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Photomodulation of Conjugated Polymer Nanoparticles via Photochromic Dye Doping

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Photomoduation of Conjugated Polymer Nanoparticles via Photochromic Dye Doping

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelors of Science in Chemistry from The College of William and Mary

by

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ABSTRACT

Two types of dye-doped conjugated polymer nanoparticles that undergo fluorescence photomodulation were successfully created. The modulation of polymer nanoparticle fluorescence is possible via fluorescence resonance energy transfer (FRET). FRET occurs when an acceptor’s absorbance has good spectral overlap with a donor’s fluorescence, allowing the donor to pass its energy to the acceptor. The donor in this work is the conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and the acceptor is a photochromic dye, either a spirooxazine or a diarylethene in my case. Upon UV-irradiation spirooxazine (SO), which does not absorb visible light, is converted into merocyanine (MC), a rigid, conjugated molecule that absorbs visible light. The region of light where MC absorbs overlaps well with the fluorescence spectrum of MEH-PPV. This spectral overlap allows for FRET to take place between the polymer and the photochrome, quenching the fluorescence of the polymer nanoparticles when MC is present. However, MC is not thermally stable; after UV-irradiation is ceased, MC reverts back to SO, restoring polymer fluorescence to the nanoparticles. MeOSO-doped MEH-PPV nanoparticles are quenched to less than 10% and recover to over 95% of original fluorescence intensity. To create a polymer nanoparticle system that is stable in both quenched and fluorescent states, a diarylethene was used. Diarylenes undergo photochemically-allowed ring closures upon UV-irradiation, which creates a rigid ring structure with extended conjugation that absorbs visible light. The diarylethene used in my research, HFCP, has great absorbance spectral overlap with MEH-PPV fluorescence and is therefore a good acceptor for FRET. This dye is also stable for days in its ring-closed form, allowing for
stable fluorescence quenching. Upon ring opening, fluorescence is restored to the polymer. The quench provided by diarylethene is below 10% with over 95% recovery on average, the same as observed with spirooxazine. Fluorescence photomodulation of spirooxazine and diarylethene doped MEH-PPV nanoparticles has potential in many applications such as optical data storage, as sensors, and as probes for high-resolution microscopy.
**BACKGROUND**

The absorption of a photon by matter has the potential to excite an electron to an energy level above the ground state in which it resides. Allowed transitions for electrons are quantized and depend fully on the wavelength of the incoming photon. The energy gap between the ground state and the excited state can be found using the following equation: $\Delta E = h\nu$. Once in an excited state, an electron has multiple pathways for dissipating its energy, two of the most common forms being though luminescence and molecular movements. The dissipation of energy via luminescence can occur by fluorescence or phosphorescence. Fluorescence is the emission of light induced by an electron’s transition from a singlet-excited state to the ground state while phosphorescence is the emission of light from an electron’s transition from a triplet-excited state to the ground state. Since fluorescence involves an allowed transition between singlet-state and ground state, it happens faster than that of the forbidden triplet-state-to-ground-state transition of phosphorescence and is normally on the nanosecond time scale. The Jablonski Diagram (Figure 1) illustrates the processes that occur between absorption and emission of photons.
**Figure 1**: Jablonski Diagram

As shown in the Jablonski Diagram by the magnitude of absorption and fluorescence arrows, the energy of absorption is usually higher than that of fluorescence; this is because of internal conversion of the electron once in the excited state. Internal conversion is the vibrational relaxation of an electron to the lowest vibrational level of an excited state. Due to the loss of energy during this process, the photon emitted has less energy than the photon absorbed and therefore occurs at longer wavelengths inducing a red shift of fluorescence, known as a Stokes’ shift. Figure 2 shows the absorbance and fluorescence of a molecule; the fluorescence occurs at higher wavelengths and, therefore, lower energy than the absorption.¹
It is also apparent in Figure 2 that the fluorescence spectrum (dotted line) is a mirror image of the absorbance spectrum (solid line). This phenomenon is quite typical of fluorescent molecules, commonly referred to as fluorophores, and is attributed to the transitions involved in absorbance and fluorescence. The Born-Oppenheimer approximation and the Frank-Condon Principle explain how electron transitions induce this phenomenon as well as the Stokes’ Shift. The Born-Oppenheimer approximation allows for the separation of electron and nuclear motion. Electrons move orders of magnitude faster than nuclei and therefore see nuclei as stationary point charges. The slow motion of nuclei allows electrons to be excited and deactivated before the nuclei change position. This causes the excitation and the decay of electrons to be linear, as stated by the Frank-Condon Principle. The Frank-Condon Principle also states that the most probable absorption transition will also be the most probable fluorescence transition. When an electron is excited from the ground state to the excited state, the vibrational level of the electron also changes. This specific electronic and vibrational change will be mirrored during the relaxation transition. For example, if the absorption
transition is from the zeroth vibrational level of the ground state to the second vibrational level of the excited state, the fluorescence transition will occur from the zeroth vibrational level of the excited state down to the second vibrational level of the ground state. The Jablonski diagram (Figure 1) elucidates this idea via visual representation of the Frank-Condon linearity principle where the lengths of the absorption and fluorescence arrows indicate the magnitude of energy.

Molecular rigidity increases the likelihood of fluorescence due to the lowered probability of losing energy via molecular motion and other non-radiative processes. Fluorophores with large quantum yields, a large ratio of photos emitted per photons absorbed, are commonly aromatic compounds. Aromatic compounds are rigid conjugated ring structures, resulting in delocalization of the pi electrons. As the length of conjugation increases, the energy level of the molecule’s exited states is lowered; this results in a red shift of fluorescence. Figure 3 shows an example of a conjugated system and Figure 4 shows some common aromatic systems.

**Figure 3:** An example of a conjugated system. Notice the alternating single and double bonds.

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\begin{center}
\includegraphics[width=0.5\textwidth]{conjugated_system.png}
\end{center}
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**Figure 4:** Common aromatic systems. Left to right: benzene, naphthalene, anthracene.

