# Phototriggered Fluorescence Color Changes in Azobenzene-Functionalized Conjugated Polymers

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We report fluorescence studies of phototriggered changes in spectral position and shape for two azobenzene-functionalized poly(*p*-phenylenevinylene) derivatives, poly(2-methoxy-5-(4-phenylazophenyl-4′-(1,10-dioxydecyl))-1,4-phenylenevinylene) (MPA-10-PPV) and poly(2-hexyloxy-5-(4-phenylazophenyl-4′-(1,10-dioxydecyl))-1,4-phenylenevinylene) (HPA-10-PPV). Upon trans → cis azobenzene photoisomerization, small (ca. 1 nm) blue shifts in spectral position are observed for MPA-10-PPV in 100% toluene, a good solvent for this polymer. These shifts are reversed upon visible irradiation and can be cycled many times. To probe the dependence of these shifts on initial polymer conformation, a dichloromethane−methanol cosolvent study was performed in which the solvent quality was decreased incrementally to induce a reduction in polymer coil dimensions. Unirradiated dichloromethane solutions of both MPA-10-PPV and HPA-10-PPV showed a red shift and reduction in quantum yield with increasing methanol concentration as expected based on literature results for other poly(*p*-phenylenevinylene) derivatives. These changes have been attributed to a dramatic conformational collapse by others and occur for these azo polymers over the 30−60% (v/v) methanol range. While little or no light-induced spectral shifting was observed at low (≤20%) and high (≥70%) methanol concentrations, significant spectral shifts were observed for both polymers upon azobenzene photoisomerization in solutions with 30−60% methanol, the same range over which the polymer undergoes collapse to a highly coiled state. The largest shifts are visible to the eye, with a 65:35 (v/v) dichloromethane−methanol solution of HPA-10-PPV showing yellow-orange fluorescence when the azobenzenes are trans, green fluorescence when they are cis, and yellow-orange again after the azobenzenes are returned to the trans state. We attribute these color changes to a reversible UV-phototriggered expansion of polymer coil dimensions that occurs as a result of trans → cis azobenzene side chain isomerization and provide temperature data to support this conclusion.

## Introduction

The photophysical properties of poly(*p*-phenylenevinylene) (PPV) derivatives are a subject of continued investigation due to the many optoelectronic applications of these multichromophoric, light-emitting polymers.[1−4] Numerous studies have demonstrated that PPV fluorescence properties in both dilute solutions and thin films are highly dependent on polymer chain conformation.[5−9] Although most PPV-based applications involve films, a detailed understanding of polymer conformation in solution is also important because polymer chains in films have been shown to retain “memory” of their solution phase conformation.[7,8] Polymer conformational differences manifest themselves in solution in the form of variations in the wavelength of maximum fluorescence ($\lambda_{max}$) and the quantum yield. In dilute solution the $\lambda_{max}$ of the well-studied MEH−PPV varies from 556 nm in THF to 565 nm in chlorobenzene[10] while its quantum yield in THF is 70% of its value in chlorobenzene.[11] Dynamic light scattering studies have demonstrated the conformational basis for these results by showing that MEH−PPV forms a more compact coil with a smaller hydrodynamic radius in THF than in chlorobenzene.[11] In general, PPV conformation affects both the conjugation length and energy migration to lower energy chromophores and hence has a substantial effect on the observed fluorescence.

Significant research effort has been expended in recent years to control and to tune PPV emission properties, and control of conformation is one strategy for emission tunability. Conjugated polymer conformations have been manipulated in solution via addition of a cosolvent,[12−17] variation of temperature,[10,12] and attachment of side chains that respond to an external signal such as light.[18−20] These stimuli share the ability to modulate polymer coil dimensions, which in turn can affect the observed fluorescence through changes in conjugation length, intrachain energy transfer, and formation of nonemissive species. Several groups have investigated the effect of PPV conformational collapse on fluorescence properties by using a cosolvent to incrementally decrease the solvent quality of a polymer solution.[12,13,15,16] Typically, the PPV is dissolved in a solvent in which it has good solubility, and measured amounts of a poor solvent for the polymer under study are added. As the concentration of poor solvent increases and the overall solvent quality decreases, the fluorescence spectrum shifts significantly to the red and the quantum yield decreases substantially. The spectral shift and quantum yield reduction typically occur over a narrow range of cosolvent compositions, and this sudden change in fluorescence properties has been interpreted as the result of a dramatic conformational collapse.[12] Heating a solvent mixture with collapsed polymer chains has been shown to reverse the conformational change due to heat-induced expansion of the coil dimensions.[12]

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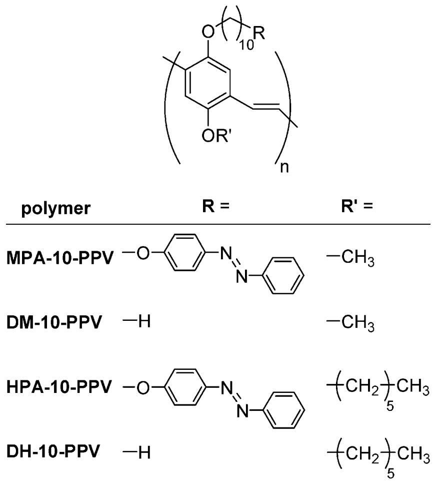
**SCHEME 1**



