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Solvent effects on phototriggered conformational changes in an azobenzene-functionalized poly(*p*-phenylene vinylene)

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Abstract

Poly(2-hexyloxy-5-((10-(4-(phenylazo)phenoxy)decyl)oxy)-1,4-phenylene vinylene) (HPA-10-PPV) is an azobenzene-functionalized poly(*p*-phenylene vinylene) derivative that previously has been shown to undergo changes in the position and shape of its fluorescence spectrum in response to *trans* → *cis*-azobenzene photoisomerization. This effect was initially observed in a binary dichloromethane-methanol solution and was attributed to a phototriggered expansion of polymer coil dimensions. In this report we explore the mechanism by which azobenzene isomerization induces this conformational change and the solvent properties that govern the magnitude of the change. Phototriggered fluorescence shifts are observed in mixtures of dichloromethane and each of 12 cosolvents, 7 protic and 5 aprotic. The shifts are largest in protic solvents but do not correlate with any single solvent parameter or combination of parameters. Smaller shifts are observed in mixtures with aprotic cosolvents, and the magnitude of these shifts correlates with solvent polarity/polarizability. The conformational changes responsible for the fluorescence shifts are attributed to a change in polymer–solvent interactions induced by the difference between properties of the *trans*- and *cis*-azobenzene isomers. Isomerization to the more polar *cis*-azobenzene promotes an increase in polymer–solvent interactions. These results suggest a means by which the magnitude of phototriggered fluorescence changes could be increased in future derivatives.

Keywords: Poly(*p*-phenylene vinylene); Azobenzene; Fluorescence

1. Introduction

The light-emitting properties of soluble poly(*p*-phenylene vinylene) (PPV) derivatives have been intensively investigated in recent years due to potential applications in organic light-emitting diodes and other optoelectronic devices [1,2]. PPV is a multichromophoric molecule in which each polymer chain is composed of many "quasi-chromophores" separated by tetrahedral defects or kinks in the backbone [3]. Functionalization of PPV with alkoxy side chains confers solubility in organic solvents, which enables formation of thin films via spin casting from solution. Our work focuses on PPV derivatives in which one of the alkoxy side chains has been modified with a photochromic moiety that enables control of PPV emission properties with light. We have studied a family of azobenzene-functionalized PPV derivatives and determined that the azobenzene photoisomerization can affect the fluorescence of the PPV backbone in two major ways in solution: by photomodulating the fluorescence intensity via electronic energy transfer [4] and by inducing spectral shifts due to conformational change [5]. In this report we investigate the mechanism by which azobenzene side chain isomerization induces conformational change in the polymer backbone.

The conformation of PPV derivatives in the solution phase has been shown to influence not only the fluorescence properties of the solution itself [6] but also that of nanostructures [7] and films [8–10] formed from polymer solutions. Polymer backbone conformation can affect the conjugation length of the quasi-chromophores, formation of aggregated species, and the efficiency with which energy is transferred among chromophores. These properties, in turn, manifest themselves in the steady-state fluorescence spectrum through the position and shape of the spectrum and the quantum yield. A number of investigators have observed variations in the wavelength of maximum fluorescence (λ_{max}) and quantum yield as a function of solvent in PPV derivatives [6,11,12].

Systematic conformational change in PPV derivatives can be induced through incremental reduction of solvent quality

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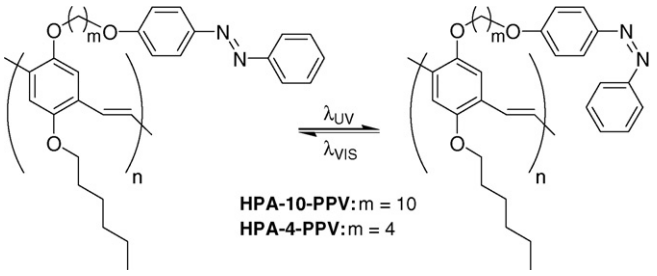

Scheme 1.

via addition of a cosolvent that is a poor solvent for the polymer [13–16]. As the proportion of poor solvent is increased, polymer–solvent interactions become less favored. Over a fairly narrow range of cosolvent compositions, the polymer chain undergoes a conformational collapse that has two major effects on the fluorescence spectrum: a substantial red-shift in position (ca. 30 nm) and a major reduction in intensity due to a drop in the quantum yield. These effects have been attributed to the formation of well-packed states with spectral properties resembling those of polymer thin films [14]. Similar fluorescence red shifts have also been observed in aggregated oligo(*p*-phenylene vinylene)s [17–19] and poly(distyrylbenzene)s [20].