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\begin{center}
\includegraphics[width=0.5\textwidth]{aromatic_systems.png}
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Conjugated polymers are made from conjugated monomers that often contain aromatic rings. A few common conjugated polymers can be seen in Figure 5. The
absorbance spectra of conjugated polymers as well as the fluorescence are often classified as broadband. The term broadband refers to the fact that polymers absorb a wide range of wavelengths. The wavelengths absorbed and emitted are dependent upon the length of polymer chains and the twisting of chains. Longer conjugated polymer chains show absorption and emission of longer wavelengths of light than shorter chains due to increased conjugation and therefore increased delocalization of electrons. The twisting of polymer chains has the potential to break the planarity of the system, therefore breaking the conjugation and causing the chain to absorb and fluoresce at higher energy, or “bluer” wavelengths. The mixture of these high and low energy polymer chains in a single sample causes both the absorbance and the emission to be broad.\(^5\)

**Figure 5:** Examples of conjugated polymers

Though absorbance and fluorescence spectra of conjugated polymers are both considered broadband, the absorbance spectra are normally broader. This is due to energy funneling between monomers of a polymer chain. High-energy monomers can funnel their energy to low-energy monomers, which reduces the bluer emission of the polymer. The funneling of energy decreases the polymer’s blue fluorescence and increases the red. This results in a less broad emission spectrum.
MODULATION OF FLUORESCENCE

Modulation of emission in the visible region of light can be used for optical data storage, sensors, or probes for high-resolution microscopy. Fluorescence can be modulated via electron transfer (ET) or fluorescence resonance energy transfer (FRET). FRET, the system of interest to the Harbron group, involves the transfer of energy from a donor to an acceptor. In the Harbron group, conjugated polymers are used as donors and photochromic dyes are used as the acceptors. A photochrome is a molecule that undergoes a conversion between two isomers upon irradiation with ultraviolet (UV) light. The two isomers of a photochrome usually have different absorbance spectra, one of which overlaps the fluorescence of the donor while the other one does not. By alternating between the two forms of the photochrome, the fluorescence of the polymer oscillates between an “on” state and an “off” state. FRET occurs when the photochrome absorbs the polymer’s fluorescence, thereby quenching the emission. The use of photochromes to manipulate emissions of fluorophores is well studied.

There are many factors that influence FRET, the most important being the overlap of the donor’s fluorescence with the acceptor’s absorbance. If the overlap is poor, the likelihood of energy transfer is low. The distance between the donor and the acceptor also determines the rate of energy transfer. The donor and the acceptor must be within the Förster Radius to have efficient FRET. The Förster Radius is the distance at which the fluorescence quenching is 50% efficient. For most donor-acceptor systems this distance is 20-60 Ångstroms. The equation used to determine the rate of energy transfer is 

$$k_T = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

where $k_T$ is the rate of transfer, $R_0$ is the Förster Radius, $\frac{1}{\tau_D}$ is the decay
of the donor alone, and \( r \) is the radius between donor-acceptor. The donor-acceptor distance equals the Förster Radius when the energy transfer is at 50\%.\(^{16}\)

The modulation of conjugated polymer emission with photochomic dyes can be studied using various sample geometries. Some examples include polymer films, covalently bound photochrome-fluorophore units, and non-covalently bound photochrome-fluorophore nanoparticles.\(^6,8\) Synthesizing conjugated polymers with covalently attached photochromes has proven difficult in the Harbron lab since photochromic dyes are sensitive to the conditions needed for polymerization. Films of polymer and dye tend to undergo phase separation during spin coating resulting in unknown and irreproducible polymer/dye proportions.\(^8\) To circumvent these issues, dye-doped conjugated polymer nanoparticles and organic dyes are used to create a system of non-covalent interaction between photochrome and fluorophore. Nanoparticles self-assemble upon injection into water due to the disfavored solvation of the hydrophobic entities by water; the nanoparticles are stable as suspensions in water.\(^{17}\) The diameter of the spherical nanoparticles is also easily manipulated during preparation. These particles are preferred for polymer/dye FRET analysis due to their easy reprecipitation preparation and their well-defined structure.\(^6,18,19\) The difficulties in film and polymerization studies leave nanoparticles as the most efficient, reproducible way to study FRET using conjugated polymers and photochromic dyes.
EXPERIMENTAL SECTION

MATERIALS

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with an average MW of 260,000 was purchased from American Dye Source, Inc. and used without further purification. 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (HFCP) and 4,4′-dimethyltriphenylamine (triphenylamine) were purchased from TCI America and used without further purification. 9′-methoxy-1,3,3-trimethylspiro(indoline- 2,3′-[3H]-naphth[2,1-b][1,4]oxazine) (MeOSO) was synthesized following literature procedures. Poly(vinyl alcohol) (PVA) (MW 16000) was purchased from Acros Organics. FisherFinest Premium Cover Glass slides were used for solid samples. The filtering apparatus used was a glass microanalysis filter holder assembly from Fisherbrand. Two types of filter papers purchased from Millipore were used with this filtering assembly: 0.22 micrometer GV Durapore Membrane Filters and 0.7 micrometer Glass Fibre Prefilters.

CHARACTERIZATION

UV-irradiation was performed using a Spectroline Long Wave UV Pencil Lamp (365nm) and a Spectroline Short Wave UV Pencil Lamp (254nm). Absorbance spectra and kinetics were measured using a Varian Cary 50 Bio UV-Visable Spectrophotometer and fluorescence spectra and kinetics were measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. Solid samples were spin coated onto glass slides using Chemat Technology Spin-Coater KW-4A and studied on a Zeiss Axiovert 200 Microscope.
SAMPLE PREPARATION

Nanoparticles, both control and dye-doped, were prepared following a reprecipitation method proposed by Jason McNeill.¹⁷

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] Control Nanoparticles and Methoxy-Spiroanapthoxazine Doped PPV Nanoparticles:

