Refractive Index Engineering of Advanced Optoelectronics Materials

I. C. Khoo
Electrical Engineering Department
The Pennsylvania State University
University Park, PA 16802 USA

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* AFOSR * NSF [MRSEC] * ARO * DARPA
Recent Publications


Absorption spectrum (ground state) of some organic Liquid and Liquid Crystals

Absorbance (cm\(^{-1}\)) vs. Wavelength (nm)

Broadband Limiting Application
400 nm – 900 nm
Multiple-Time-Scale
(fs - ps - ns - μs - ms - cw)

1mm cell
Chemical synthesis and molecular engineering to provide new functionalities – extending bandwidth of response

- Potential function dictates the energy levels
- Dielectric constant:
  \[ \varepsilon \sim \varepsilon (\rho_{ii} - \rho_{jj}; d_{ij}); \mu \sim \mu_0 \]

\[
\left( \frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_{\text{ext}}(\vec{r}, t) - i\hbar \frac{\partial}{\partial t} \right) \Psi(\vec{r}, t) = 0
\]
New neat Nonlinear optical organic liquids quantum molecular energy levels calculation

DPY1: diphenyl acetylene
DPY1-L34: 4-propyl 4'-butyl diphenyl acetylene
DPY2: 1,4-diphenylbutadiyne
DPY2-L44: 4,4'-butyl 1,4-diphenylbutadiyne
DPY3: 1,6-diphenylhexatriyne
1. The calculations were performed using TD-DFT method. The relevant molecular orbitals for ground state $^1\text{Ag}$ are listed below.

$\pi$-type Occupied Orbitals

- HOMO (b3u)
- HOMO-1 (au)
- HOMO-2 (b1g)
- HOMO-3 (b2g)
- HOMO-4 (b2u)

$\pi$-type Unoccupied Orbitals

- LU MO (b2g)
- LU MO+1 (b1g)
- LU MO+2 (au)
- LU MO+3 (b3u)
- LU MO+4 (b2u)
Excited State absorption of neat liquid DPY1-L34 containing DPY2-L44

$\lambda_{\text{exc}} = 410 \text{ nm}$

$\lambda_{\text{exc}} = 480 \text{ nm}$

Observed peaks at 410 nm and 480nm are in agreement with theoretical calculations for DPY1-L34 and DPY2-L44. Transient excited state measurements at PSU and WPAFB [to be published].
Chemical synthesis and molecular engineering + intermolecular correlations $\rightarrow$ liquid crystalline phases with emergent properties otherwise absent in the constituents molecules

Self-organization via local and long-range order (molecular correlations) – usually non-polar arrangement of dipoles

$\equiv$ + others

nematic  smectic  cholesteric
Liquid Crystals for very Broadband Optical Applications

400 nm – 12 microns – Terahertz - Microwave

Molecular structures of liquid crystals and their broadband birefringence.


Samble - Microwave Region,” Liquid Crystals, 30, pp599-602 [2003]

Electro-Optics Display
Crossland, Coles, Collings…et al
http://www-g.eng.cam.ac.uk/photonics
Motivations:

1. Design and create new materials with unique and useful functionalities and emergent properties so that the materials will enable new processes or vastly improve current performance of switches, filters, imagers, sensors, and sensor protection devices….etc

2. Learn new physics, chemistry, nano-technologies,

3. Materials with index ~1 and low loss will be very useful
   New material design guidelines, compact high performance devices, …. so on
Meta-materials - Design and Engineering Real and Imaginary Parts of

\[ \varepsilon(\omega_1, \omega_2, \omega_3...) = \varepsilon'(\omega'S) + i\varepsilon''(\omega'S) \text{ and } \mu(\omega'S) = \mu' + i\mu'' \]

so that \( n = (\mu\varepsilon)^{1/2} \) can be <1, 0 or <0

Tuning of the material enabled by the electro-optics and/or nonlinear optical response of one of the constituents.
Liquid Crystal Optical Metamaterials - ‘dispersion engineering’ for emergent “unconventional” optical properties

