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14. ABSTRACT
The objective of this project was to develop a new approach to 3-D metamaterials. A key step was developing materials with large optical activity. A series of chiral polymers, based on thiophene, fluorene, and fluorene-quinoxaline motif with chiral side chains were synthesized, post-processed and characterized in both solution and film phases. A new concept of chirality enhancement via coupling with plasmonic, excitonic and magnetic nanoparticles was introduced for the first time and verified experimentally. Theoretical models were proposed to explain the enhancement. The enhancement of nonlinear optical activity by utilizing pi-conjugated molecular building blocks was proposed and experimentally realized. Writing of sub-wavelength metal-nanoparticle-containing metamolecules was demonstrated via simultaneous photoreduction of a gold precursor and crosslinking of a photoresist using two-photon excitation, opening the way to a faster and more cost efficient "top down" manufacturing of metamaterials. Photopatternable polymer nanocomposites of chiral polymer and SU-8 photoresists were produced and photopatterning was demonstrated. Joint papers with researchers at AFRL in Dayton have been published, thus aiding in transitioning of our concepts to AFRL.

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**Development of Bottom-Up Chemical Approaches to 3-D Negative Index
Meta-Materials: Two Photon Lithographic Approach-Chiral Chemical
Synthesis Approach**

Principal Investigator

Paras N. Prasad, Ph.D.
Distinguished Professor
Executive Director
Institute for Lasers, Photonics and Biophotonics
The State University of New York at Buffalo
427 NSC
Buffalo, NY 14260-3000
Phone: (716)645-6900 ext 2098
Fax: (716)645-6945
Email: pnprasad@acsu.buffalo.edu

Submitted by:

Institute for Lasers, Photonics and Biophotonics
The State University of New York at Buffalo

Submitted to:

Air Force Office of Scientific Research
ATTN: Dr. Charles Lee
875 North Randolph Street
Suite 325, Room 3112
Arlington, VA 22203-1768

FINAL REPORT

Abstract: The objective of this project was to develop a new approach to 3-D metamaterials. A key step was developing materials with large optical activity. A unique combination of "bottom up" and "top down" approaches to produce nanostructures was successfully applied. Multiscale modeling was used to design chiral polymers. A series of chiral polymers, based on thiophene, fluorene, and fluorene-quinoxaline motif with chiral side chains, exhibiting extremely large chirality, were synthesized, post-processed and characterized in both solution and film phases. A new concept of chirality enhancement via coupling with plasmonic, excitonic and superparamagnetic nanoparticles was introduced for the first time and verified experimentally. Theoretical models were proposed to explain the enhancement. The enhancement of nonlinear optical activity by utilizing pi-conjugated molecular building blocks was proposed and experimentally realized. Writing of sub-wavelength metal-nanoparticle-containing metamolecules was demonstrated via simultaneous photoreduction of a gold precursor and crosslinking of a photoresist using two-photon excitation, opening the way to a faster and more cost efficient "top down" manufacturing of metamaterials. Photopatternable polymer nanocomposites of chiral polymer and SU-8 photoresists were produced and photopatterning was demonstrated. Joint papers with researchers at AFRL in Dayton have been published, thus aiding in transitioning of our concepts to AFRL.

Chemical synthesis and Bottom up approach:

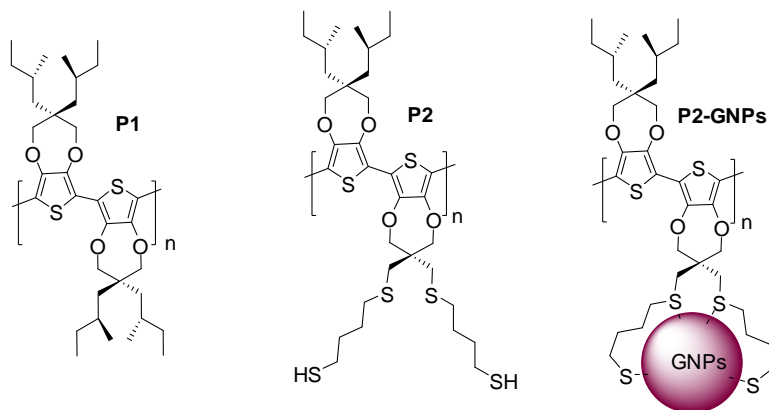


Figure 1. Thiophene-based chiral polymers.