A poly(p-phenylene vinylene) derivative, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), was dissolved in anhydrous tetrahydrofuran (THF) in a 1mg:1mL proportion and was stirred for at least 1 hour under argon. Throughout the stirring process the solution was covered by aluminum foil to protect against ambient light exposure. After stirring, the polymer/THF solution was filtered through 0.7-micrometer filters; this filtration step was implemented to remove large aggregates of polymer. To make control MEH-PPV nanoparticles, the filtered polymer solution was diluted to either a 20 ppm or 40 ppm concentration using anhydrous THF. To obtain dye-doped nanoparticles, a 100 ppm methoxy-spiroanapthozazine (MeOSO)/THF solution was added to the concentrated polymer solution to create the desired weight percent of dye:polymer. This dye/polymer mixture was then diluted with anhydrous THF until the polymer concentration reached 20 ppm or 40 ppm. The resulting solution, control or dye-doped, was then sonicated for 30 seconds to guarantee homogeneity. A 1 mL portion of the sonicated solution was then injected into 8 mL of sonicating ultra-pure water, creating nanoparticles. After 2 minutes of additional sonication, excess THF was removed by rotary evaporation. The resulting solution consisted of MEH-PPV (dye-doped or control) nanoparticles suspended in ultra-pure water. This suspension was filtered through 0.22-micrometer filters to remove aggregated nanoparticles.
1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene and 4,4'-Dimethyltriphenylamine Doped MEH-PPV Nanoparticles:

The preparation of 1,2-Bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (HFCP) and 4,4'-dimethyltriphenylamine (triphenylamine) doped MEH-PPV nanoparticles mirrors that of MeOSO-doped MEH-PPV nanoparticles. The MEH-PPV derivative MEH-PPV was dissolved in anhydrous, unstabilized THF in a 1 mg:1 mL solution. From here, the solution was stirred for at least 1 hour under argon while covered in aluminum foil. The polymer solution was then filtered through 0.7-micrometer filters to remove polymer aggregates. A desired amount of a 100 ppm HFCP/THF solution was added to polymer solution to create a specified weight percent mixture of HFCP:MEH-PPV. A 100 ppm amine solution was then added to the mixture to create a 3:1 mole ration of HFCP:amine. This solution of HFCP/amine/MEH-PPV was then diluted until the MEH-PPV concentration reached 20 ppm. The solution was sonicated for 30 seconds to guarantee homogeneity and a 1 mL portion of the sonicated mixture was injected into nano-pure water. The purification procedure for removing THF and filtering out nanoparticle aggregates is the same as that of the MeOSO/MEH-PPV nanoparticles previously discussed.

Liquid Samples:

Nanoparticle samples were examined in quartz fluorimeter septum screw top micro-cuvette from Starna. The nanoparticles were degassed in order to reduce photo-oxidative damage. This is done by bubbling argon gas through the sample for an extended period of time.
Solid Samples:

For solid samples on glass slides, poly(vinyl alcohol) (PVA) was dissolved in nano-pure water to a concentration of 10 wt% and 0.4 mL of the PVA solution was then added to 0.8 mL of nanoparticles. This solution was sonicated to allow for mixture of the viscous PVA solution with the thin nano solution. After sonication, the entire 1.2 mL sample was spin-coated onto glass cover slides and studied on a fluorescence single molecule microscope described previously.  

NANOPARTICLE CHARACTERIZATION

Atomic Force Microscopy (AFM) studies showed the nanoparticles to have an average diameter of 8 nm. This measurement yields the hypothesis that each nanoparticle is made from one polymer chain, which contains about 100 chromophores. Due to the cylinder-like tip on the AFM probe and the fluidity of the nanoparticles, the specific shape of the particles cannot be fully determined using this type of microscopy. Also, due to the diffraction limit of light (~\(\lambda/2\)) the exact shape cannot be determined using fluorescence microscopy studies either. However, the particles appear round in AFM scans and the fluorescence studied using microscopy alludes to round particles; the particles are therefore thought to be in sphere-like with shape variations.
RESULTS AND DISCUSSION

MeOSO-DOPED MEH-PPV NANOPARTICLES

Poly (p-phenylene vinylene) (PPV) is a conjugated polymer that exhibits fluorescence in the visible region of light. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (Figure 6) is a derivative of PPV that has strong absorbance in the blue-green and emission in the green-yellow region of the visible spectrum when in solution (Figure 7). This polymer’s strong fluorescent properties make it a good candidate for fluorescence photo-modulation.

**Figure 6:** MEH-PPV

![MEH-PPV structure](image)

**Figure 7:** MEH-PPV absorbance (solid line) and fluorescence (dotted line) in anhydrous THF

![Absorbance and fluorescence spectra](image)
The photochrome chosen for fluorescence modulation of MEH-PPV via FRET was 9′-methoxy-1,3,3-trimethylspiro(indoline- 2,3′-[3H]-naphth[2,1-b][1,4]oxazine (MeOSO) (Figure 8). When this dye is in the spironaphthoxazine (SO) form, it shows no absorbance in the visible region of light. Upon irradiation with 365nm light, the photochrome undergoes an isomerization where the spiro-bond is broken and a quinodal group is formed. This isomer is called photomerocyanine (MC).

**Figure 8:** MeOSO in SO (left) and MC (right) isomers.

The SO form of MeOSO does not absorb in the visible region of light, while the MC form shows strong absorbance in this region (Figure 9). This drastic change in absorbance in the visible region of light between SO and MC is highly desirable for FRET.
**Figure 9:** MeOSO absorbance in THF. SO (solid line) and MC (dotted line).

The absorption spectrum of MC has good spectral overlap with the fluorescence of MEH-PPV. The drastic change of absorption between SO and MC in the region of light where MEH-PPV emits is highly desirable for FRET. Figure 10 depicts the spectral overlap of MC absorbance and MEH-PPV fluorescence.

**Figure 10:** MC absorption (solid line) overlap with MEH-PPV nanoparticle fluorescence (dotted line)
The hypothesized mechanism for fluorescence modulation of MEH-PPV emission using MeOSO can be seen in Scheme 1. When SO is present, it is thought that MEH-PPV will fluoresce without interference. Upon UV irradiation SO converts to MC and the emission of the polymer will hopefully be absorbed, resulting in the termination of fluorescence.

**Scheme 1:** MEH-PPV and MeOSO fluorescence modulation model

![Scheme 1](image1.png)

A depiction of this hypothesized process in nanoparticles can be seen in Scheme 2. The dye-doped polymer nanoparticles will be fluorescent until UV exposure induces SO→MC conversion, quenching MEH-PPV fluorescence.