Conventional Wisdom:
Vacuum $n = 1$
Materials: $n > 1$ ; $n > 0$

Meta-materials:
Appropriate ‘combining’ of material constituents of dielectric constant $\varepsilon_i(r)$
and creating effective dielectric constant $\varepsilon_{\text{eff}} \sim \varepsilon_{\text{eff}} \{\varepsilon_3, \varepsilon_2, \varepsilon_1, \mu\}$’s
Avô Permeability $\mu_{\text{eff}} \sim \mu_{\text{eff}} \{\varepsilon_3, \varepsilon_2, \varepsilon_1, \mu\}$’s

Resulting in refractive index that could range from sub-unity to below zero $n = (\mu_{\text{eff}}\varepsilon_{\text{eff}})^{1/2} \{ > 1, < 1, =0, < 0\}$
Sub-unity, Zero and Negative index materials
-a revisit of basic EM-

\[ n = n' + in'' \]
\[ n = \pm \sqrt{\varepsilon_r |\mu_r|} \exp\left(i \frac{\theta_\varepsilon + \theta_\mu}{2}\right) \]

• To simplify, we define a normalized permittivity and permeability

\[ \varepsilon_N' + i\varepsilon_N'' = \frac{\varepsilon_r'}{|\varepsilon_r|} + i\frac{\varepsilon_r''}{|\varepsilon_r|} = \cos \theta_\varepsilon + i \sin \theta_\varepsilon \]
\[ \mu_N' + i\mu_N'' = \frac{\mu_r'}{|\mu_r|} + i\frac{\mu_r''}{|\mu_r|} = \cos \theta_\mu + i \sin \theta_\mu \]

\[ n_N = \pm \sqrt{\varepsilon_N \mu_N} = \pm \exp\left(i \frac{\theta_\varepsilon + \theta_\mu}{2}\right) = \exp\left(i \frac{\theta_\varepsilon + \theta_\mu}{2} + i \pi\right) = n_N' + in_N'' \]

• The normalized refractive index
Sub-unity, Zero and Negative index materials
-a revisit of basic EM-(contd)

• The power flow in the +z direction is given by:

$$P_z = \frac{1}{2} \dot{z} \cdot \text{Re}\{E(z) \times H^*(z)\} = \text{Re}\left\{\left(\frac{n}{\mu_r}\right)^* \frac{|E_0|^2}{2\eta_0} \exp(-2k_0n^*z)\right\}$$

• From the condition of power flow in the positive z direction, we require

$$\text{Re}\left\{\left(\frac{n}{\mu_r}\right)^*\right\} = \text{Re}\left\{\frac{n}{\mu_r}\right\} = \text{Re}\left\{\pm \sqrt{\varepsilon_0|\mu_r| \exp\left(i\frac{\theta_\varepsilon + \theta_\mu}{2}\right)}\right\} = \text{Re}\left\{\pm \sqrt{\varepsilon_0|\mu_r| \exp\left(i\frac{\theta_\varepsilon - \theta_\mu}{2}\right)}\right\} > 0$$

• which means we need to choose the sign so that

$$\pm \cos\left(\frac{\theta_\varepsilon - \theta_\mu}{2}\right) > 0$$
Plug back to the definition of refractive index, we have

\[ n = \text{sign} \left( \cos \left( \frac{\theta_e - \theta_\mu}{2} \right) \right) \sqrt{\varepsilon_r \mu_r} \exp \left( i \frac{\theta_e + \theta_\mu}{2} \right) \]

Equivalently, \( n \) is given by:

\[ n = \text{sign} \left( \cos \left( \frac{\theta_e - \theta_\mu}{2} \right) \cos \left( \frac{\theta_e + \theta_\mu}{2} \right) \right) \sqrt{\varepsilon_r \mu_r} = \text{sign} \left( \cos \theta_e + \cos \theta_\mu \right) \sqrt{\varepsilon_r \mu_r} \]