Optical properties of a series of newly synthesized chiral polythiophene polymers mixed with metallic (gold, diameter ~5nm) and nonmetallic (CdS, diameter ~5nm) nanoparticles (NPs) were studied. Absorption, reflection and circular dichroism (CD) spectra of pure polymers, polymer/Au NP and polymer/CdS NP solutions, and spin- and spray-coated films were recorded. The chiral polymer and NPs were mixed in organic solvents that both dissolved the polymer and stably dispersed the NPs. In solid films, addition of Au NPs resulted in intensity redistribution among bands in the CD spectrum, while in solution the shape of the spectrum remained the same for both pure polymer and polymer/Au NP mixtures. In the case of nonmetallic NPs of similar size and surface capping, this effect was not observed. This provided clear evidence of plasmonic interaction between Au NPs and the chiral polymers. The polythiophene polymers are optically

active at visible wavelengths (around 500 nm). This overlap of optical activity with the localized surface plasmon resonance (LSPR) of the Au NPs, which peaks near 530 nm, facilitates plasmonic enhancement of molecular chirality by NPs.

Synthesis of functionalized and solubilized π -conjugated chiral polymers (**P1** and **P2** in Fig. 1) was performed. The chiral polymers were synthesized by Grignard metathesis polymerization. Helicity with an enantiomeric excess was sterically induced by the incorporation of chiral pendant groups into the polythiophene backbone. Attachment of appropriate chiral pendants not only produced optical activity of the helical backbone, but also improved solubility and processability of the rigid backbone for improved device fabrication. Repeating units of helical polythiophene (**P2**) can be further functionalized with one more substituent (e.g., phenyl group with or without π -electron donor/acceptor) to immobilize gold nanoparticles and obtain uniform distribution of gold NPs throughout the chiral polymer (**P2-GNPs**).

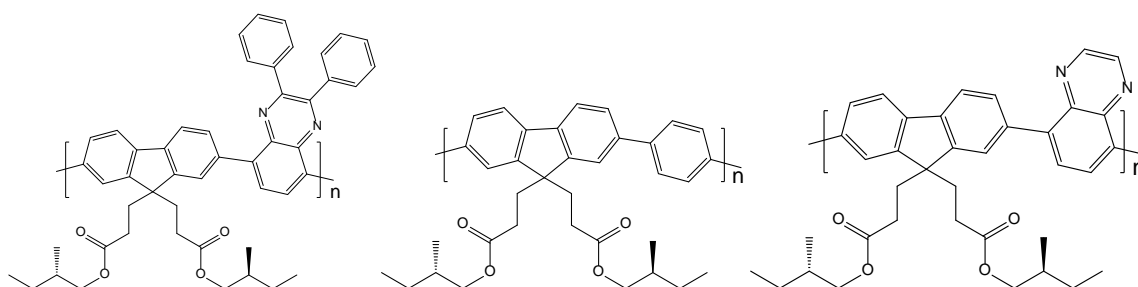


Figure 2. Newly synthesized chiral polymers. From left to right: Poly3, Poly5, Poly 6

Poly 3: poly(9,9-bis(3-((S)-2-methylbutylpropanoate))fluorene-alt-5,8-(2,3-bis(phenyl)quinoxaline))

Poly 5: (9,9-bis(3-((S)-2-methylbutylpropanoate))fluorene-alt-1,4-phenyl)

Poly 6: poly(9,9-bis(3-((S)-2-methylbutylpropanoate))fluorene-alt-5,8-(quinoxaline))

We have synthesized three new chiral fluorene-based polymers (Fig. 2) with much higher optical activity as pure films than poly(fluorenebenzothiadiazole) (PFBT) that we used in our previous studies. Poly 5 shows chirality parameter of -0.02 at 360 nm without any doping. The high intrinsic optical activity of these new chiral polymers showed great promise for achieving even higher ultimate values of chirality parameter, if their interactions with plasmonic nanoparticles and quantum dots, as well as their supramolecular organization, can be optimized.

We have synthesized a series of chiral alternating polymers, based on a fluorene-quinoxaline motif with chiral ester side chains. Theoretical calculations revealed a correlation between the topological conformations of oligomers and the simulated CD spectra. Along with the experimental data, this helped clarify the mechanism of optical activity enhancement and provided an insight into strategies for further enhancement of chirality.

Plasmonic enhancement of optical activity:

Optical properties of a newly synthesized chiral polyfluorene polymer (PFBT) mixed with gold and silver, diameter 4 nm and 10 nm, nanoparticles (NPs) were studied. Absorption and circular dichroism (CD) spectra of pure polymers, polymer/Au NPs and polymer/Ag NPs spin-coated films were recorded. Plasmonic interaction between Au and Ag NPs and the chiral polymer resulted in more than *three orders* of magnitude enhancement of chirality in the visible (500 nm). The chirality parameter, obtained with new polymer, reached 0.02 which is a remarkably high value for an organic nanocomposite. They were directly obtained as solid films and showed

more than one order of magnitude improvement over the previously synthesized chiral polythiophene system.