**Scheme 2:** MeOSO-doped MEH-PPV nanoparticles undergoing fluorescence quenching.

![Scheme 2](image2.png)

In order to study the FRET between SO and MEH-PPV, polymer nanoparticles doped with MeOSO were prepared. It is important to note that when going from organic
solution to water, as in nanoparticle preparation, MEH-PPV fluorescence shows a
bathochromic shift; this red shift is attributed to the bundling of polymer chains. In
organic solvent, the polymer is suspended freely and polymer chains are able to “stretch
out”. In this case, a small amount of energy is funneled between high-energy and low-
energy monomers, which reduces the broadness of the fluorescence spectrum. In
nanoparticles, polymer chains are suspended in water and, due to the hydrophobicity of
the polymer, are bundled into spherical-like shapes. The bundled conformation allows
high-energy monomers to be closer in space to low-energy monomers. This causes a
larger reduction of blue fluorescence because the close proximity of high and low energy
monomers increases energy funnelling. The end result of the bundling of polymer chains
upon nanoparticle formation is a red shift of MEH-PPV fluorescence, as seen in Figure
11. The red shift of MEH-PPV fluorescence is also visible in films.

**Figure 11:** MEH-PPV fluorescence in anhydrous THF (solid line) and in nanoparticles
(dotted line)

Once MeOSO-doped MEH-PPV nanoparticles were successfully prepared via
reprecipitation, the ability for SO to undergo conversion to MC in nanoparticles was
studied. A change in nanoparticle absorption in the region where MC absorbs would indicate the ability for SO to successfully convert to MC. After UV irradiation, absorbance of the nanoparticles did increase in the red region of visible light, specifically at 600 nm (Figure 12).

**Figure 12:** 28 wt% MeOSO-doped MEH-PPV nanoparticle absorption before UV irradiation (solid line) and after 10 seconds of UV irradiation (dotted line).

Subtraction of pre-UV nanoparticle absorbance from the post-UV absorbance yields a difference spectrum. This difference spectrum shows the change in absorbance in response to UV exposure. The difference spectrum was very similar to that of the MC absorbance spectrum; therefore, the change in nanoparticle absorption upon UV irradiation is attributed to SO$\rightarrow$MC conversion. Figure 13 shows the difference spectra overlaid with MC absorbance. By using Beer’s Law, the number of dye molecules converted can be determined where more opened dyes, i.e., a larger difference spectrum absorbance, yields a better fluorescence quench because more quenchers are present.
**Figure 13:** MC difference spectrum (dotted line) overlaid with 28 wt% MeOSO-doped MEH-PPV nanoparticle subtraction spectrum and subtraction fit (solid lines).

After SO/MC conversion in nanoparticles was proven successful, fluorescence-quenching studies were performed to see if SO→MC conversion would successfully quench MEH-PPV fluorescence. Figure 14 shows the fluorescence spectra of MeOSO-doped MEH-PPV nanoparticles during irradiation with UV light. It is obvious that the nanoparticles do undergo fluorescence quenching upon SO→MC conversion.
Since the fluorescence quenching of MEH-PPV nanoparticles is caused by MC formation, the stability of the quench state is dependent upon the thermal stability of MC. MeOSO is not thermally stable in the MC form and reverts to SO quickly, thereby restoring polymer fluorescence to the nanoparticles with a half-life of 2 seconds in solution and 4 seconds in nanoparticles (Figure 15). This increase in half-life is attributed to the increased spatial constriction of dye molecules in nanoparticle form; the polymer is wrapped around the dyes, hindering the ability of the spiro-bond to reform as rapidly as it does in solution. The kinetics of MC→SO reversion in both solution and nanoparticles is first order.
Figure 15: Kinetic scans of MeOSO in a) THF and in b) MEH-PPV nanoparticles.

Kinetics scans of the nanoparticle polymer emission maximum were used to determine the amount of UV irradiation time needed to obtain an optimal quench. These studies indicate that 10 seconds of 365 nm light exposure is ample exposure to induce a maximum quench (Figure 16). Since the MC form of MeOSO is thermally unstable, the nanoparticles needed constant exposure to UV in order to quench and, as expected, once UV exposure ceased the nanoparticles regained their fluorescence.

Figure 16: Fluorescence kinetic scan of 28 wt% MeOSO-doped MEH-PPV nanoparticles at 590 nm. UV light exposure from second 9 to 19, maximum quench after 10 seconds. Once the UV light was turned off, the nanoparticle fluorescence returned.
The next major hurdle in this project was to find the amount of MeOSO needed to obtain a “perfect quench,” one in which the fluorescence of the particles is completely absent. After multiple trials with different weight percent ratios of MeOSO to MEH-PPV, 28 wt% nanoparticles were found to have the most complete quench. Though this concentration is quite large, the actual number of dye molecules opening up is quite small. The small fraction of dyes actually undergoing SO→MC conversion is thought to be a direct result of the constriction of the SO dyes in polymer nanoparticles. However, on average it only takes one dye molecule undergoing SO→MC conversion to quench 1.4 polymer chains.\(^6\) Since each nanoparticle is thought to contain one polymer chain, this number is also the average number of dye molecules needed to quench one nanoparticle.

The photochromic dyes are predicted to be located within the nanoparticle as well as on the outer surface due to the entropically disfavored segregation of dye completely into the center or completely on the surface of a polymer particle. Dye molecules on the surface of the nanoparticle, which have more space due to their location, are hypothesized to be the quenchers of polymer fluorescence. The fluorescence spectra of 28 wt% nanoparticles before, during, and after UV exposure can be seen in Figure 17. The sample in this figure quenched to 7.72% of the original fluorescence intensity. This percent was determined using the following equation:

\[
E_{\text{quench}} = \frac{I}{I_0} \times 100\%
\]

where \(E_{\text{quench}}\) is the quench efficiency, \(I_0\) is the initial intensity of the nanoparticles, and \(I\) is the intensity during UV irradiation.
**Figure 17**: The fluorescence spectra of 28 wt% MeOSO-doped MEH-PPV nanoparticles before (solid line), during (dotted line), and after (dash-dot line) UV exposure.