The sign of the refractive index is therefore given by:

\[ \text{sign} \left( \cos \theta_e + \cos \theta_\mu \right) \]
(a) Regions in ‘phase space’ of positive index (reddish) and negative index (blue) behavior and 3-D plot of the real normalized refractive index. (b) Regions in phase space where the material is lossy (reddish) or exhibits gain (blue) and 3-D plot of the imaginary normalized refractive index.
Nano-Dispersed Liquid Crystals [NDLC] for Electro-Optical and Nonlinear Optical NIM-ZIM and LIM

NDLC - Aligned nematic liquid crystal containing nano coated-spheres

Response of a Nano-sphere Dispersed Liquid Crystal (NDLC)

Core - Polaritonic Material Response (LiTaO₃):
\[ \varepsilon_1 = \varepsilon(\infty) \left( 1 + \frac{\omega_p^2 - \omega_1^2}{\omega_p^2 - \omega_1^2 - i\omega\gamma_1} \right) \]

Shell - Drude material
\[ \varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_2} \]

Host - Birefringent nematic liquid crystal (NLC):
\[ \varepsilon_3 = \frac{\varepsilon_∥ \varepsilon_⊥}{\varepsilon_∥ \cos^2 \theta + \varepsilon_⊥ \sin^2 \theta} \]
\[ k_3 = \sqrt{\varepsilon_3 k_0} = \left( \frac{\varepsilon_∥ \varepsilon_⊥}{\varepsilon_∥ \cos^2 \theta + \varepsilon_⊥ \sin^2 \theta} \right)^{1/2} k_0 \]

Effective permittivity
\[ \varepsilon^{\text{eff}} = \varepsilon_3 \frac{k_3^3 + j4\pi N\alpha r}{k_3^3 - j2\pi N\alpha r} \]

Effective permeability
\[ \mu^{\text{eff}} = \frac{k_3^3 + j4\pi N\beta r}{k_3^3 - j2\pi N\beta r} \]

Nano-Dispersed Liquid Crystals [NDLC] Tunable NIM-ZIM and LIM

**Challenges of current work:**
Volume Fraction; Loss

Optical Region

Terahertz Region
Model selection

A. D. Rakic, A. B. Djurisic, J. M. Elazar and M. L. Majewski,
Figure 4. Real part ($n$) and imaginary part ($k$) of refractive indices of gold nanoparticles dispersed at various volume fractions in $n$-dodecane. (a) Experimental results. (b) Calculated results.

Coated nanoshells

- Calculation of the real part ($n$) and the imaginary part ($k$) of the refractive index for silica-gold core-shell nanospheres dispersed in a NLC, the radius for the silica core is 10nm with a permittivity of 3.8, and the thickness for the shell (gold) is 5nm. The filling fraction is 0.25. The permittivity of the host medium (NLC) is varied from 2.0 to 4.0 in step of 0.5.

- Calculation of the real part ($n$) and the imaginary part ($k$) of the refractive index for silica-silver core-shell nanospheres dispersed in a NLC, the radius for the silica core is 10nm with a permittivity of 3.8, and the thickness for the shell (silver) is 5nm. The filling fraction is 0.25. The permittivity of the host medium (NLC) is varied from 2.0 to 4.0 in step of 0.5.
Photonic Crystals-Dispersed Liquid Crystalline Metamaterials
Liquid Crystal Infiltration

- Hydrophilic (untreated) samples
  - Infiltrated with pure 5CB at 50°C.
  - Drop at gap of the sample cell.
  - Immediate color change.

- Hydrophobic (treated) samples
  - Infiltrated with a mixture of 5% 5CB in ethanol at 20°C.
  - Drop at edge of partially open cell.
  - Gradual color change with repeated application
  - Post infiltration ensured ethanol removal.