Conformational change can also be induced by light if the polymer is functionalized with suitable photoactive moieties. Azobenzenes, in particular, have been used extensively for this purpose in a variety of synthetic polymers, and the use of azobenzene photoisomerization to induce conformational change in polymers has been reviewed.[21−23] The azobenzene trans−cis photoisomerization reaction is known to proceed cleanly with few side reactions, and the azobenzene's large geometric change upon isomerization makes it an excellent candidate for inducing structural changes in macromolecules.[24,25] Numerous conjugated polymers with azobenzenes in their main chains[18,26,27] and side chains[19,20,28−36] have been synthesized, and some of these polymers have been shown to undergo conformational changes in the polymer backbone as a result of azobenzene photoisomerization. Izumi et al. synthesized poly(*p*-phenylene) derivatives with azobenzenes in the main chain and demonstrated that trans → cis azobenzene photoisomerization induced a reversible change in the hydrodynamic volume of the polymer in solution.[18] Lévesque and Leclerc found that the absorbance of polythiophenes with azobenzene side chains changed upon trans → cis isomerization in a manner consistent with main chain conformational change.[19] Our work also involves azobenzene-induced conformational change in polymers but with the emphasis on the effect of such change on *fluorescence* properties of conjugated polymers.

Our work focuses on PPVs functionalized with azobenzene side chains and the manipulation of PPV fluorescence properties via side chain photoisomerization. Our initial efforts focused on poly(2-methoxy-5-(4-phenylazophenyl-4′-(1,10-dioxydecyl))-1,4-phenylenevinylene) (MPA-10-PPV), a PPV derivative with alkoxy-tethered azobenzene side chains that was first synthesized by Yoshino and co-workers.[28−31] The structure of MPA-10-PPV is shown in Scheme 1. In preliminary studies of energy transfer in MPA-10-PPV, we determined that its emission intensity in dilute solution is partially quenched by nonradiative energy transfer from the PPV backbone to the azobenzene side chains.[37] Energy transfer occurs to both azobenzene isomers but with a higher apparent efficiency to the cis form. This efficiency differential enables modulation of the polymer emission intensity via cycling of the side chain isomeric state with UV and visible light. The energy transfer process also sensitizes cis → trans azobenzene isomerization in this system.

We recently determined that not only PPV emission intensity but also spectral position and shape (i.e., color) can be modulated by controlling the isomeric form of the azobenzene side chains with light. Azobenzene trans → cis photoisomerization triggers a blue shift in the PPV fluorescence spectrum, and cis → trans back-isomerization prompts a return to initial PPV spectral position. The magnitude of the fluorescence color shift is highly dependent on the initial conformation of the polymer chains, which can be manipulated via addition of a cosolvent that is a poor solvent for the polymer. We find that the largest phototriggered fluorescence color changes are observed in the chain collapse region, which is the range of cosolvent compositions over which the polymer coil collapses. The magnitude and nature of the shape changes are also dependent upon polymer structure, and we present data for MPA-10-PPV and a hexyloxy-substituted analogue, HPA-10-PPV (Scheme 1). We believe that the color changes are due to PPV main chain conformational changes triggered by side chain azobenzene photoisomerization and provide temperature data to support this hypothesis. This work extends our efforts to control PPV fluorescence properties with light.

## Experimental Section

**Sample Preparation.** The synthesis and characterization of the polymers are described in the Supporting Information. All solvents for spectroscopic experiments were spectral grade from Acros and were used as received. Stock solutions of polymer in good solvent (toluene, dichloromethane, or chloroform) were freshly prepared on the day of study by sonicating, filtering to remove any suspended particles, and diluting to $5 \times 10^{-5}$ M. Cosolvent solutions were prepared by combining 0.3 mL of this stock solution with the appropriate amounts of good solvent and methanol to bring the total volume of the solution to 3.0 mL and the polymer concentration to $5 \times 10^{-6}$ M. Solutions were prepared in septum-sealed cuvettes (Starna) and degassed for 15 min with nitrogen prior to study.

**Spectroscopy.** Absorption spectra were measured on a Varian Cary 50. Fluorescence experiments were conducted on a PerkinElmer LS55 with a thermostatted sample holder used in conjunction with a circulating heater/chiller. The excitation wavelength for all fluorescence experiments was 488 nm. Azobenzene trans → cis isomerization was induced by irradiating through the side of the cuvette with a 365 nm pencil lamp (Spectroline). UV irradiation periods were determined separately for each azo-functionalized polymer by measuring the irradiation time required to reach the photostationary state concentration of cis azobenzenes for that polymer. The UV irradiation time was 45 s for MPA-10-PPV and 30 s for HPA-10-PPV in dichloromethane. The same irradiation times were used for each polymer's corresponding control polymer. Visible irradiation was induced by the 488 nm line of an air-cooled argon-ion laser (Melles Griot) delivered to the top of the cuvette by liquid light guide (PTI). A visible irradiation period of 4 min was used for all samples.