The normalized fluorescence spectra of the quenched and unquenched nanoparticles have roughly the same shape (Figure 18). The emission spectrum of the quenched nanoparticles has a blue edge in comparison to the emission spectrum of the nanoparticles in their fluorescent state. This is thought to be a result of preferential polymer chain quenching. Polymer chains with lower energy fluorescence have lower energy, which allows them to more easily participate in FRET with the MC. This results in more quenching of red emission than blue emission, leaving a blue edge in the emission spectrum. This blue shift of fluorescence during PPV polymer fluorescence quenching has been observed before in the Harbron lab.\(^{22}\)
Figure 18: Normalized fluorescence spectra for 28 wt% MeOSO-doped MEH-PPV nanoparticles from Figure 17 above, before (solid line), during (dotted line), and after (dash-dot line) UV exposure.

The 28wt% nanoparticles also showed extremely good fatigue resistance. This means the SO→MC conversion was successful multiple times in a row with the same efficiency. The nanoparticles quenched to an average of 5.9% of the initial intensity through the 21 cycles and recovered to an average of 97.7% of the initial intensity. Figure 19 shows the fluorescence intensity modulation through the cycling of UV exposure and thermal relaxation.
**Figure 19:** The graph below depicts the fatigue resistance of the 28 wt% MeOSO-doped MEH-PPV nanoparticles. The negative slope segments represent UV exposure which induces the formation of the MC isomer while the positive slope segments represent thermal relaxation of the dye to the SO isomer.

At concentrations lower than 28 weight percent, quenching ability is decreased and it is hypothesized that there are not enough SO dyes converting to MC to attain sufficient quenching. In parallel with the theory of dye molecules on the surface causing the quenching, this low quenching capability would indicate that lower concentrations do not have enough dyes with sufficient space to undergo SO→MC conversion. When concentrations larger than 28 wt% were studied, the quenching ability also decreased. This is thought to be from over-doping nanoparticles. Since the polymer concentration was constant while the dye concentration was varied, the larger amount of dye overwhelms the nanoparticles and the polymer chains are no longer able to fold in their optimal size and shape. This conformational change affects the nanoparticles enough to reduce quenching ability of the dyes.

The Stern-Volmer equation was used to study the relationship between nanoparticle weight percent and fluorescence quench.
Stern-Volmer Equation: \( \frac{I_0}{I} = 1 + K_{SV}[Q] \)

where \( I_0 \) is the initial fluorescence intensity of the nanoparticles, \( I \) is the intensity after SO→MC conversion, \( K_{SV} \) is the Stern-Volmer constant, and \( [Q] \) is the concentration of the dye dopant. According to the Stern-Volmer equation, the ratio of initial emission intensity to quenched intensity is linearly related to the amount of quencher present with a slope of \( K_{SV} \). The y-intercept is normally 1 as seen by the \( b \) value of the \( y=mx+b \) equation above.

A Stern-Volmer plot for MeOSO-doped MEH-PPV nanoparticles can be seen in Figure 20. This plot indicates that quench ratio does have a linear relationship with the amount of quencher present. The nanoparticle Stern-Volmer constant was found to be 1.4, indicating an average of 1.4 polymer chains, or about 100 chromophores, quenched per MC molecule.\(^6\)

**Figure 20:** Stern-Volmer plot showing the relationship between quenching and number of MC dyes per polymer chain.
The inability for the nanoparticles to attain a “perfect quench,” one in which the fluorescence turns completely off, is very intriguing. There are two hypotheses which explain the residual quenching: (a) some nanoparticles do not attain a complete quench due to either lack of dyes in/on those particles or the inability for dyes in/on those particles respond to UV irradiation, or (b) all the nanoparticles are only quenched to about 5% of their original intensity. Single molecule fluorescence microscopy studies of nanoparticles on slides can help to determine which of these two hypotheses is correct, or if there is another explanation for the residual fluorescence.

**CONTROL EXPERIMENTS**

In order to confirm that fluorescence quenching was caused by the dye dopant and not polymer photo bleaching, absorbance studies were performed on MEH-PPV control nanoparticles; control nanoparticles consist only of polymer. When photo bleaching takes place, the absorbance peak of the polymer decreases. This is due to destruction of the polymer itself, which reduces the ability for the polymer to absorb. The absorbance of the control polymer nanoparticles does not decrease in intensity upon UV exposure as seen in Figure 21. This leads to the conclusion that polymer bleaching is not the cause of fluorescence quenching. Another piece of evidence against polymer bleaching being the source of quenching is that polymer bleaching disables quenching recovery, which is evident in nanoparticles.
Unfortunately, the control nanoparticles do experience some self-quenching, as seen during fluorescence kinetic studies. The self-quench does not supply the same magnitude of quenching that dye-doped nanoparticles show. Figure 22 shows the kinetics of fluorescence quenching for control MEH-PPV nanoparticles. Notice the control nanoparticle fluorescence is only quenched to 58% of the original intensity wherein dye-doped nanoparticles fluorescence is quenched to less than 10% of the original intensity.
Control nanoparticle fluorescence quenching also differs from that of dye-doped nanoparticles in the kinetic decay of the quench. Figure 23 shows the difference in the kinetics of fluorescence return; control nanoparticles take longer to restore fluorescence than MeOSO-doped nanoparticles. This difference in kinetics shows that dye-doped nanoparticles do not undergo the same mechanism for quenching as control nanoparticles.
The mechanism through which control nanoparticle fluorescence is quenched is thought to be a phenomenon called hole polaron quenching. Hole polaron quenching is possible when a polymer irradiated with UV light excites an electron to a higher energy orbital.\(^5\) The electron can then travel through conjugation across polymer chains leaving a radical cation, or hole, behind.\(^5,23\) This charge separation induces a small amount of polymer fluorescence quenching in closely wound polymer molecules, such as nanoparticles.\(^23,24\) To stop hole polaron quenching, the charge separation produced by the excited electron must be terminated; one way to do this is to “plug” the radical cation hole. The sequestering of radical cations by tertiary amines is well known.\(^25-28\) These amines donate an electron from their lone pair to the polymer, which neutralized the polymer radical cation and causes the amine to become cationic (Scheme 3).\(^25,26\) Since MeOSO contains a tertiary amine, MeOSO-doped MEH-PPV nanoparticles were protected from hole polaron quenching and this form of quenching became apparent only upon MEH-PPV control nanoparticle studies. Hole polaron quenching, however,
explains why the Stern-Volmer plot for MeOSO-doped MEH-PPV nanoparticles does not have a y-intercept of one.

