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**Low Bandgap, Highly Polarizable, and Intrinsically Conductive Polymers**

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Phthalocyanine and porphyrin systems were investigated in thin film form and found to have large Verdet constants. Metallocenes with open electronic shells were found to be promising magneto-optical systems. Novel methods to induce chirality were also developed and liquid crystal systems were design that assemble into chiral structures with the application of electric fields.

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# Low Bandgap, Highly Polarizable, and Intrinsically Conductive Polymers

Final Report, July 2021

AFOSR Grant # 17RT0904, FA9550-18-1-0341

PI: Timothy M. Swager, Massachusetts Institute of Technology

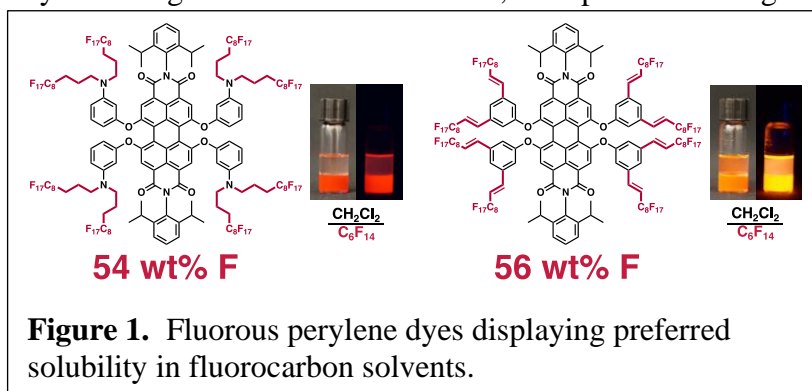
## Abstract

This program is directed at developing novel  $\pi$ -conjugated organic materials for magneto-optical and conductive properties. The target materials require new synthetic routes and the development of novel strategies. We established that chirality in conjugated polymers, specifically helical structures, plays a major role in dictating the magnitude and sign of the Verdet constant, which is a measure of the response. This result has helped focus our research on exploring different forms of chiral materials. We focused on the polymerization of functional conjugated polymers, their chiral assembly, and post-polymerization cyclization reactions. We completed the construction of a magneto-optical spectrometer that has the ability to measure the Faraday rotation with high precision over a range of wavelengths. This latter system has enabled deeper insights into the origin of magneto-optical behavior in different materials systems. Phthalocyanine and porphyrin systems were investigated in thin film form and found to have large Verdet constants. Metallocenes with open electronic shells were found to be promising magneto-optical systems. Novel methods to induce chirality were also developed and liquid crystal systems were design that assemble into chiral structures with the application of electric fields.

## Results

In this program we have been broadly interested in developing molecules and polymers with useful and interesting electronic and molecular structures. The organization of materials is critical. Crystalline organic materials are difficult to work with and tend to be fragile and prone to cracking. Liquid crystals and amorphous molecular materials offer good alternatives. Polymers are inherently disordered materials and polymer single crystals without any defects are so statistically improbable that they do not exist. This feature is also in part the result of their polydispersity. However, polymers with delocalized  $\pi$ -electronic systems can create electronic coherence over distances and if the disorder is managed appropriately new and/or enhanced properties can emerge. Organization of materials can be accomplished by creating selected conformations and we have focused on chiral/helical structures. Additionally, creating materials that segregate based on chemical potentials/solubility are also useful and we have investigated the creation of diverse new electronic materials that have fluororous properties that can promote organizations of interest.

Perfluorinated liquids can exhibit immiscibility with organic solvents and water, and provide orthogonal opportunities in chemistry. Examples of emissive dyes that display only fluororous phase solubility are limited, despite the many potential applications. Perylene bisimides are among the most versatile dyes and are known for their outstanding stability and high quantum yields. We reported the synthesis of two new “fluorofluorescent” perylene bisimide dyes (Figure 1) as well as other chromophores, designed to be soluble in the fluororous