In our previous work, we used a cosolvent strategy to vary the conformation of HPA-10-PPV, an azobenzene-functionalized PPV derivative (Scheme 1) [5]. When methanol, a poor solvent for HPA-10-PPV, is added to a dilute solution of the polymer in dichloromethane (DCM), the fluorescence spectrum undergoes a red shift in position and reduction in intensity analogous to that observed for other PPV derivatives. *Trans* → *cis*-azobenzene photoisomerization triggers a partial reversal of the effect of the poor solvent: the spectrum undergoes a blue shift and matches the appearance a *trans*-polymer spectrum measured at a lower methanol concentration. The initial spectrum is restored upon *cis* → *trans*-azobenzene back-isomerization. Heating the polymer solution, which is known to expand polymer coil dimensions, reproduces the effect observed upon *trans* → *cis*-photoisomerization whereas cooling, which induces contraction of the polymer coil, returns the spectrum to its initial position and shape [5]. Thus, the azobenzene isomerization provides us with a photoswitch to convert between collapsed and extended conformational states of this PPV derivative. The phototriggered fluorescence effects are independent of concentration down our lowest measurable value (6×10^{-7} M), indicating that they represent changes in individual chains rather than aggregates [5].

Our previous work on phototriggered fluorescence changes in HPA-10-PPV left two open questions: (1) How does azobenzene isomerization trigger conformational changes in the polymer backbone? (2) What factors govern the magnitude of the conformational change? To answer these questions, we present studies of the phototriggered fluorescence changes as a function of azobenzene tether length and cosolvent identity. We determine that the observed effects are dependent on the poor solvent component of the cosolvent mixture. Phototriggered fluorescence changes that qualitatively match those observed in DCM:methanol are observed when methanol is replaced by any of six different protic solvents. Variations in the magnitude of the effects among the protic cosolvents do not appear to correlate with any single solvent parameter. When an aprotic solvent is used as the poor solvent, the magnitude of phototriggered fluorescence changes is much smaller than observed with protic solvents and correlates with the polarity/polarizability of the solvent. Collectively, these results indicate that fluorescence changes triggered by azobenzene photoisomerization are due to a change in solvation that occurs because of the different properties of *trans*- and *cis*-azobenzene. This work continues our efforts to control the fluorescence properties of polymers with light.

2. Experimental

The synthesis of poly(2-hexyloxy-5-((10-(4-(phenylazo)phenoxy)decyl)oxy)-1,4-phenylene vinylene) (HPA-10-PPV) has been described previously [5]. Poly(2-hexyloxy-5-((4-(4-(phenylazo)phenoxy)butoxy)oxy)-1,4-phenylene vinylene) (HPA-4-PPV) was synthesized by the same method. Solvents for spectroscopic experiments were spectral grade from Acros and were used as received. Particularly hygroscopic solvents were obtained as anhydrous grade in septum-sealed bottles from Aldrich or Acros. Stock solutions of polymer in good solvent (dichloromethane or chloroform) were prepared freshly the day of use by sonicating, filtering to remove suspended particles, and diluting to an absorbance of 0.5 for the PPV peak. Cosolvent solutions were prepared by adding 0.3 mL of stock solution to 2.7 mL of the appropriate solvent mixture so that the final absorbance at the PPV peak of each solution was approximately 0.05. All solutions were prepared in septum-sealed cuvettes (Starna) and degassed for 15 min with nitrogen prior to study. Absorption spectra were measured with a Varian Cary 50, and fluorescence spectra were obtained with a Perkin-Elmer LS55 with 488 nm excitation. *Trans* → *cis*-azobenzene isomerization was induced by holding a 365 nm pencil lamp (Spectroline) next to the sample cuvette for 30 s, which was determined by absorption measurements to be sufficient to reach the photostationary state. The reversibility of all ultraviolet-induced phenomena was confirmed by inducing azobenzene back-isomerization with the 488 nm line of an argon-ion laser (Melles Griot).