Photopatterning of chiral polymers:

Optical properties of various blends of chiral polyfluorene polymer (PFBT) with achiral photoresist SU-8 were studied. Absorption and circular dichroism (CD) spectra of pure annealed polymer films, PFBT/SU-8 annealed films, and PFBT/SU-8 photo-patterned films were recorded. Structural reorganization of PFBT helical fibrils within the SU-8 matrix resulted in substantial enhancement of chiral response (75 times that of pure PFBT film) in the visible (500 nm). The maximum chirality parameter, obtained with patterned PFBT/SU-8 film, reached 0.017, which is a remarkably high value considering the optical densities of pure film and the blend were the same. We have measured blanket-exposed (SU-8 fully crosslinked by UV-exposure) and annealed films and films annealed without exposure. Films that were only annealed (without UV exposure) exhibited about 50% higher CD than films that were crosslinked by UV-exposure then annealed. However, these results are somewhat sensitive to the sample history; i.e. the pre-baking prior to UV-exposure results in some degree of annealing. For the fully-crosslinked films, the maximum chirality parameter was about -0.003 (for a 1:40 PFBT:SU-8 ratio) perhaps somewhat higher for those annealed without UV-exposure than for blanket-UV-exposed films, but not dramatically so. The greater increase in chirality parameter occurs when the SU-8 is removed from the nominally unexposed areas of a patterned film. In that case, the CD goes up while the average film thickness goes down (due to SU-8 removal). Thus, the chirality parameter increases. The most notable features of these PFBT/SU8 nanocomposites are:

- (1) A fixed amount of PFBT yields not only higher CD when dispersed in SU-8, but actually yields higher chirality parameter and dissymmetry ratio (g -factor). That means that, in some sense, the chiral PFBT diluted in an achiral matrix has higher optical activity than the pure chiral PFBT.
- (2) Removal of the SU-8 matrix, followed by annealing, leads to a further increase in maximum CD, despite the fact that material is removed in this process. This suggests that the high chirality parameter results from structural effects in the PFBT and not any transfer of chirality from the PFBT to the achiral SU-8. Comparing the PFBT aggregates left behind after SU-8 removal to the pure SU-8 film, the former has almost two orders of magnitude higher CD. This really illustrates the potential of supramolecular or nanoscale ordering to have dramatic effects on chirality that would not be observed in other processes. For example, it would be very difficult to imagine a dye whose absorbance increases by a factor of 75 upon some change in supramolecular configuration.

Excitonic enhancement of optical activity:

We explored the excitonic enhancement of chirality by a variety of semiconductor nanocrystals (quantum dots). CdTe/ZnS core-shell quantum dots (QDs) have shown the greatest enhancement of PFBT chirality. Excitonic coupling between the helical polymer molecule and single QDs as well as the coupling between QDs resulted in enhancement that was superior to plasmonic enhancement obtained with gold NPs (chirality parameter of 0.03 obtained).

We synthesized chiral polyfluorene and chiral poly(fluoreneethiophene), which have higher chirality as pure films than the poly(fluorenebenzothiadiazole) (PFBT) that we have been using in the above-described studies. However, to date, the enhancement of their chirality upon addition of plasmonic particles has been much smaller than that observed with PFBT. Thus, the

highest values of chirality parameter obtained to date are from PFBT nanocomposites with plasmonic NPs or quantum dots. Nonetheless, the higher intrinsic chirality of these other chiral polymers showed a promise for achieving even higher ultimate values of chirality parameter, if their interactions with plasmonic nanoparticles and quantum dots, as well as their supramolecular organization, can be optimized.

From a theory standpoint, chiral patterns will have CD response in the visible (where we have molecular chirality) only when they are shrunk to scales below visible wavelengths. When the two chiralities are spectrally overlapped, then the resonance will be split into two hybridized components, blue- and red-shifted with the respect to the original resonances. One of them will show constructive interference whereas the other one - destructive. A situation is possible when we can get a very sharp and intense Fano-like resonance which depends on the ratio between HWHMs of the overlapped original resonances. We explored this concept computationally. We calculated geometry-induced chirality of dielectric meta-molecules (e.g. Y-shapes) predicting significant chiral optical activity ($\kappa = 0.018$, at ~ 4400 nm, for micron-scale Y-shaped structures that can easily be written). Combining this with the molecular chirality required changing the equations used in the computational electrodynamics to include natural optical activity. Likewise, on the experimental side, we continued to push to write smaller structures (that will allow the geometric chirality to overlap the molecular chirality) by optimizing the experimental setup with higher N.A. objective and other improvements, and to do characterization at longer wavelengths (where geometric chirality is more easily achieved).