## Results and Discussion

MPA-10-PPV is an azobenzene-functionalized PPV derivative that is well-solvated by moderately polar aliphatic solvents (THF, chloroform, dichloromethane) and benzene derivatives (toluene, chlorobenzene). Figure 1A shows absorption spectra of MPA-10-PPV in dilute toluene solution. Prior to irradiation, the azobenzene side chains are in the trans form and show an intense peak for the $\pi \rightarrow \pi^*$ transition at 352 nm and a weaker n $\rightarrow \pi^*$ peak that is obscured by the absorption of the PPV backbone ($\lambda_{\max} \sim 477$ nm). Trans → cis azobenzene isomerization is induced by a brief period of UV irradiation, and the trans $\pi \rightarrow \pi^*$ peak is greatly diminished while the weaker cis azobenzene $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ peaks show increased

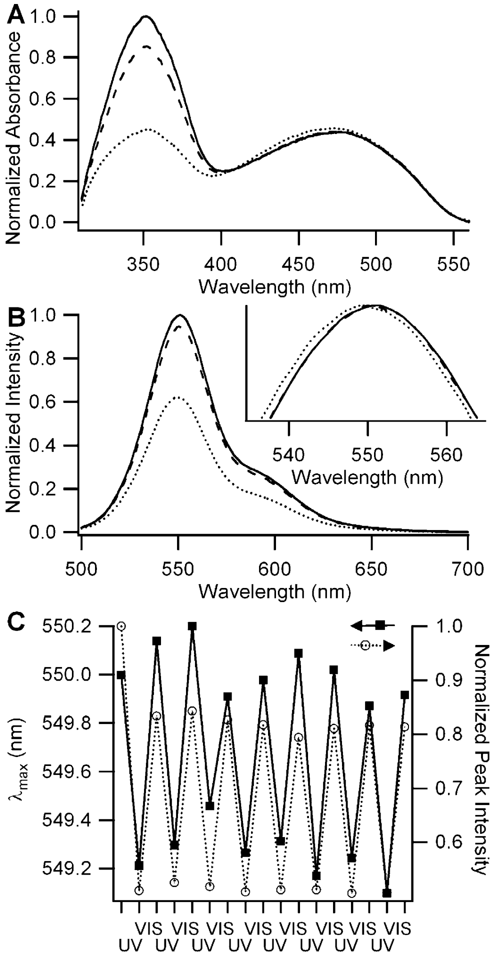


**Figure 1.** (A) Absorption spectra of MPA-10-PPV in 100% toluene before irradiation (solid line), after 30 s of 365 nm irradiation (dotted line), and after 4 min of 488 nm irradiation (dashed line). (B) Fluorescence spectra of the solution depicted in (A) before irradiation, after UV irradiation, and after 488 nm irradiation. The solid, dotted, and dashed lines have the same meaning in (B) as in (A). Inset: normalized spectra. (C) Cycling of $\lambda_{max}$ (left axis) and peak intensity (right axis) through eight cycles of 365 and 488 nm irradiation.

absorbance although they are obscured by the absorbance of the toluene solvent and the polymer backbone. Irradiation with visible (488 nm) light induces cis → trans back-isomerization via two pathways, direct excitation of the cis azobenzene isomer and sensitized isomerization due to the energy transfer. The trans $\pi \rightarrow \pi^*$ peak recovers most of its initial intensity upon back-isomerization, and the incomplete recovery is consistent with previous results in THF.[37]

Figure 1B shows typical fluorescence behavior of MPA-10-PPV in the same dilute toluene solution as a function of azobenzene side chain isomeric form. The PPV backbone fluoresces with a $\lambda_{max}$ of 550 nm when the azobenzene side chains are in the trans form. The PPV fluorescence spectrum following UV-induced trans → cis isomerization is quenched to 50−60% of initial peak intensity. The intensity quenching is consistent with previous measurements in THF and is due to nonradiative energy transfer from the PPV backbone to the nonfluorescent azobenzene side chains.[37] Upon irradiation with visible light, the peak intensity recovers to 94% of its initial value as a result of the cis → trans azobenzene back-isomerization.

The normalized spectra shown in the inset to Figure 1B reveal an additional effect that is observed in conjunction with the intensity quenching. When the azobenzene side chains are cis, the fluorescence spectrum is slightly blue-shifted from its position when the azobenzenes are trans. Upon trans → cis back-isomerization, the spectrum recovers its initial position. Although this shift in spectral position is very slight and not readily apparent without comparison of the normalized spectra, it is highly reproducible. Figure 1C shows the modulation of both spectral position, as expressed by the fluorescence $\lambda_{max}$, and peak intensity through eight cycles of UV and 488 nm irradiation. The $\lambda_{max}$ values were obtained from Gaussian fits of the spectral peak and show that the fluorescence spectrum is consistently blue-shifted by ca. 0.8−1.0 nm when the azobenzene side chains are cis than when they are trans. The spectral shifts are not observed in control polymer DM-10-PPV, which has the same alkoxy substituents as MPA-10-PPV but lacks the azobenzene (data not shown). This result indicates that the shifts are not the result of photoinduced processes in the main chain, and the reversibility of the phenomenon argues against photobleaching or other reactions as an explanation.