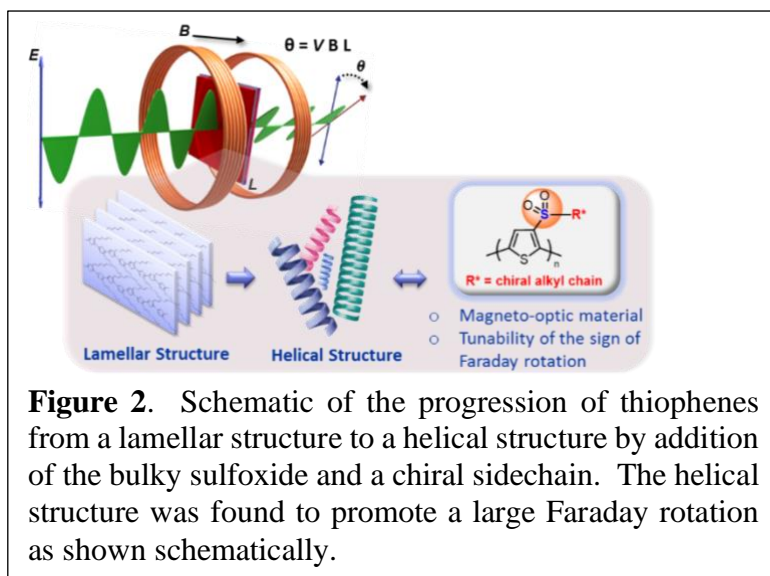


phases.<sup>1</sup> These two dyes possess unique photophysical properties, including dramatic increases in fluorescence quantum yields when treated with Brønsted acids as well as aggregation in the fluoruous phase. In the latter case the organization produced what is known as a J-aggregate, which has enhanced absorption and emission characteristics.

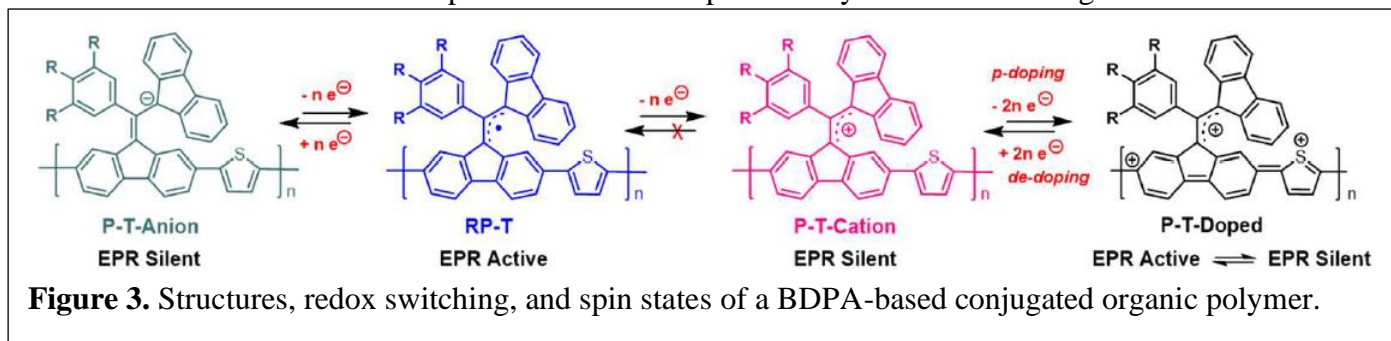
Materials with magneto-optic (MO) properties have enabled critical fiber-optic applications and highly sensitive magnetic field sensors. Although traditional MO materials are inorganic in nature, new generations of MO materials based on organic semiconducting polymers could allow increased versatility for device architectures, manufacturing options, and flexible mechanics. However, the origin of MO activity in semiconducting polymers is far from understood. In this paper, we report high MO activity observed in a chiral helical poly-3-(alkylsulfone)thiophene (**P3AST**), which confirms a new design for the creation of giant Faraday effect with Verdet constants up to

$(7.63 \pm 0.78) \times 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$  at 532 nm (Figure 2).<sup>2</sup> We have determined that the sign of the Verdet constant and its magnitude are related to the helicity of the polymer at the measured wavelength. The Faraday rotation and the helical conformation of **P3AST** are modulated by thermal annealing, which is further supported by DFT and MD simulations. Our results demonstrate that helical polymers exhibit enhanced Verdet constants, and expand the previous design space for polythiophene MO materials that was thought to be limited to highly regular lamellar structures. The structure property studies herein provide insights for the design of next generation MO materials based upon semiconducting organic polymers.

Investigations of magnetism in electronically coupled polyradicals have largely focused on applications in photonic and magnetic devices, wherein radical polymers were found to possess molecularly tunable and cooperative magnetic properties. Polyradicals with non-conjugated insulating backbones have been intensively investigated previously, however the integration of radical species into conducting polymer backbones is at an early stage. We reported 1,3-bisdiphenylene-2-phenylallyl (BDPA)-based conjugated radical polymers (Figure 3) that display ambipolar redox-activities and conductivities.<sup>3</sup> Moreover, these radical polymers were demonstrated to be promising magneto-optic (MO) materials with Faraday rotations wherein the sign is modulated by the radical character and display absolute Verdet constants up to  $(2.80 \text{ } 0.84) \text{ } 10^4 \text{ deg T}^{-1} \text{ m}^{-1}$  at 532 nm. These values rival the performance of the present-day commercial inorganic MO materials. The