**Scheme 3:** Polymer hole polaron formation and tertiary amine electron donation

Once it was determined that fluorescence quenching of dye-doped nanoparticles was an effect of the dye dopants, the importance of nanoparticle structure was examined. To make sure nanoparticle structure was needed for FRET, a 1 mL aliquot of 28 wt% MeOSO-doped MEH-PPV solution was injected into 7 mL of THF. This yielded an 8mL sample of dye and polymer in THF as apposed to injecting the 1 mL stock solution into 8mL of water, which yields 8 mL of nanoparticles after THF removal. The fluorescence and absorbance of this sample upon UV irradiation were then studied. Figure 24 shows
the absorbance spectra of the 28 wt% stock solution injected into THF sample. There is no change in absorbance upon irradiation indicating a lack of SO→MC conversion.

**Figure 24:** Absorbance of 28 wt% MeOSO/MEH-PPV solution in THF before UV exposure (solid line), after 10 seconds 365 nm irradiation (dotted line) and after 1 minute of recovery (dot-dash line).

![Absorbance spectra](image)

Figure 25 shows the fluorescence before, during, and after UV irradiation. The lack of change in fluorescence upon irradiation further supports the idea that SO is not converting to MC and therefore is unable to quench polymer fluorescence. The combination of the absorbance and fluorescence spectra from this control sample indicates that in order to obtain FRET, both the dye dopant and polymer must be in nanoparticle form.
**Figure 25:** Fluorescence spectra of 28 wt% MeOSO/MEH-PPV solution in THF before UV exposure (solid line), after 10 seconds 365 nm irradiation (dotted line) and after 1 minute of recovery (dot-dash line).

After studying dye and polymer interaction in solution and nanoparticle from, the next step was to examine a mixture of nanoparticles and solution. To do this, nanoparticles were “killed” by adding small amounts of THF to the water solution, specifically 0.4 mL of THF to a 0.8 mL aliquot of nanoparticles. The intention behind this was to swell the nanoparticles and see if FRET was still possible. Since THF is relatively non-polar in comparison to water, upon injection into water the non-polar nanoparticles “soaks” up the THF. The addition of solvent to nanoparticles therefore causes the polymer and dye to become less tightly bound upon each other and induces a more fluid-like environment. The fluorescence spectra of “killed” nanoparticles (Figure 26) show a large blue shoulder caused by the solution-like environment of the polymer. As noted above, MEH-PPV shows bluer fluorescence when in solution due to the extended conformation of polymer chains. This shows the THF did swell the nanoparticles and induce a more fluid like environment.
**Figure 26:** Fluorescence spectrum of “killed” nanoparticles

Since the dye is still within nanoparticles, which happen to be swollen, SO→MC conversion should still be observed upon UV exposure and is apparent in the absorbance spectra in Figure 27.

**Figure 27:** Absorbance of “killed” nanoparticles before UV exposure (solid line) after 10 seconds 354nm irradiation (dotted line) and after 1 minute (dot-dash line).
As expected, “killed” nanoparticles did not exhibit fluorescence modulation upon UV irradiation due to the expanded size of the nanoparticles. It is thought that in swollen nanoparticles, the dye and polymer are no longer within Förster Radius and therefore are unable to FRET to each other. Figure 28 shows the fluorescence kinetics of “killed” nanoparticles at 590 nm; it shows no modulation.

**Figure 28:** Fluorescence kinetics of “killed” nanoparticles at 590 nm. The sample was exposed to 360 nm light at for 10 seconds between second 7 and second 20.

The result of these control experiments shows polymer fluorescence in nanoparticles is quenched by the dye dopant and the extent of the quench depends on the concentration of the dopant in the nanoparticles.

**HFCP-DOPED MEH-PPV NANOPARTICLES**

In order to determine why the nanoparticles are not completely quenched, nanoparticles on glass slides were studied using a fluorescent microscope. The lack of thermal stability of MeOSO makes microscopic studies of the MeOSO-doped MEH-PPV
nanoparticles impossible; the dye reverts from MC to SO and restores fluorescence to the polymer before a scan of quenched nanoparticles can be taken on the fluorescence microscope. To circumvent this issue, a thermally stable photochrome is needed.

1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (HFCP) (Figure 29) is a diarylethene that is thermally stable in both its ring-closed and ring-opened isomers. The ring-opened form does not absorb in the visible region of light while the ring-closed form absorbs in the region where MEH-PPV fluoresces (Figure 30). HFCP ring closure is a concerted reaction that is conrotatory and involves 6 pi electrons; it is therefore thermally forbidden and photo-chemically allowed. In order for the ring to undergo disrotary ring opening, which is thermally allowed, a large activation energy must be overcome. Since the activation energy is so large, the ring system is unlikely to undergo disrotary ring opening and is therefore thermally stable in the ring closed form. Exposure to visible light induces a conrotary ring opening, stopping FRET and allowing MEH-PPV to once again fluoresce.

**FIGURE 29:** HFCP in its opened (left) and closed (right) forms
FIGURE 30: Absorbance of HFCP in ring-open (solid line) and ring-closed (dotted line) forms in THF

The absorbance of HFCP in the closed form overlaps nicely with MEH-PPV fluorescence as seen in Figure 31.

FIGURE 31: HFCP absorbance in THF (solid line) and MEH-PPV nanoparticle fluorescence (dotted line)
One difficulty in using HFCP, however, is that irradiation with 365 nm light does not induce as high of a conversion from ring-opened to ring-closed form as 254 nm light. As seen in Figure 32, 5 seconds of irradiation with 254 nm light results in an absorption 16 times that of 5 seconds of irradiation with 365 nm light. Since MEH-PPV is easily degraded upon intense, high-energy light exposure, the amount of irradiation time of the nanoparticles must be limited. After several absorption studies of HFCP in THF, it was found that about 2 seconds of exposure was suitable for an acceptable ring closure conversion rate. Fluorescence kinetics of HFCP-doped MEH-PPV nanoparticles were then measured to confirm this observation. Figure 33 shows the fluorescence kinetics at 590 nm of HFCP-doped MEH-PPV nanoparticles 254 nm light exposure. It is clearly visible that 2 seconds provides an ample quench. Absorbance spectra taken before irradiation and after recovery from irradiation (Figure 34), indicates no polymer degradation from the 2-second irradiation.