5CB

$C_5H_{11}$ \(-\) \(\begin{array}{c} \text{CN} \\ \end{array} \)

$n = 1.522$ to $1.706$
Electric Field Tuning: 
TiO$_2$ Large-pore inverse shell opals

- Reflectance spectra for increasing applied electric field (bipolar square wave at 1 kHz) for 2 large-pore samples.

Hydrophobic treated 
Hydrophilic

Periodic Metallo-Dielectric Structures

Frequency Selective Surfaces

Introducing electro-optical and all-optical tuning and modulation capabilities with the incorporation of liquid crystals

Utilizing the broadband and Large Birefringence and Nonlinearity of liquid crystals for low power threshold and broadband [optical – microwave] application
(Conventional) FSS - Introduction

- AC Current induced on metal at wavelength resonant with periodic geometry
- Surface looks like solid perfect electric conductor at this wavelength
- Energy at this wavelength reflected

- Frequency response scales with element dimensions
  - FSS designs developed at microwave and RF can be adapted to IR and visible by using micro- or nanofabrication to scale the dimensions
P-FEBI (Finite Element Boundary Integral) for Bi-Anisotropic Materials

\[
\begin{align*}
D &= \varepsilon_0 \varepsilon_\text{r}(r) \cdot E + \sqrt{\varepsilon_0 \mu_0} \zeta_\text{r}(r) \cdot H \\
B &= \sqrt{\varepsilon_0 \mu_0} \zeta_\text{r}(r) \cdot E + \mu_0 \mu_\text{r}(r) \cdot H \\
\nabla \times E &= -j \omega B \\
\nabla \times H &= j \omega D + J_i
\end{align*}
\]

**Frequency-domain implementation**
- FE-BI formulas for bi-anisotropic materials
- Brick element for FE part; Rooftop basis for BI part
- Ewald transformation for Periodic Green’s function
- For scattering and radiation problems

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**Top surface: BI**
- Periodic Green’s function \((\varepsilon_\text{r}, \mu_\text{r})\)

**Bottom surface: BI**
- Periodic Green’s function \((\varepsilon_2, \mu_2)\)

**Inhomogeneous Bi-anisotropic materials**

**FEM applied**

**External source**

**Internal source**
Electromagnetic Analysis and Optimization of NIMs and ZIMs

- **Periodic MoM** (metallo-dielectric FSS structures)
- **Periodic FDTD Method** (including anisotropic, chiral, and bi-anisotropic materials)
- **Periodic FEBI Method** (inhomogeneous all-dielectric structures)

**Particle Swarm Optimization**

**Genetic Algorithms**

1. Define Parameters & Fitness Function
2. Encode Parameters into Binary String
3. Randomly Generate Initial Population
4. Evaluate Fitness of Each Member
5. Fitness Goal Achieved?
   - YES: Stop
   - NO: Fill New Generation
     - Tournament Mate Selection
     - Single-point Crossover
     - Mutate Randomly
     - Keep Current Best Member
All-Dielectric FSS with Liquid Crystal Tunable Superstrate

Unit Cell of DFSS – side view

3.04 μm

1.52 μm

1.14 μm

ε₁

ε₂

Top view

Wavelength (μm)

Frequency (THz)

Transmission (dB)

Exemplary Theories and Experimental Results on FSS

Modeled (blue) and measured (red) transmission with two strong (>20 dB attenuation) stop-bands in the mid-IR. (inset) SEM of metallo-dielectric filter. Scale, 1.5 µm.

(Top) Modeled neff for a ZIM, Scale: 4 µm.
(Bottom) Modeled (line) & measured transmission ellipsometry.
Rigorous Anisotropic Analysis (tuning the magnetic resonator)

Latest (7/14/2008) Results (Feasibility of Optical tuning in very thin sample):

Observed degenerate four wave mixing in 250 nm thick dye-doped liquid crystals. Diffraction efficiency corresponds to an index change of \( \sim 0.1 \)

Feasibility of Optically Tunable Nano-structured Meta-materials!
Self-diffraction efficiency and nonlinear index coefficients of very thin aligned nematic liquid crystal layer