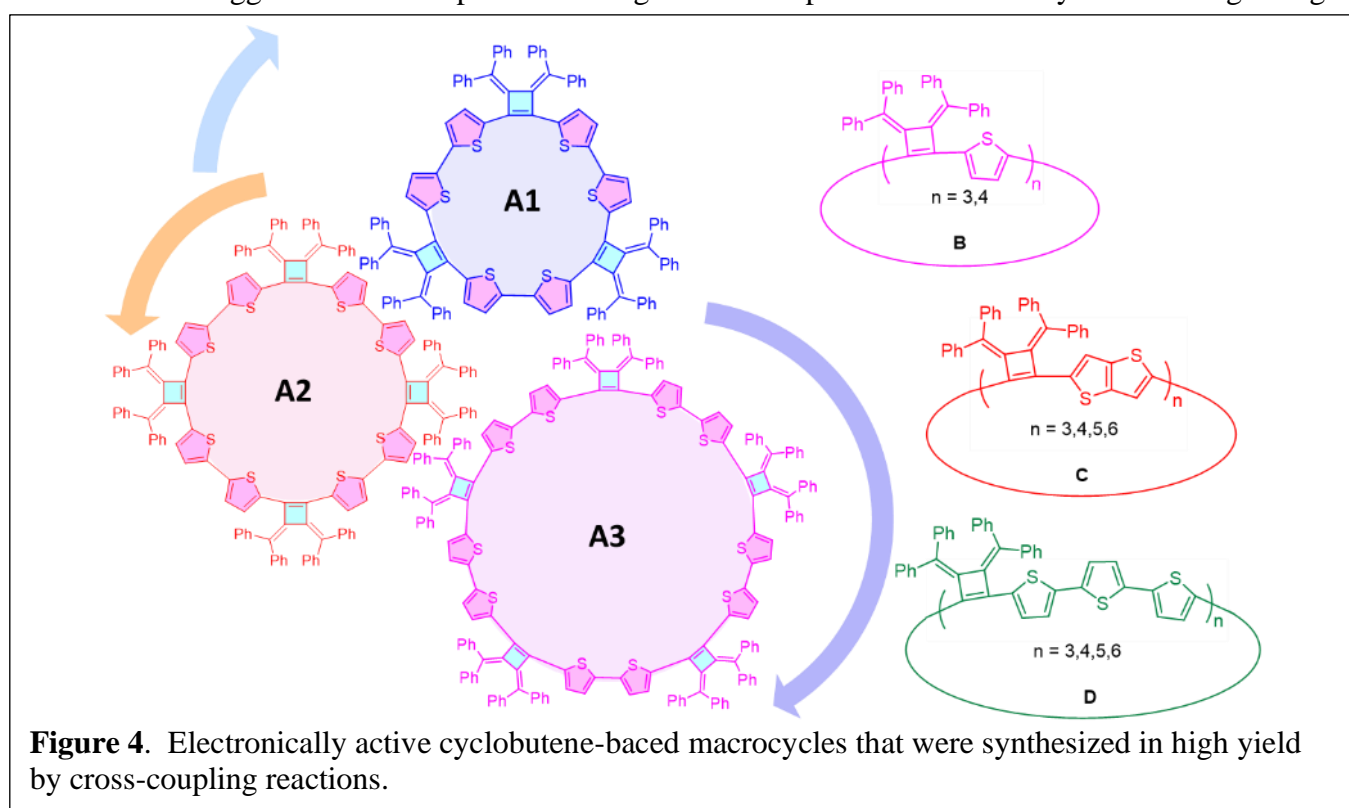
**Figure 2.** Schematic of the progression of thiophenes from a lamellar structure to a helical structure by addition of the bulky sulfoxide and a chiral sidechain. The helical structure was found to promote a large Faraday rotation as shown schematically.



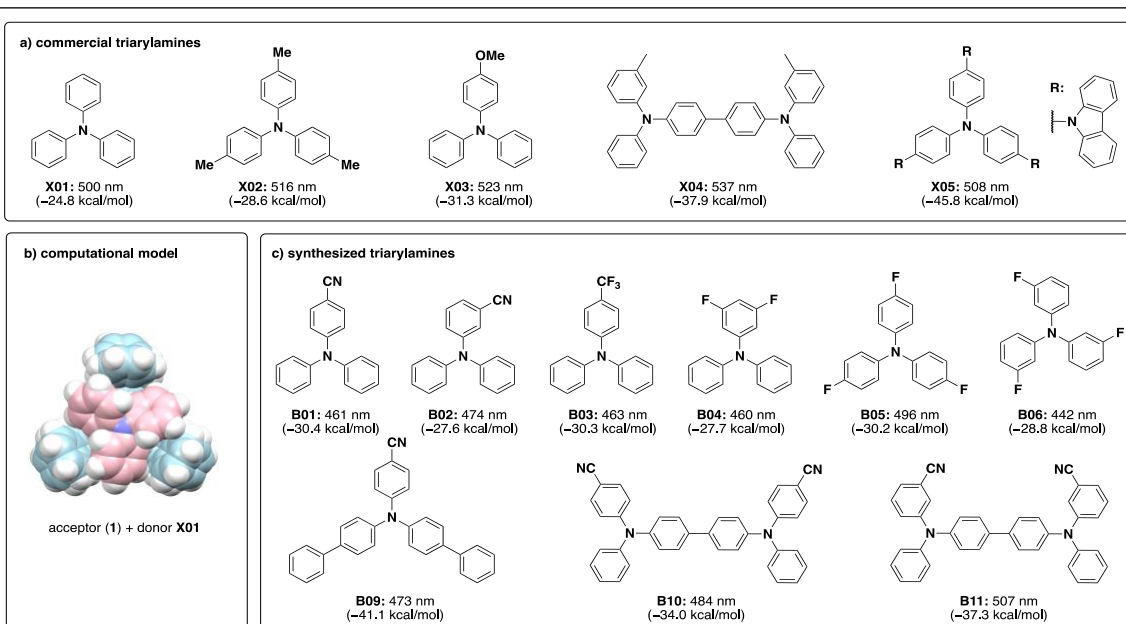
**Figure 3.** Structures, redox switching, and spin states of a BDPA-based conjugated organic polymer.