**FIGURE 32:** The absorption of HFCP in THF before irradiation (solid line), upon 5 seconds of irradiation with 365 nm light (dot-dash line), and upon 5 seconds of irradiation with 254 nm light (dotted line).
FIGURE 33: The fluorescence kinetics of HFCP-doped MEH-PPV nanoparticles at 590 nm. 254 nm light was irradiated from seconds 3 to 9. Two seconds of irradiation, however, is enough for a maximum quench. 1:1 mole ratio of HFCP:MeOSO

A second difficulty in using HFCP is hole polaron quenching. This form of quenching was not prevalent during MeOSO nanoparticle studies due to the protective affect of the tertiary amine in the MeOSO dye structure. A tertiary amine was therefore

FIGURE 34: The absorption of 28 wt% HFCP-doped MEH-PPV nanoparticles before 2 seconds of irradiation with 254 nm light (solid line) and after irradiation and fluorescence recovery (dotted line). 1:1 mole ratio of HFCP:MeOSO
added to HFCP nanoparticles in order to control hole polaron quenching. MeOSO was initially used for this purpose until a better tertiary amine was found: 4,4'-dimethyltriphenylamine (triphenylamine) (Figure 35). Figure 36 shows the fluorescence kinetics at 590 nm of HFCP nanoparticles without the amine. The inability for this sample to reach a stable quench is attributed to the absence of amine in the sample.

**Figure 35:** 4,4'-dimethyltriphenylamine

![Image of 4,4'-dimethyltriphenylamine](image)

**Figure 36:** Fluorescence kinetics at 590 nm of 28 wt% HFCP-doped MEH-PPV nanoparticles.

To study the quenching ability of HFCP in MEH-PPV nanoparticles, the techniques used for MeOSO in MEH-PPV nanoparticles were repeated. Absorbance data showed that HFCP was successfully opening in nanoparticles upon UV irradiation (Figure 37).
**Figure 37:** Absorbance spectra of 28 wt% HFCP-doped MEH-PPV nanoparticles with a 3:1 mole ratio of HFCP:MeOSO before irradiation with 365 nm light (solid line) and after irradiation (dotted line). Inset: the difference spectrum (solid line) over laid with HFCP difference spectrum (dotted line). The difference between the difference spectrum and HFCP absorbance from 500 to 550 nm is most likely due to a small amount of polymer bleaching.

To study the thermal stability of ring-closed HFCP, a sample of nanoparticles was irradiated for 5 seconds to induce ring closure and then left in the dark for an extended period of time (Figure 38). This is the sample from Figure 33 above in which it was found that 2 seconds provides ample ring closure; therefore, the extra 3 seconds of irradiation might have bleached the polymer. If the polymer was bleached, the quench would not be as good as reported below but the stability of the quench, which is being examined with this sample, would not change. The nanoparticles show an initial quench to 6% of the original intensity and remained at a stable 8% for over 38 hours. During this 38 hour stretch of time, the nanoparticles were irradiated with 497 nm light every 20 seconds to measure the fluorescence intensity. This constant irradiation slowly bleached
the polymer. Because of this, the fluorescence of the sample did not return to its original intensity upon exposure to visible light. Again, the percentage of the quench may not be accurate due to polymer bleaching but the stability of the quench during the first few hours would not be affected.

**FIGURE 38:** Fluorescence kinetics of 28 wt% HFCP-doped MEH-PPV nanoparticles with a HFCP:MeOSO mole ratio of 1:1 at 590 nm.

![Fluorescence kinetics graph](image)

After determining that HFCP is stable for an extended period of time in the ring-closed form in nanoparticles, experiments in which the fluorescence of the nanoparticles was turned “off” and back “on” were preformed. Since HFCP undergoes ring opening upon exposure to visible light, a LED flashlight was used. This flashlight supplied more intense white light exposure than ambient room light and therefore allowed HFCP ring opening to occur at a faster rate than without the light. Figures 39 and 40 show the absorption kinetics data for HFCP samples in THF in which ambient room light or LED flashlight was applied for ring opening. The samples were both irradiated with 254nm light for 5 seconds and the kinetic scan was started immediately. Since the scans were
started immediately, the ring-closed dye was not dispersed evenly throughout the sample. Therefore, for the first few seconds of kinetic data for the LED light treated sample and the first few hundreds of seconds for the ambient light treated sample contain various increases in absorbance (Figure 40). Once the HFCP dyes completely diffuse throughout the THF sample, the absorbance decay kinetics stabilize.

**FIGURE 39:** Normalized absorbance kinetics at 590 nm of HFCP in THF with irradiation from ambient room light (solid line) and white light (dotted line).
FIGURE 40: The first 1000 seconds of the above kinetics data (Figure 39) expanded.

Fluorescence kinetics studies were measured to study the quenching and returning of MEH-PPV fluorescence in HFCP-doped MEH-PPV nanoparticles (Figure 41). The sample in Figure 41 is 28 wt% HFCP-doped MEH-PPV nanoparticles with a 3:1 mole ratio of HFCP:triphenylamine. The fluorescence intensity at 590 nm was recorded as a function of time to yield the kinetics data shown in Figure 41. Upon 2 seconds of irradiation with 254nm light (seconds 5 to 7), the intensity dropped to 8% of the original intensity. After relaxation of hole polaron quenching, the nanoparticles stabilized to 13% of the original fluorescence intensity. The quench to 13% is attributed in full to the HFCP ring closed isomer. At 50 seconds, the nanoparticles were exposed to ambient room light and at 75 seconds the nanoparticles were exposed to white light with the LED flashlight. During white light exposure, MEH-PPV restores its fluorescence up to a certain percentage, in this case to 69%. The flashlight applies intense white light to the nanoparticles that is thought to induce hole polaron quenching, which dissipates with time as seen after removal of the white light at second 563. The end result of the white
light exposure was a 95% recovery of fluorescence. This sample experienced no polymer bleaching from any of the irradiation periods (UV and white light) as shown in the absorbance spectra in Figure 42.