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Input Beam Power (mW)</th>
<th>1st. Order Diffracted beam power (μW)</th>
<th>Diffraction Efficiency</th>
<th>Nonlinear coefficient n2 (cm²/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>50</td>
<td>25</td>
<td>5 x 10⁻⁴</td>
<td>7.5 x 10⁻²</td>
</tr>
<tr>
<td>0.8</td>
<td>54</td>
<td>33</td>
<td>6.11 x 10⁻⁴</td>
<td>2.4 x 10⁻²</td>
</tr>
<tr>
<td>1.2</td>
<td>50</td>
<td>850</td>
<td>170 x 10⁻⁴</td>
<td>9 x 10⁻²</td>
</tr>
<tr>
<td>1.7</td>
<td>38</td>
<td>245</td>
<td>64.5 x 10⁻⁴</td>
<td>5.3 x 10⁻²</td>
</tr>
</tbody>
</table>
Recent Publications


End
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- **Fundamental Concepts**
  - Mie-Scattering Theory, Material Models, Definition of Negative index material

- **Dispersion of nanoparticle in NLC**
  - Model selection, Solid spheres, Coated nanoshells
Consider an incident plane wave with magnetic field

\[ H_{\text{inc}} = H_0 \exp(\imath k_o z) \hat{y} \]

To calculate the scattered electric and magnetic field coefficients

\[ a_n \quad b_n \]

C. F. Bohren and D. R. Huffman, "Absorption and Scattering of Light by Small Particles" Wiley, 2004
Mie-Scattering Theory

- The scattered magnetic dipole is shown as followed

\[ H_{\text{sca}} = \frac{3}{2} i H_0 b_1 e^{ik_0r} \frac{k_0^2 (\hat{r} \times \hat{y}) \times \hat{r} + [3(\hat{y} \cdot \hat{r}) \hat{r} - \hat{y}]}{r^2} - \frac{ik_0}{r} \] 

- The standard expression of magnetic dipole radiation

\[ H_{\text{dipole}} = \frac{1}{4\pi} \frac{e^{ik_0r}}{r} \{k_0^2 (\hat{r} \times \hat{m}) \times \hat{r} + [3(\hat{m} \cdot \hat{r}) \hat{r} - \hat{m}]}{r^2} - \frac{ik_0}{r} \} \]

- Compare these two equations, the effective polarizability:

\[ \alpha_m = 6\pi b_1 / k_0^3 \]
Mie-Scattering Theory

• From the Clausius-Mossotti equation, the polarizability is also equal to

\[ \alpha_m = \frac{3}{N} \left( \frac{\mu_{\text{eff}}}{\mu_{\text{eff}} + 2} \right) \]

\[ f = \frac{4\pi N r_1^3}{3} \]

N is the volume density of the spheres, and the filling fraction of the composite will be

• Effective Permeability

\[ \mu_{\text{eff}} = \frac{k_3^3 + j4\pi Nb_1}{k_3^3 - j2\pi Nb_1} \]

• Effective Permittivity

\[ \varepsilon_{\text{eff}} = \varepsilon_0 \left( \frac{k_3^3 + j4\pi Na_1}{k_3^3 - j2\pi Na_1} \right) \]
Maxell-Garnett mixing rule

• Effective Permittivity

\[ \varepsilon_{av} = \varepsilon_m \left[ 1 + \frac{3 f \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} \right)}{1 - f \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} \right)} \right] \]

• Effective Permeability

\[ \mu_{av} = \mu_m \left[ 1 + \frac{3 f \left( \frac{\mu - \mu_m}{\mu + 2 \mu_m} \right)}{1 - f \left( \frac{\mu - \mu_m}{\mu + 2 \mu_m} \right)} \right] \]
Material Models

• Metals

\[ \varepsilon_r(\omega) = \varepsilon_r^{(f)}(\omega) + \varepsilon_r^{(b)}(\omega) \]

• The intraband part is described by the free-electron Drude model:

\[ \varepsilon_r^{(f)}(\omega) = 1 - \frac{\Omega_p^2}{\omega (\omega + i\Gamma_0)} \]

\[ \Omega_p = \sqrt{\frac{f_0}{f_0}} \omega_p \]

\( \Omega_p \) is the plasma frequency associated with intraband transitions with oscillator strength and damping constant.
Electron-free path

- The small size of the nanoparticles will result in a limit of the mean free path for the free electrons.