structure property studies detailed herein reveal the promise of multi-functional conjugated radical polymers as responsive MO materials.

Nanoscopic macrocycles could have unusual magnetic, optical, and electronic properties when compared to their linear counterparts. Conjugated  $\pi$ -systems in unsaturated macrocycles are particularly interesting as they have no end groups that limit electronic delocalization in equivalent linear oligomers. The rigid four-membered ring structure in 3,4-bis(methylene)cyclobutene with vicinal connections provides a vertex with an angle slightly less than  $90^\circ$ , which promotes macrocycle formation.<sup>4</sup> We reported a facile high-yielding synthesis of a series of 3,4-bis(methylene)cyclobutene-based  $\pi$ -conjugation macrocycles (Figure 4). The structure-property studies reveal that the smaller macrocycles are rigid crystalline frameworks and display symmetrical conformations in solution. The electrochemical, photophysical and magnetic properties of these macrocycles were also studied with a framework of characterization methods, revealing their size- and linkage-dependent properties. Density functional theory (DFT) calculations and molecular dynamics (MD) simulations at the molecular level suggest that several possible configurations are possible for macrocycles with larger ring sizes.

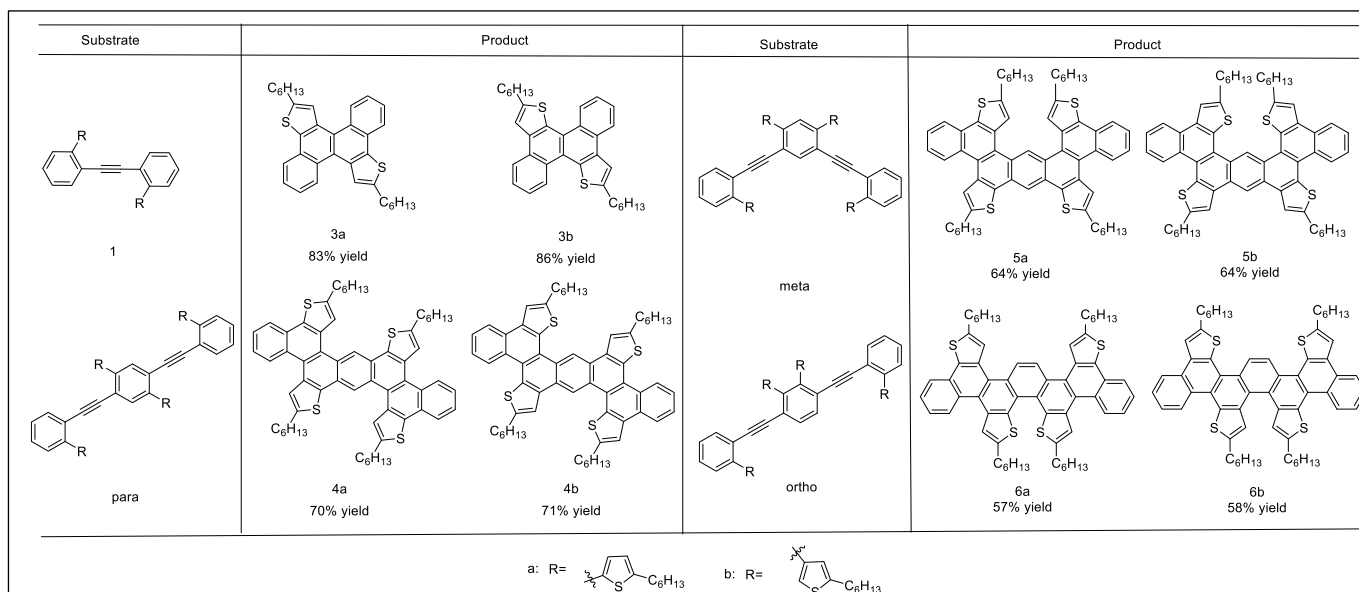