We hypothesize that the spectral shifts are due to polymer main chain conformational changes triggered by the azobenzene photoisomerization. If this hypothesis is correct, the phototriggered conformational change will be dependent upon the initial dimensions of the polymer coil, which are in turn solvent-dependent. The Figure 1 data were measured in toluene, a solvent in which MPA-10-PPV is very soluble and adopts a more open coil than it would in a solvent of lesser quality. Addition of a cosolvent that lowers the solvent quality of the polymer solution (i.e., a “poor solvent”) is a well-known means of inducing the transition to a more coiled structure for PPVs.[12−17] Given the conformational hypothesis, we expect to find a cosolvent regime in which the spectral changes observed upon azobenzene photoisomerization are larger than they are in solutions of good solvents such as toluene. We have performed cosolvent studies for MPA-10-PPV and its hexyloxy-substituted analogue, HPA-10-PPV, with dichloromethane (DCM) and methanol as the good and poor solvent, respectively. DCM was selected because both MPA-10-PPV and HPA-10-PPV are very soluble in it, and methanol was chosen because it is known to be a poor solvent for these polymers. The DCM−methanol solvent pair has been employed in previous studies of MEH−PPV.[12]

Fluorescence spectra of unirradiated MPA-10-PPV were measured in 100% DCM and in DCM−methanol mixtures ranging from 10% to 90% (v/v) methanol. As shown in Figure 2, spectra in solvent mixtures with small amounts of methanol ($\leq$20%) show reduced emission intensities but are not shifted in position relative to the 100% DCM spectrum, which is centered at 550 nm. Beginning at 30% methanol, the spectra undergo a gradual red shift in position as they continue to decrease in intensity. In solutions with 60% or more methanol the polymer has $\lambda_{max}$ values of approximately 580 nm, which do not change appreciably in position as the proportion of methanol is increased. Collison et al. studied the red shift and intensity decrease observed as the concentration of poor solvent is increased for MEH−PPV and concluded that only two species are present: isolated chains, with bluer emission and higher quantum yields, and well-packed structures, with redder emission and lower quantum yields.[13] They observed reduced torsional motion for MEH−PPV in solutions with poor solvent quality and found that the decreased mobility yields longer conjugation lengths, which produce redder emission than isolated chain segments. The well-packed structures also favor formation of nonemissive interchain excitations, which explains the reduced quantum yield in poor solvent mixtures.[14]

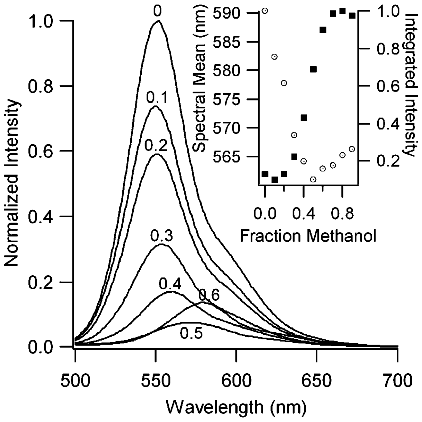


**Figure 2.** Fluorescence spectra of unirradiated MPA-10-PPV in 100% DCM and DCM−methanol mixtures with 10−60% v/v methanol. Each spectrum is labeled with the volume fraction of methanol. Spectra from solutions with >60% methanol were omitted for clarity. Inset: spectral mean (squares, left axis) and integrated intensity (open circles, right axis) as a function of fraction of methanol in DCM−methanol mixtures.

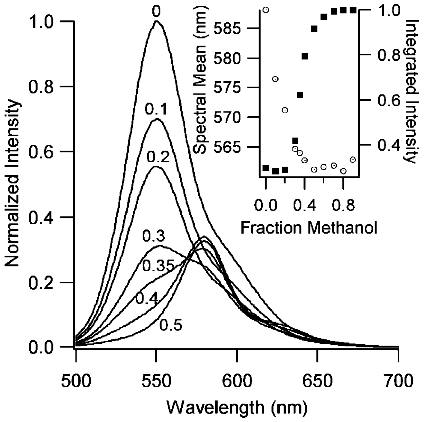


**Figure 3.** Fluorescence spectra of unirradiated HPA-10-PPV in 100% DCM and DCM−methanol mixtures with 10−50% v/v methanol. Each spectrum is labeled with the volume fraction of methanol. Spectra from solutions with >50% methanol were omitted for clarity. Inset: spectral mean (squares, left axis) and integrated intensity (open circles, right axis) as a function of fraction of methanol in DCM−methanol mixtures.