- This effect is taken into account by adding to the damping constant in the free-electron Drude model a surface scattering rate:

  \[ \sigma_s = A v_F / r \]

  where \( v_F \) is the Fermi velocity, \( A \) is a proportional factor.

- The intraband expression is modified to:

  \[ \hat{e}_r^{(f)}(\omega) = 1 - \frac{\Omega_p^2}{\omega (\omega + i(\Gamma_0 + A v_F / r))} \]
Material Models

- The interband part is described by the simple semi quantum model resembling the Lorentz result for insulators:

\[
\hat{\varepsilon}_{r}^{(b)}(\omega) = \sum_{j=1}^{k} \frac{f_j \, \sigma_p^2}{(\sigma_j^2 - \omega^2) + i \omega \Gamma_j}
\]

where \(\sigma_p\) is the plasma frequency, \(k\) is the number of oscillators with frequency \(\sigma_j\), strength \(f_j\) and lifetime \(1/\Gamma_j\)

- Usually the Gaussian line shape is a much better approximation for the broadening function than the Lorentzian line shape
Material Models

- The BB model of Gaussian line shape can be used to describe optical properties of a wide range of materials including metals.

\[ \hat{\varepsilon}_r^{(b)}(\sigma) = \sum_{j=1}^{k} \chi_j(\sigma) \]

\[ \chi_j = \frac{i \sigma_j}{2\sqrt{2\alpha_j}} \{ U[1/2,1/2,-(\alpha_j-\sigma_j)^2] + U[1/2,1/2,-(\alpha_j+\sigma_j)^2] \} \]

\( U[1/2,1/2,z^2] = \sqrt{\pi \varepsilon^2} \text{erfc}(z) \) is the Kummer functions of the second kind.

\[ \alpha_j' = \frac{\sigma_j}{\sqrt{2}} \{[1+(\Gamma_k/\sigma_j)^2]^{1/2}+1\}^{1/2} \]

\[ \alpha_j'' = \frac{\sigma_j}{\sqrt{2}} \{[1+(\Gamma_k/\sigma_j)^2]^{1/2}-1\}^{1/2} \]

Other material models

• The polaritonic materials’ relative permittivity is shown as

\[
\varepsilon_r(\omega) = \varepsilon(\infty)(1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2 - i\omega\gamma})
\]

where \(\varepsilon(\infty)\) is the high-frequency limit of the permittivity, \(\omega_T\) is the transverse optical phonon frequency, \(\omega_L\) is the longitudinal optical phonon frequency, and \(\gamma\) is the damping coefficient.

• The permittivity of the host medium

\[
\varepsilon_{\text{host}} = \frac{\varepsilon_\parallel \varepsilon_\perp}{\varepsilon_\parallel \cos^2 \theta + \varepsilon_\perp \sin^2 \theta}
\]

Model selection

- Comparison of experimentally measured and theoretically calculated refractive indices of pure dodecane and gold nanoparticles dispersed in dodecane at a volume fraction of 1.0%.

Solid line: calculated results using LD model for Au, a constant value of $A=1.4$; markers: experimental results.

Conclusion

• The nanoparticles dispersed NLC is one of those perfect combinations for the Metamaterials
• Method: by varying the parameters of this combination, e.g. the structure and the material, the dimension and filling fraction, the permittivity of the host medium and so on
• Result: it is possible for us to obtain a metamaterial with a tunable refractive index from negative to zero to positive over a very broad wavelength region (from visible to IR)
• These materials have a dramatically increased birefringence for the index so it can be called as ultra-nonlinear optical materials