We have combined synthetic supramolecular chemistry and materials science to develop novel exciplexes for thermally activated delayed fluorescence (Figure 5).<sup>5</sup> Our approach starts from a bowl-shaped acceptor molecule for which we synthesize tailor-made donors that bind in a lock-and-key fashion. The donor design is guided by extensive density functional theory calculations of three independent donor families. The investigation of a large number of custom-synthesized donors allows us to derive empirical relationships for the prediction of the exciplex emission color. Incorporated within organic light-emitting devices, the lock-and-key exciplexes yield external quantum efficiencies of up to 5.4%, with potentially tunable emission color across the blue and green visible spectrum.



**Figure 5.** An iptycene acceptor produces an array of highly emissive exciplexes with donor guests to generate tunable emission wavelengths and thermally delayed activated fluorescence.

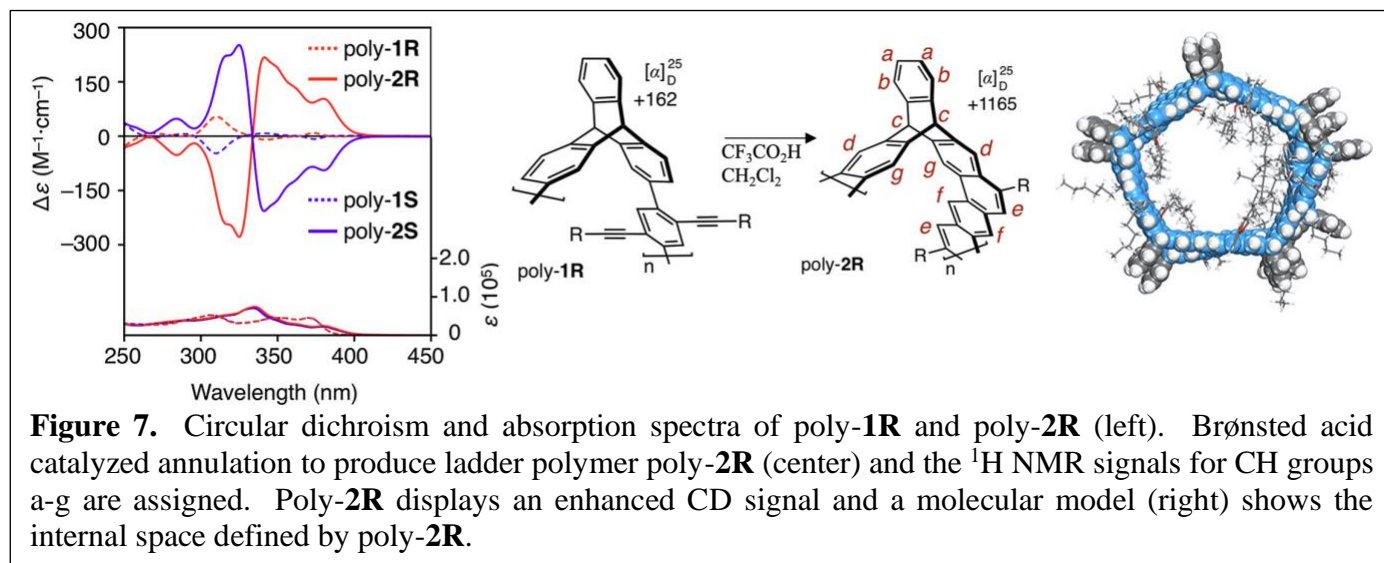
Efficient syntheses that incorporate thiophene units into different extended conjugation systems are of interest as a result of the prevalence of sulfur-rich aromatics in organic electronics (Figure 6).<sup>6</sup> Self-organization by using liquid crystal properties is also desirable for optimal processing of organic electronics and optical devices. In this article, we describe a two-step process to access extended regioisomers of polyaromatics with different shapes. This method involves an efficient single or double benzannulation from an alkyne precursor followed by Scholl cyclization. In spite of their unconventional nondiscoid shape, these materials display stable



**Figure 6.** Substrates and produces from new catalytic annulation reactions to produce thiophene based organic ribbon structures.