As shown in the Figure 2 inset, the changes in spectral position and intensity can be quantified by the spectral mean, which is the centroid of the spectrum, and the integrated emission intensity. Spectral position is quantified by the spectral mean rather than $\lambda_{\max}$ because the latter provides an incomplete description of intermediate spectra that contain substantial components at both 550 and 580 nm. Likewise, the integrated intensity is a more complete measure of these spectra than the peak intensity. Examination of the spectral mean as a function of methanol composition shows that the transition from the "560 nm spectrum" to the "590 nm spectrum" is fairly sharp, occurring over a narrow range of cosolvent compositions between 30% and 60% methanol. The decline in integrated intensity begins at lower methanol concentrations and is more gradual. The changes in spectral position and intensity with increasing amounts of poor solvent are consistent with those observed by Padmanaban and Ramakrishnan for MEH−PPV and are believed to be the product of dramatic conformational collapse of the polymer coil.[12] We refer to the 30−60% methanol range over which this collapse occurs for MPA-10-PPV as the "chain collapse region." Figure 3 shows the fluorescence spectra of unirradiated HPA-10-PPV, which has a hexyloxy side chain in place of MPA-10-PPV's methoxy substituent. The same general phenomena observed for MPA-10-PPV as the proportion of methanol in solution is increased are observed for HPA-10-PPV with the most notable difference being that the HPA-10-PPV spectra are more structured than their MPA-10-PPV counterparts, particularly for solutions with between 30% and 40% methanol. As was the case for MPA-10-PPV, the chain collapse region for HPA-10-PPV occurs between 30% and 60% methanol and involves a shift in spectral mean from 560 to 590 nm.

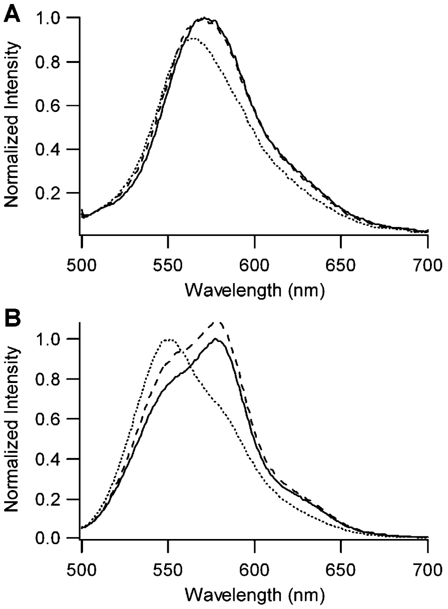


**Figure 4.** (A) Fluorescence spectra of MPA-10-PPV in 50:50 v/v DCM−methanol before irradiation (solid line), after 45 s of 365 nm irradiation (dotted line), and after 4 min of 488 nm irradiation (dashed line). (B) Fluorescence spectra of HPA-10-PPV in 65:35 v/v DCM−methanol before irradiation, after UV irradiation, and after 488 nm irradiation. The solid, dotted, and dashed lines have the same meaning in (B) as in (A).

The fluorescence spectra of MPA-10-PPV and HPA-10-PPV in 100% DCM and in each of 9−10 cosolvent mixtures were measured prior to irradiation, when the azobenzenes are in the trans form; after UV irradiation, when the azobenzenes are at the photostationary state (PSS) concentration of cis isomer; and following 488 nm irradiation, when the azobenzenes have returned to the PSS concentration of trans isomer. Figure 4 illustrates this procedure, showing the preirradation, post-UV irradiation, and post-488 nm irradiation spectra for MPA-10-PPV in a solution with 50:50 (v/v) DCM−methanol (panel A) and HPA-10-PPV in 65:35 DCM−methanol (panel B). Both sets of spectra exhibit changes in spectral position or shape upon UV irradiation that are almost completely reversed upon 488 nm irradiation. These fluorescence changes can be reproduced over multiple cycles (see the Supporting Information). The spectral mean is calculated for each spectrum, and a "blue shift," which is equal to the difference between preirradiation and post-UV spectral means, is computed for each set of spectra. The term blue shift will be used throughout the discussion as a general means of describing the UV-photoinduced changes. Some of these changes involve differences in spectral shape more than position, but all result in a reduction in the spectral mean, hence the blue-shift terminology.

The phototriggered spectral shape and position changes for MPA-10-PPV and HPA-10-PPV have significant qualitative differences that are exemplified by the sets of spectra shown in Figure 4. Both polymers show excellent recovery of their initial spectral shape, position, and intensity upon photoinduced (488

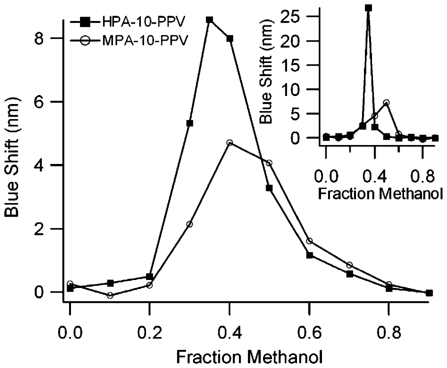


**Figure 5.** Blue shift as a function of methanol composition in DCM−methanol mixtures. The blue shift is the difference between the spectral means prior to irradiation and after UV irradiation. Inset: blue shift calculated from $\lambda_{max}$ values rather than spectral means.

