implementation of new processing techniques such as laser-assisted electric field poling.<sup>14</sup>

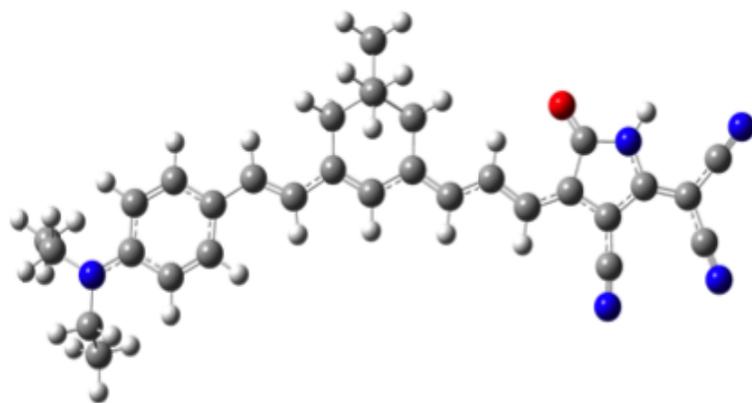
It is important in discussing OEO materials to note that although theory-assisted design has resulted in the improvement of  $\langle \cos^3\theta \rangle$  and  $r_{33}$  by approximately an order of magnitude,  $\langle \cos^3\theta \rangle$  values are still only on the order of 0.2. If improved  $\beta$  chromophores under development can be translated to even this level of poling-induced acentric order then electro-optic activity should increase by a factor of 2 to 4. Statistical mechanical simulations suggest that with appropriate modification of the cores of new chromophores, acentric order should be capable of being improved by at least 50% while maintaining acceptably high chromophore number density. Moreover, the longer lengths (and somewhat red shifted interband transitions) should yield somewhat increased index of refraction values, which should also help to somewhat reduce  $U_{\pi}L$  values. Variable angle spectroscopic ellipsometry (VASE) measurements, shown in Fig. 5 illustrate the change of index of refraction ( $n$ ) with changing chromophore length. Of course, longer chromophore lengths and greater poling efficiency can lead to greater poling induced index of refraction anisotropy that will need to be taken into account in the analysis of device performance, e.g., for estimation of in-device  $r_{33}$  values from measured  $U_{\pi}L$  values. Although measurement of both odd,  $\langle \cos^3\theta \rangle$ , and even,  $\langle \cos^2\theta \rangle$ , order parameters together with measurement of the anisotropy of  $k$  and  $n$  have been pursued for earlier chromophores, the low order parameters together with the offset of operational telecommunication wavelengths from material resonances resulted in such small anisotropies in the refractive index that they could be neglected in the analysis of in-device  $r_{33}$  and device performance.<sup>41</sup> However, it should be noted that VASE measurements have been very helpful in understanding subtle features of chromophore organization and matrix dimensionality when the linear dichroism of different components of the OEO material could be followed simultaneously by examining non-overlapping resonances (linear optical transitions).<sup>12,13,15,41</sup>

Higher level of analysis and utilization of multiple characterization methodologies have been a hallmark of evolving OEO research, e.g., introduction of variable angle polarization referenced absorption spectroscopy (VAPRAS); measurement of both  $r_{33}$  and  $r_{13}$  using attenuated total reflection (ATR): measurement of  $\langle \cos^3\theta \rangle$  by vibrational sum frequency generation spectroscopy; etc.<sup>1</sup> These have been particularly important because of the low poling-induced order associated with electric field poled OEO materials (as contrasted to highly ordered crystalline electro-optic materials). Such low order is obviously a challenge to characterize with high accuracy. Use of covalent bonds to define acentric order as pursued in the sequential synthesis/self assembly method<sup>1</sup> may be a way to significantly increase order beyond values of 0.3, but this will require theoretical guidance as the same intermolecular interactions addressed in electric field poling still come into play.

Minimization of the attenuation of electro-optic activity with decreasing waveguide width (electrode separation for plasmonic modulators) is a critical concern. Although this phenomenon has been observed for all OEO materials investigated to this point in time<sup>16</sup>, it is clear (as demonstrated by the comparison of the behaviors of JRD1 and DLD164) that chromophore structure (particularly with respect to steric or site isolation characteristics) impacts the observed behavior. So for the narrowest waveguides, it may be appropriate to somewhat sacrifice chromophore number density to achieve improved acentric order (or more precisely, to recover some of the acentric order lost to interfacial interaction effects). Synthetic feasibility has been demonstrated on some of the most promising chromophores (see Figs. 7 and 8) under consideration; it remains to appropriately modify these chromophores to address the issues discussed above. Surface modification of electrodes is also being explored in an effort to reduce unwanted interfacial interactions that attenuate poling efficiency. Finally, we note that theoretical calculations and experimental measurements are being extended to include a more first principles evaluation of index of refraction properties as well as electro-optic properties in order to refine the analysis of material and device performance. Such analysis is appropriate and important if acentric

order can be increased while achieving high chromophore number densities as this will lead to index of refraction anisotropy that will need to be considered.