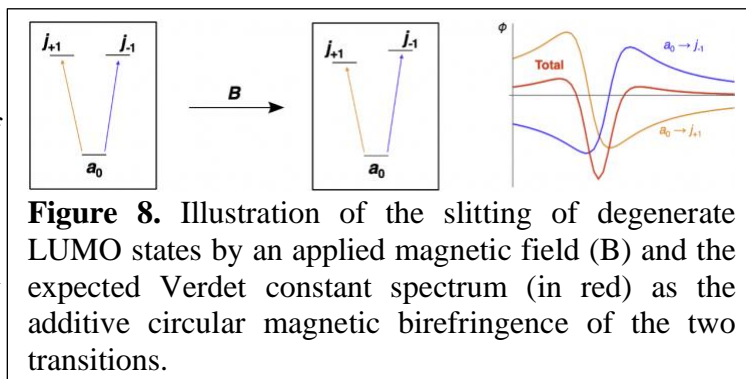
columnar liquid crystal phases. We examine the photophysical and electrochemical properties and find that structurally very similar thiophene-fused polyaromatics display significant differences in their properties.

Our prior measurements on chiral helical polythiophenes revealed a strong correlation with the chirality and the sign and magnitude of  $V$ , and values reached as high as  $8 \cdot 10^4 \text{ degT}^{-1}\text{m}^{-1}$ . However, these helical polymers required the aggregation and/or solid-state annealing to create helical structure. To create more robust helical structures, we developed rigid resolvable chiral triptycene monomers.<sup>7</sup> We recently demonstrated the ability of these building blocks to produce persistent helical ladder polymers (Figure 7).<sup>8</sup> The ladder polymer synthesis makes use of the powerful annulation reaction that we introduced in the early 1990s to create graphene ribbons.<sup>9</sup> The helical structure in this case is present in solution and doesn't require aggregation to exist. Although the aromatic structure is interrupted by the triptycene groups, extended conjugation is maintained as a result of homo-conjugation.



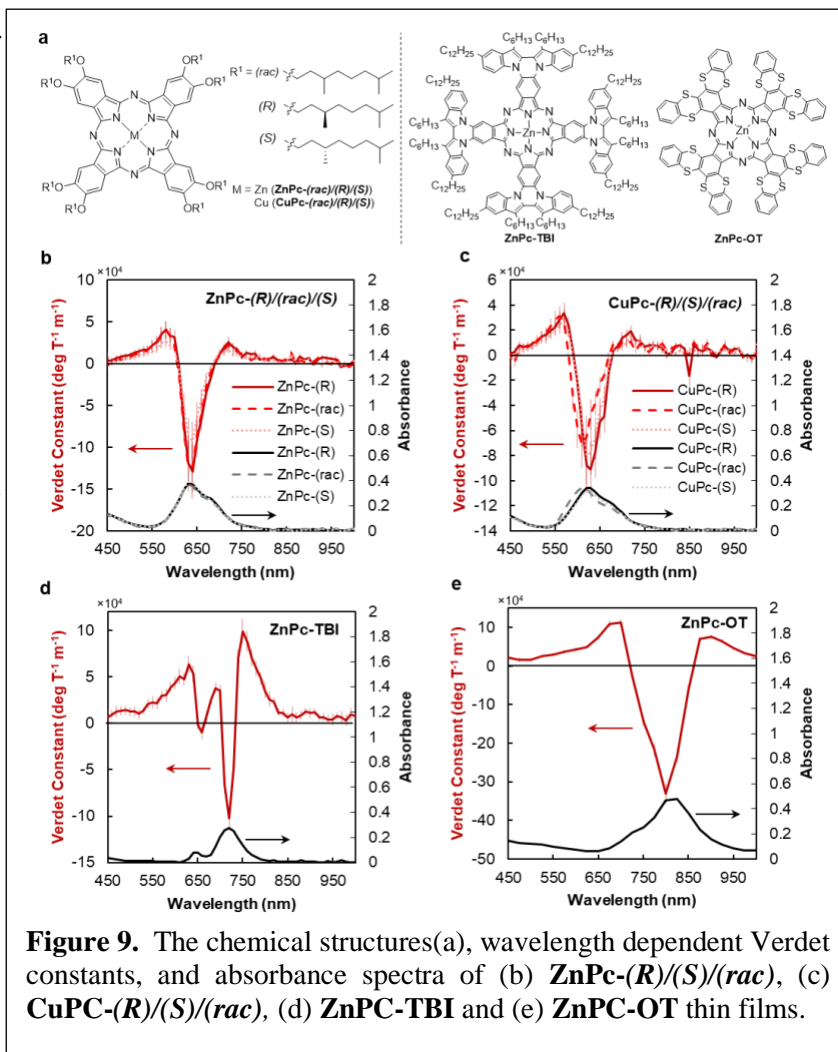
The Faraday effect in molecular materials was described years ago in a seminal paper by Buckingham and Stephens.<sup>10</sup> The MO effects are largest when the electronic dipole of the electronic transitions are perpendicular and the magnetic transition moments are parallel to the applied magnetic field. Such alignments generally require 3D electronic delocalization that is not common in organic  $\pi$ -conjugated structures. Additionally, this theory recognized three different interactions, represented as A-, B-, and C-Terms, that produce MO behavior. Over the course of the last funding period, we have recorded Verdet constants over a range of wavelengths in order to deduce the origins of the MO effects in different materials.