**FIGURE 41:** Fluorescence kinetics for 28 wt% HFCP-doped MEH-PPV nanoparticles with 3:1 mole ratio of HFCP:triphenylamine. Irradiation with 254 nm light from seconds 5-7, ambient light exposure at 50 seconds, white light exposure at 75 seconds, dark at 563 seconds. Insert: first 100 seconds expanded.

**FIGURE 42:** Absorption spectra from the sample in Figure 41 before (solid line) and after (dotted line) the kinetics study.
SINGLE NANOPARTICLE STUDIES

The reason for making stable nanoparticles was to study single nanoparticles on slides to determine if residual fluorescence was due to: (a) all nanoparticles only being quenched to a certain percent of the original intensity, or (b) if most of the nanoparticles attained a complete quench but some larger particles still fluoresced. In order to do this, dye doped nanoparticles were spin coated onto glass slides in poly(vinyl alcohol) (PVA), an optically transparent polymer matrix. For slides, 5 seconds of irradiation with 254 nm light was used to induce ring closure of HFCP. Solid slide samples needed more irradiation time than liquid samples due to the hindrance of molecular movement, in this case HFCP ring closure, that occur in solid form. Figure 43 shows a 20-micron x 20-micron glass slide sample before UV irradiation, after UV irradiation, and after LED white light irradiation. The series of images show that upon UV irradiation, most nanoparticles undergo fluorescence quenching but still have residual fluorescence. It is also apparent that some nanoparticles do not quench.

FIGURE 43: Nanoparticles in PVA on glass slide sample before irradiation (left) after 5 seconds of 254 nm irradiation (middle) and after white light irradiation (right).
Figure 44 shows two individual nanoparticles on a glass slide. The residual fluorescence of nanoparticles after UV irradiation and their ability to restore fluorescence after white-light irradiation are more clearly depicted in these images than in Figure 43.

**FIGURE 44:** Fluorescence quenching and recovery of two individual 28 wt% HFCP doped MEH-PPV nanoparticles with a 3:1 mole ratio of HFCP:triphenylamine.

Studying HFCP-doped MEH-PPV nanoparticles on glass slides allowed for the question of residual fluorescence to be answered on a nanoparticle by nanoparticle basis. The nanoparticles that do not undergo considerable quenching upon UV exposure are thought to be aggregates that do not have enough conversion of SO to MC to quench the collective fluorescence of aggregated polymer chains. Why nanoparticles do not obtain a complete quench is still under examination.
CONCLUSIONS AND FUTURE WORK

The photomodulation of polymer fluorescence was successful upon doping polymer nanoparticles with photochromic components. The photochrome dopant was either a spirooxazine (MeOSO) or a diarylethene (HFCP), which allowed for modulation of polymer fluorescence via FRET upon UV-irradiation. Both photochrome-fluorophore systems obtained quenching of polymer fluorescence to less than 10% and recovery to more than 95% of initial intensity.

Nanoparticles made using MeOSO as the dopant were useful in exploring the capability of the photochrome-fluorophore nanoparticle system to undergo FRET. MeOSO undergoes rapid SO→MC conversion upon UV exposure and rapidly reverts from MC back to SO after UV exposure is ceased. The ability for MeOSO to quench MEH-PPV fluorescence was, therefore, seen immediately upon UV exposure. This characteristic of MeOSO was paramount in determining what concentration of dye dopant is needed to obtain an optimal quench of fluorescence. It was possible to study multiple concentrations of dye dopant daily because of this, allowing for the optimal concentration of dye dopant to be found after about four months. If the dye dopant needed an excessive amount of UV exposure to convert between its colorless form and its visible light absorbing form, or needed extensive relaxation time, the analysis of this photochrome-fluorophore system would have taken much longer.

MEH-PPV nanoparticles doped with MeOSO never attained a complete quench, where the intensity of the polymer’s fluorescence reached zero, upon dopant concentration variations. There are two hypotheses for this: either all the nanoparticles in a sample have residual fluorescence or most nanoparticles are completely quenched while
some aggregated particles still fluoresce. To determine if either of these hypotheses were correct, single nanoparticle studies were performed. By studying the nanoparticles with a fluorescence microscope, it is possible to determine the source of the residual fluorescence. The rapid conversion rate between SO and MC forms of MeOSO makes it impossible to use MeOSO-doped MEH-PPV nanoparticles in single nanoparticle studies; fluorescence scans via microscope take longer than the conversion rates between SO and MC. The thermally stable diarelethene HFCP was therefore used for single nanoparticle studies.

Single nanoparticle studies showed that most nanoparticles have some residual fluorescence and that there are also some aggregates that do not undergo fluorescence quenching. It is hypothesized that there are not enough HFCP molecules on the outside of the nanoparticle to completely quench the polymer’s fluorescence. In order to determine if this hypothesis is correct, the concentration of HFCP needs to be varied. Another possibility for residual fluorescence is that the HFCP molecules are sterically hindered in nanoparticles. Therefore, there could be enough HFCP molecules in the nanoparticles to obtain a complete quench, but not enough of dye molecules can undergo ring closure to quench polymer fluorescence.

To further understand the cause of residual fluorescence, a new dye-polymer pair will be studied. If residual fluorescence occurs in this new dye-polymer system, nanoparticles of different dye concentrations will be studied with the microscope to see if the number of aggregated polymer particles is dependent on the amount of dopant. Also, different sizes of filters will be used to try to filter out aggregates from nanoparticle
solutions. Hopefully these studies will lead to a dye-doped polymer nanoparticle that obtains complete quenching of fluorescence upon UV exposure.

Stable polymer nanoparticles that undergo fluorescence modulation can be used for optical data storage systems, sensors, and high-resolution spectroscopy probes. Upon exposure to UV light by laser techniques, dye-doped nanoparticles on glass slides can be selectively quenched, which is a step towards optical data storage. Beth Childress of the Harbron lab is currently working on the selective quenching of polymer nanoparticles using diarylethenes as the dye dopants. Metivier et. al. have created 2-D fluorescent images with a pyrromethene donor and diarylethene acceptor that undergo fatigue resistant writing and erasing. The goal of the Harbron group nanoparticle project is to accomplish this type of re-writable sample using dye doped polymer nanoparticles.
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