In-device electro-optic activity can likely be significantly improved (by a factor of 3-6) through improvements in molecular first hyperpolarizability and acentric order while maintaining chromophore number densities at current levels. Somewhat larger index of refraction values associated with longer chromophore lengths may also contribute to small improvements in device performance, i.e., reduction in  $U_{\pi}L$ . Much larger improvements can be achieved for the narrowest waveguide widths by modifying chromophores or electrode surfaces or both to reduce the attenuation of electro-optic activity that now occurs with decreasing waveguide width. In summary, it is not unreasonable to anticipate that an order of magnitude improvement in performance can be achieved, although it should be kept in mind that in-device electro-optic activity will likely continue to vary for different device architectures and poling conditions and different OEO materials may well be required for different applications.

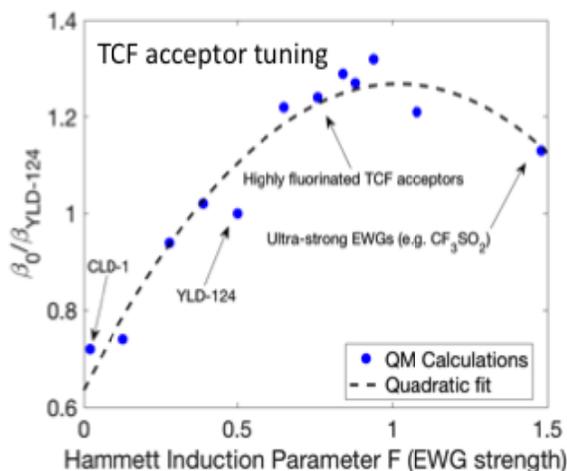


### TCP-CLD vs. YLD-124

Rel.  $\beta_0$ : 1.6

Rel.  $\mu$ : 0.87

$\Delta\lambda$ : +92 nm



Modification type	Best Improvement vs. YLD-124 $\beta_0$
TCF Acceptor tuning	1.32x
TCP Acceptor tuning	1.95x
Bridge extension	1.77x
Novel donors	2.25x
Best combined effect	4.5x

Fig. 8. The recently-synthesized TCP-CLD chromophore (top) is predicted to have a significant improvement in static hyperpolarizability vs. YLD-124 and JRD-1, while preserving a favorable dipole moment and exhibiting a large red-shift of its primary charge transfer peak that could contribute to increased resonance enhancement and higher index of refraction values at operating wavelengths. A wide variety of modifications have been studied computationally (bottom) using QM calculations at the M062X/6-31+G(d) level of theory in PCM chloroform, indicating particularly large potentials from longer bridges, new donors, and TCP acceptor variants. These effects can combine to produce chromophores with performance predicted to be greatly in excess of YLD-124. EWG stands for electron withdrawing group.

Quantum mechanical calculations (see Fig.8) have been used to investigate the potential impact of various chromophore core modifications (bridge extension, donor modification, acceptor modification) on molecular first hyperpolarizability,  $\beta$ . The various modifications shown are not simply additive, but quantum calculations permit evaluation of the cumulative effects and illustrate the range of change that is possible with each type of modification. Fig. 8 also illustrates that the strongest acceptors (and strongest donors—not shown) need to be avoided as they drive chromophores toward the zwitterionic limit leading both to attenuation of  $\beta$  and increase in  $\mu$ . The dipole moments,  $\mu$ , of zwitterionic chromophores are so large as to make it difficult to achieve desired poling efficiency by chromophore core derivatization (e.g., addition of site isolation moieties). Since the dipole moments of the new “neutral ground state” chromophores are very similar to previously studied chromophores such as YLD-124 and since the core structures are not radically different, it can be anticipated that the chromophore core derivatizations that have worked well in the past will work well for newly synthesized chromophores. Coarse-grained statistical mechanical simulations are currently being run for putative modifications and are being used to guide derivatization of the most promising new chromophores (shown in blue in Fig. 7).

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