The A-Term is often the largest effect in organic molecules and is the result of a Zeeman splitting of degenerate unoccupied electronic states by the applied magnetic field. This orbital configuration creates a Verdet constant wavelength profile as shown in Figure 8. An issue with that A-term, and indeed the other contributions to the Faraday effect,



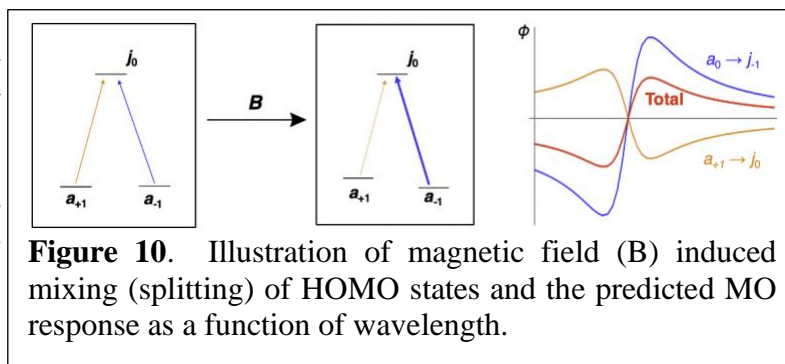
is that the effect is largest when it is close or overlapping an electronic transition, which reduces the transmitted light signal.

Phthalocyanines have degenerate LUMOs and we have examined a number of structures.<sup>4g</sup> As shown in Figure 9, the Faraday rotations (Verdet constants) have the signature profile of the A-term. The materials shown all have  $V > 10^5 \text{ deg T}^{-1} \text{ m}^{-1}$  and the novel phthalocyanines with extended disk shapes (Figure 9, top right) produce optical quality films with a discotic nematic organization.<sup>11</sup> Multiple synthetic innovations were needed to produce the extended disc structures, but are not detailed as a result of space considerations. It is important to note that the discotic nematic phase generates a negative uniaxial optical structure that readily aligns with the optic axis perpendicular to the substrate plane. This alignment is highly desirable as it minimizes optical scattering, a key attribute of an optical material, and orients the  $\pi$ -plane for optimal coupling of the electric transition dipole with the light beam. One surprising finding in this study is that the Verdet constants for **Zn-Pc** and **Cu-Pc** were insensitive to chirality. Additionally, although we expected the unpaired electrons to enhance the interactions with applied magnetic fields and thereby enhance the Verdet constant, we find that the  $S = \frac{1}{2}$  **Cu-Pc** has a slightly lower MO effect than the diamagnetic **Zn-Pc**. Nevertheless, magnetic materials can produce enhancements in Verdet constants. This concept has been extensively studied by the University of Arizona group,<sup>12</sup> but as we now appreciate simply incorporating paramagnetic ions into organic materials does not necessarily enhance the MO behavior.

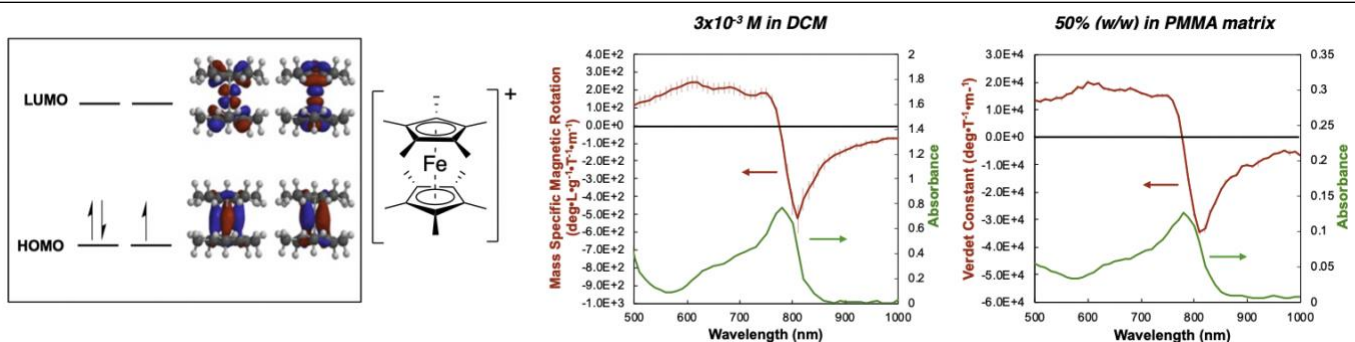


**Figure 9.** The chemical structures(a), wavelength dependent Verdet constants, and absorbance spectra of (b) **ZnPc-(R)/(S)/(rac)**, (c) **CuPc-(R)/(S)/(rac)**, (d) **ZnPC-TBI** and (e) **ZnPC-OT** thin films.