Magneto-optic effect:

We considered the use of magneto-optics for achieving negative refractive index. Faraday rotation in an external magnetic field combined with natural optical activity of chiral polymer nanocomposites and geometrical chirality of planar patterned elements may lead to a value of chirality parameter sufficient for obtaining negative refractive index. The value of magneto-optical chirality parameter projected to polyfluorene from experimental measurements of Faraday rotation by polythiophene molecules can be as large as, or even larger than, that originating from natural optical activity, depending on the strength of the external magnetic field. We doped our nanocomposites with (ferro)magnetic nanoparticles and organic bi-radicals to enhance the effect. Blends with organic bi-radicals revealed unprecedented values of Verdet constant - on the order of 10^5 grad/(T m). Moreover, nonlinear Faraday rotation has been observed which proves the existence of unusually strong magnetic coupling in the blends.

Chiral nonlinear optical effect:

For the first time we demonstrated that our previously reported PFBT/QDs nanocomposites have an exceptionally large value of the effective nonlinear refractive index for the right-circularly polarized light, 2.4×10^{-3} cm²/GW. This value is more than one order of magnitude larger than that of very promising twisted π -system chromophore TMC-2 that we characterized earlier. For the left-circularly polarized wave the value of the effective nonlinear refractive index was measured to be less than 0.6×10^{-3} cm²/GW. Therefore, the value of the nonlinear chirality parameter can be roughly estimated as 0.9×10^{-3} cm²/GW which is comparable with the value of the nonlinear refractive index itself. This provides strong evidence of the enhanced magnetic coupling in the nanocomposite and opens the door to chiral control of optical nonlinearities.

We have measured the intensity-dependent circular dichroism and circular birefringence of chiral polyfluorene thick film samples using a polarimetric z-scan technique. The intensity dependent refractive index is found to be more than two orders of magnitude larger than that of

the quartz plate standard for both senses of the circular polarization. At the same time, the nonlinear chirality parameter is estimated to be of the same order of magnitude as the nonlinear refractive index itself, which makes these chiral polyfluorene films highly suitable for realizing chiral control of optical nonlinearities for a wide range of applications, such as all-optical switching. Strong evidence of the enhanced magnetic coupling in the nanocomposite opens the door to new magneto-optic materials.

Top down approach:

Simultaneous photo-reduction of a gold precursor (HAuCl_4) and crosslinking of a photoresist (SU-8) using two-photon excitation with a femtosecond near-IR laser was demonstrated as an effective means of writing sub-wavelength metal-nanoparticle-containing features. Conductivity measurements of these sub-wavelength structures were carried out, showing a resistivity comparable to bulk gold. The writing process was sensitized with an Air Force two-photon dye (AF380), which transfers energy to a conventional photoacid generator (photoinitiator, PC2506). The photoacid initiates both cationic polymerization of the SU-8 and reduction of Au^{3+} ions to metallic gold (Au^0) nanoparticles. Writing lines and planar structures with linewidths as narrow as 200 nm was demonstrated. A simple mathematical model of the writing process was developed to accurately reproduce trends of linewidth vs. laser power and writing speed. Diffraction gratings were manufactured to demonstrate that the process provides sufficient control and reproducibility to create optically active structures. Arrays of chiral structures were also produced. Computational analysis of those structures showed that they should be optically active, rotating the plane of polarization of light. Components of negative index materials, including planar arrays of split rings and fishnet structures were also prepared, but at dimensions that should lead to negative index behavior in the infrared region of the spectrum.

We employed two-photon lithography to produce micropatterns of Ag nanoparticles (NPs) with chiral ligands that preserve chirality of the individual NPs after patterning. The technique uses a photothermal reaction induced by two-photon direct laser writing. The individual chiral Ag NP were produced using a facile surface treatment of silver NPs functionalized with thermally cleavable chiral ligands: N-(tert-butoxycarbonyl)-L-cysteine methyl ester. The ligand cleavage initiated by a femtosecond-pulsed-laser-induced thermal reaction results in a significant change in dispersibility of the nanocrystals, thereby enabling a solvent selective development process after photo-patterning. We analyzed the optical chirality of the Ag NP films before and after micropatterning. The two-photon absorption process occurs at the localized surface plasmon resonance of Ag NPs. It is the strong two-photon absorption of the Ag NPs that allows this highly localized photochemistry to be initiated in subwavelength domains *without addition of any photosensitizer*.

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