nm) cis → trans back-isomerization.[38] In general, the MPA-10-PPV spectra are less structured than their HPA-10-PPV counterparts, and their UV-phototriggered spectral shifts can be characterized as blue shifts in positions with little, if any, change in spectral shape (Figure 4A). By contrast, the HPA-10-PPV spectra shown in Figure 4B are more vibronic, and UV-phototriggered changes entail a significant change in shape that involves a decrease in the spectral component at 580 nm and an increase in that at 550 nm. The origin of this qualitative difference between MPA-10-PPV and HPA-10-PPV may involve the relative stiffness of the polymers. A previous study has shown that increasing the bulk of a PPV side chain increases the stiffness of the polymer, and that this change in stiffness can affect fluorescence properties.[39]

Control polymers with the same structures as MPA-10-PPV and HPA-10-PPV but lacking the azobenzene in the side chain were synthesized and subjected to the same experimental conditions as the azo polymers. The fluorescence spectra of unirradiated solutions of both control polymers DM-10-PPV and DH-10-PPV show the same drop in quantum yield and red shift observed for the azo polymers as the proportion of methanol in the solution is increased (data not shown). In response to successive UV and 488 nm irradiations, both control polymers show either no response or changes consistent with mild, irreversible photodegradation at all cosolvent compositions (see the Supporting Information, Figure 2). The fact that the intensity either does not change or decreases slightly without recovery indicates that the effects demonstrated in Figure 4 for MPA-10-PPV and HPA-10-PPV cannot be reproduced in a polymer lacking the azobenzene but otherwise identical in structure.

Figure 5 shows the blue shift, calculated as described above, as a function of methanol composition for both azo polymers. The fluorescence spectra of both polymers undergo little or no spectral shifting at very low (≤20%) and high (≥70%) methanol compositions. In the intermediate range of methanol compositions, however, significant blue shifts are observed for both polymers with blue shift magnitudes gradually increasing, peaking, and then decreasing as the fraction of methanol in the cosolvent mixture is increased. The range over which significant blue shifts are observed is between 30% and 60% methanol for both polymers. This is the same range of solvent compositions over which the spectral mean undergoes the rapid change indicative of chain collapse, i.e., the chain collapse region. Additionally, the largest blue shifts for each polymer coincide with the midpoint of the collapse region in the spectral mean plots, 40−50% methanol for MPA-10-PPV and 35−40% methanol for HPA-10-PPV (see Figures 2 and 3 insets and Figure 4 spectra). Aside from these differences in the solution composition at which the largest blue shifts are observed, the most notable numerical difference between MPA-10-PPV and HPA-10-PPV is in the magnitude of the blue shifts, which are larger for HPA-10-PPV. The largest blue shift is 8.6 nm for HPA-10-PPV but 4.7 nm for MPA-10-PPV.

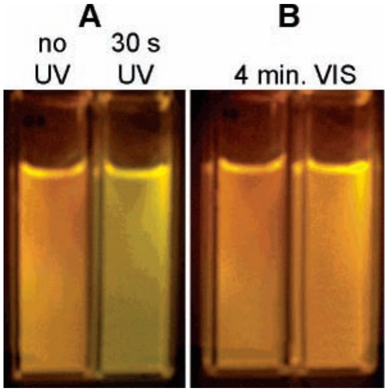


**Figure 6.** Fluorescence of HPA-10-PPV in 65:35 v/v DCM−methanol upon 488 nm excitation. (A) Left, solution not irradiated with UV; right, solution after 30 s of 365 nm irradiation. (B) Same solutions as (A) after 4 min of 488 nm irradiation. The photographs were taken through a 488 nm holographic notch filter (Kaiser Optical) to remove excitation light.

In view of the qualitative shape differences between MPA-10-PPV and HPA-10-PPV fluorescence spectra demonstrated above in Figure 4, it can be seen that calculating the UV-phototriggered blue shift (Figure 5) from spectral mean values obscures some of the differences in the behavior of the two polymers. The 50% methanol spectra for both polymers, for example, show approximately the same UV-phototriggered blue shift (∼4 nm) but different qualitative shifting behavior, as described above. Some of these differences become more apparent when the UV-phototriggered blue shift is calculated from spectral $\lambda_{max}$ values rather than from spectral means. The inset to Figure 5 shows the result of this analysis: the largest blue shift for HPA-10-PPV represents a nearly 27 nm change in $\lambda_{max}$ for the 65:35 DCM−methanol solution, and only very small or zero shifts are observed at other solvent compositions. MPA-10-PPV shows much smaller maximum shifts and nonzero shifts for more solutions than HPA-10-PPV, reflecting the fact that MPA-10-PPV tends to undergo actual blue shifts while HPA-10-PPV tends to exhibit shape changes based on differing amounts of 550 and 580 nm components.

Several of the solutions with the largest blue shifts exhibit phototriggered fluorescence color changes that are visible to the naked eye, and photographs of the color changes for the 65:35 DCM−methanol HPA-10-PPV solution are shown in Figure 6. Figure 6A shows two samples of the same solution: the left one, which was not irradiated with UV light, fluoresces yellow-orange while the right one, which was irradiated with UV light for 30 s, fluoresces green. The same two samples are shown in Figure 6B after being irradiated with 488 nm light for 4 min. The left sample still has not changed color, as expected, while the right one has returned to its original yellow-orange color. Control polymer DH-10-PPV does not change color under these irradiation conditions.