The C-Term contribution to the MO effect makes use of a degenerate HOMO that can be split by application of a magnetic field (Figure 10). The HOMO is partially occupied and the population of different states,  $a_{+1}$  and  $a_{-1}$ , is determined by a Boltzman population and the Verdet constant is enhanced by lowering the temperature.



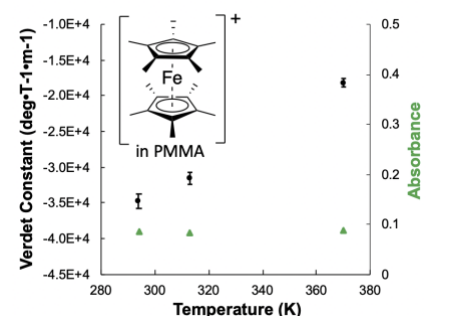
**Figure 10.** Illustration of magnetic field (B) induced mixing (splitting) of HOMO states and the predicted MO response as a function of wavelength.



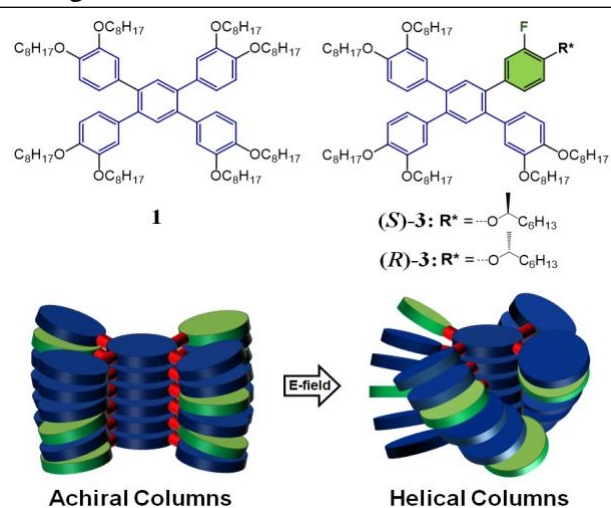
**Figure 11.** Degenerate HOMO and LUMO levels of the decamethylferrocenium cation ( $(\text{Cp}^*_2)\text{Fe}^+$ ) (left) and the MO behavior in solution and thin film (right).

We identified paramagnetic metallocenes as a class of compounds that display MO behavior as a result of a dominate C-Term.<sup>13</sup> In particular decamethyl ferrocenium cations (Figure 11) have features associated with the C-term (degenerate HOMO) as well as the A-Term (degenerate LUMO). The strong MO behavior in Figure 11 is shown both as that in solution as well as a composite film of poly(methyl methacrylate) and ferrocenium and the Verdet constant of composite films ( $4 \cdot 10^4 \text{ degT}^{-1}\text{m}^{-1}$ ) are independent of the counterion. We have determined that C-term contributes significantly to the MO behavior by performing variable temperature experiments, which reveal an increasing Verdet constant with decreasing temperature (Figure 12) as expected based on Boltzmann statistics. Solution studies of the mass specific magnetic rotation (MSMR) shown in Figure 11, allow for rapid testing and we have screened many compounds using this method. MSMR measurements performed on isoelectronic  $(\text{Cp}^*_2)\text{Mn}$  and  $(\text{Cp})_2\text{Cr}$ , which is a ground state triplet, are found to be about half that of the ferrocenium, confirming that metallocenes are promising high-performance MO materials.

To generate helical structures in novel ways we developed a novel class of tetraphenylbenzene-based discotic molecules with exceptional self-assembling properties (Figure 13).<sup>14</sup> Absorption and fluorescence studies confirmed the formation of *J*-type aggregates in solution. The discotic mesogens also show an enhancement of the emission upon aggregation. Interestingly, these discotic molecules displayed enantiotropic hexagonal columnar liquid crystal phases that can be switched into a helical columnar organization by application of an electric field. The helical columns arise from the electric-field-induced tilt of the polar fluorobenzene ring that directs all of peripheral phenyl groups into a propeller-like conformation with respect to



**Figure 12.** The Verdet constant of  $(\text{Cp}^*_2)\text{Fe}^+$  increases at low temperature without an increase in the optical absorbance.



**Figure 13.** An achiral liquid crystalline molecule, **1**, doped with chiral liquid crystalline molecules, **3**, can be organized into a helical structure by application of an electric field. This organization is the result of the coupling of the field to the conformation of **3**.

the central benzene core. A cooperative assembly process of these propeller-shaped molecules resolves into a helical columnar organization, in which the preferred helical sense is obtained from the stereogenic center proximate to the polar carbon-fluorine bond. The ease of inducing chirality in columnar LCs by electric field presents opportunities to create next-generation chiral materials for a variety of applications.

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