Figures 4−6 collectively demonstrate that UV irradiation triggers not only trans → cis photoisomerization in the azobenzene side chains but also reversible changes in the position and shape (color) of the polymer fluorescence spectra in cosolvent solutions in which the polymer coil is in an intermediate state of collapse. We believe that these reversible spectral shifts reflect

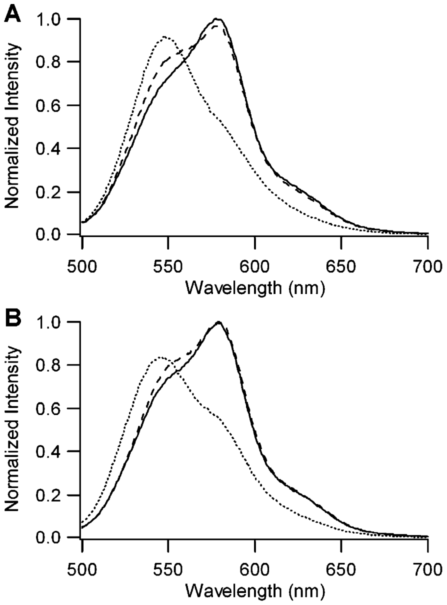


**Figure 7.** Fluorescence spectra of HPA-10-PPV in 60:40 v/v chloroform−methanol (A) before irradiation (solid line), after 1 min of 365 nm irradiation (dotted line), and after 4 min of 488 nm irradiation (dashed line) and (B) unirradiated at room temperature (solid line), at 50 °C (dotted line), and at 20 °C (dashed line).

a UV-phototriggered expansion of polymer coil dimensions, an idea supported by the fact that each post-UV irradiation spectrum closely resembles a spectrum from an unirradiated solution with lower methanol concentration, reflecting a less collapsed polymer conformation. Polymer coil dimensions in solution are known to be sensitive to temperature. In their study of MEH−PPV in cosolvent solutions, Padmanaban and Ramakrishnan showed that heating a solution of MEH−PPV in an intermediate state of collapse yielded a blue shift due to expansion of the polymer coil.[12] If it is indeed true that the observed changes in azo polymer fluorescence upon UV irradiation are due to polymer coil expansion, then it should be possible to reproduce these effects by increasing the temperature.

Chloroform was substituted for DCM in temperature experiments due to the low boiling point of DCM. Figure 7A shows HPA-10-PPV in a 60:40 chloroform−methanol solution prior to irradiation, after UV irradiation, and after 488 nm irradiation. This set of spectra is nearly identical in shape and irradiation response as the spectra measured in 65:35 DCM−methanol shown previously in Figure 4B, demonstrating that the substitution of chloroform did not alter the observed effects. Figure 7B shows the effect of temperature on unirradiated HPA-10-PPV: heating the solution to 50 °C reproduces the color change observed upon UV irradiation and cooling to 20 °C returns the spectrum nearly to its initial shape and intensity.[40] Absorption studies confirmed that heating the solution in the dark does not alter the concentration of trans azobenzenes, so the heating-induced color change can be attributed entirely to expansion of polymer coil dimensions. This result provides additional support for the hypothesis that UV irradiation triggers such an expansion. The largest MPA-10-PPV blue shift (in 50:50 chloroform−methanol) was also reproduced by heating but required just 35 °C to match the effect of UV irradiation as compared to 50 °C for HPA-10-PPV (data not shown).

We believe that the reversible color shifts reflect changes in the coil dimensions of individual polymer chains rather than multichain aggregates. It is important to note that all experiments were conducted in dilute ($5 \times 10^{-6}$ M) solutions. Addition of a poor solvent such as methanol could encourage formation of multichain aggregates. Photoisomerization of the azobenzene side chains could induce disruption of these aggregates, yielding the observed fluorescence color changes. However, the lack of a concentration dependence for the color changes argues against the presence of multichain aggregates. We measured the fluorescence spectra of HPA-10-PPV in 65:35 DCM−methanol solution before and after UV irradiation for the standard concentration ($5 \times 10^{-6}$ M) and as the concentration was dropped progressively down to nearly an order of magnitude lower ($6 \times 10^{-7}$ M) (see the Supporting Information, Figure 4). The observed UV-phototriggered color change is not altered as the concentration is lowered, indicating that the observed effects are due to self-coiling of individual chains rather than multichain aggregates.

Collectively, the results presented herein imply that trans → cis photoisomerization of the azobenzene side chains triggers polymer coil expansion while cis → trans photoisomerization induces a return to initial chain conformation. Studies of MEH−PPV in cosolvent solutions have demonstrated that just two species, isolated chains and well-packed chains, are formed by the polymer.[13,14] If the same holds true for the azo polymers studied here, azobenzene isomerization may be inducing a simple transformation of some number of well-packed chains to isolated chains and back again. The mechanism by which azobenzene isomerization induces changes in coil dimension in these particular polymers is not yet known. The 10-methylene-unit tether between the PPV backbone and the azobenzene side chains in MPA-10-PPV and HPA-10-PPV is long enough that azobenzene isomerization might not be expected to have any effect on the polymer backbone. However, there is literature precedent for isomerization of tethered azobenzenes inducing a conformational change in a macromolecular backbone in systems ranging from polypeptides[41] to polythiophenes.[19] In their study of azobenzene-substituted polythiophenes, Lévesque and Leclerc observed changes in the absorption of the conjugated polymer backbone consistent with conformational change upon side chain azobenzene isomerization.[19] These changes were independent of azobenzene tether length: the same results were observed in polymers with two methylene units, six methylene units, and four oxyethylene units in the tether.

The specific cosolvents employed in this work may also play a role in the nature and magnitude of the observed effects. Methanol, used here to reduce solvent quality, is substantially more polar than DCM and is also protic. The trans azobenzene isomer has a dipole moment of 0.5 D while the cis form is much more polar, with a dipole moment of 3.1 D.[23] The cis isomer has also been characterized as being more hydrophilic than the trans.[23] Given these facts, it seems likely that trans → cis photoisomerization significantly alters the balance of polymer−solvent interactions[23] in the azo polymers, with the cis azobenzene isomers being better solvated by the methanol cosolvent than the trans. This explanation has been invoked to explain photomodulated precipitation−dissolution of polypeptides with pendant azobenzenes.[42] Organization of azobenzene side chains through isomer-dependent stacking may also play a role in the observed color changes. Formation of trans azobenzene aggregates has been widely observed[22] in structures including dendrimers,[43,44] azo polypeptides,[42] and poly(ethylene glycol)-modified azobenzenes[45] to name just a few. Typically, stacking is disrupted upon isomerization to the cis isomer, and such a perturbation would also alter polymer−solvent interactions in a manner that could induce reorientation the polymer backbone. We believe that the nature of the poor solvent and azobenzene organization play a role in the MPA-10-PPV and HPA-10-PPV color changes.

The significant differences in the magnitude and qualitative nature of fluorescence color shifts in MPA-10-PPV and HPA-10-PPV may involve issues of solvation and stiffness. HPA-10-PPV has a higher solubility than MPA-10-PPV in solvents such as DCM and chloroform because of its longer alkyl substituents. Formation of the cis azobenzenes, which are better solvated by methanol than their trans counterparts, induces a reorientation in the polymer backbone of both polymers. HPA-10-PPV's reorientation may be larger in magnitude because it involves a shift from a state in which the polymer backbone is well-solvated to one in which the cis side chains are well-solvated. The MPA-10-PPV backbone, by contrast, is less well-solvated initially when the azobenzenes are trans, so the reorientation is less dramatic. Chain stiffness may also play a role in the different behavior of the two azo polymers. If HPA-10-PPV is indeed more stiff than MPA-10-PPV, as literature precedent suggests,[39] then it may be more likely to exist in just two states, a looser coil with a fluorescence spectrum with $\lambda_{\max} = 550$ nm and a compact coil with a spectrum with $\lambda_{\max} = 580$ nm. The more flexible MPA-10-PPV may be able to adopt a wider variety of intermediate conformations that yield fluorescence spectra with a range of $\lambda_{\max}$ values between the 550 and 580 nm extremes. Such a difference in ability to adopt certain conformations would explain MPA-10-PPV's more gradual phototriggered shifting behavior and HPA-10-PPV's shifts in proportion of just two spectral components at 550 and 580 nm.

## Conclusion

We have observed phototriggered fluorescence color changes in two PPV derivatives with alkoxy-tethered azobenzene side chains. The fluorescence changes are largest in cosolvent mixtures with 30−60% methanol in DCM, which matches the range of solvent compositions over which the polymer collapses. Further fluorescence studies indicate that the trans → cis azobenzene side chain isomerization induces an expansion in polymer coil dimensions that is reversed upon cis → trans back-isomerization. This conclusion is supported by temperature studies that reproduce the fluorescence changes induced by azobenzene forward- and back-isomerization by heating and cooling, respectively. For MPA-10-PPV, the phototriggered spectral changes are blue shifts in position with little or no change in spectral shape and are smaller in magnitude than for HPA-10-PPV, its hexyloxy-substituted analogue. The HPA-10-PPV spectra are more structured and undergo phototriggered shape changes involving an increase in 550 nm component and concomitant decrease in 580 nm component. Changes in the balance of polymer−solvent interactions upon azobenzene photoisomerization likely play a major role in inducing the polymer conformational change that is responsible for the observed changes in fluorescence. Differences in polymer solubility and chain stiffness may explain the differences in behavior for the two azo polymers. Future investigations will probe the role of specific solvent properties and polymer structural elements in the observed color changes as well as translation of the observed phenomena to thin films.

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**Supporting Information Available:** Additional fluorescence spectra of azo and control polymers, cycling data, and concentration dependence spectra are available along with synthetic and characterization details for the polymers and their precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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