3. Results and discussion

Fig. 1 shows absorption, excitation, and emission spectra for HPA-10-PPV with side chains in the trans form (*trans*-HPA-10-PPV) in dilute DCM solution. In samples prepared and stored in the dark, the azobenzenes are predominantly in the trans form and show a strong absorption at 349 nm due to the π–π^* transition of the *trans* isomer. As depicted in Scheme 1, UV irradiation induces *trans* → *cis*-azobenzene isomerization to yield a photostationary state (pss) concentration of *cis*-azobenzene side chains. Irradiation with visible light returns the azobenzene side chains to their thermally stable *trans* form. The conjugated polymer backbone shows an absorption with $\lambda_{max} \sim 470$ nm and a tail extending back into the ultraviolet (see excitation spectrum). Excitation of the polymer backbone yields green fluorescence with $\lambda_{max} = 550$ nm in 100% DCM solution. This fluorescence

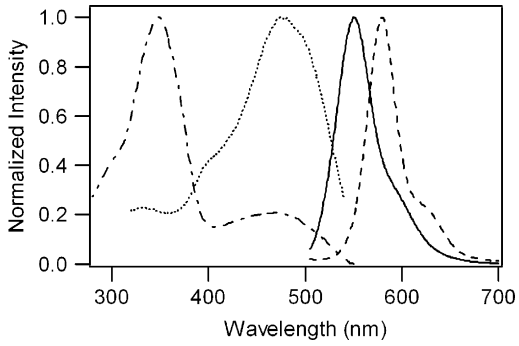

Fig. 1. Static spectra of HPA-10-PPV: absorption (dash-dot line), excitation for fluorescence at 550 nm (dotted line), and fluorescence upon 488 nm excitation (solid line) measured in dilute DCM solution, and fluorescence (dashed line) measured in DCM:methanol solution with $\chi_{MeOH} = 0.93$.

is due entirely to the PPV backbone as the azobenzene side chains are not detectably fluorescent in either isomeric form. As noted in Section 1, addition of methanol to DCM solution of the polymer induces a conformational collapse of the polymer that is evidenced by a red shift in the fluorescence spectrum. Fig. 1 shows the emission spectrum of HPA-10-PPV in a DCM:methanol solution with a methanol mole fraction (χ_{MeOH}) of 0.93. The λ_{max} of this spectrum is 580 nm, representing a shift of ca. 30 nm versus pure solvent. The two emission spectra in Fig. 1 reflect the conformational extremes of extended and collapsed polymer chains of HPA-10-PPV [5].

At intermediate cosolvent concentrations, the fluorescence spectra of HPA-10-PPV show substantial components at both 550 and 580 nm. In DCM:methanol solution with $\chi_{MeOH} = 0.46$, the fluorescence spectrum of *trans*-HPA-10-PPV has a λ_{max} of approximately 580 nm with a strong 550 nm shoulder (Fig. 2, trace b). UV irradiation of this solution induces *trans* → *cis*-azobenzene isomerization and a major change in the fluorescence spectrum of the polymer backbone. The fluorescence spectrum of HPA-10-PPV at the photostationary state (pss-HPA-10-PPV, trace a) has a λ_{max} of approximately 550 nm with a 580 nm shoulder. This dramatic change in spectral shape translates to a visible change in fluorescence color from green to yellow-orange. The spectral changes are completely reversed upon *cis* → *trans*-back-isomerization induced by 488 nm irradiation and can be cycled many times [5]. Because the λ_{max} gives an incomplete picture of spectra such as these with two strong components, we quantify the phototriggered changes in terms of the spectral mean, which is the centroid of the spectrum. For the spectra in Fig. 2, the spectral means of the *trans* and pss forms of HPA-10-PPV are 572 and 562, respectively, which equates to a phototriggered change of 265 cm^{-1}. We refer to the change in spectral mean in energy units as the "blue shift." With methanol as the cosolvent, we have observed phototriggered spectral changes of the same shape and blue shift magnitude in HPA-10-PPV solutions of chloroform and toluene as well as DCM.

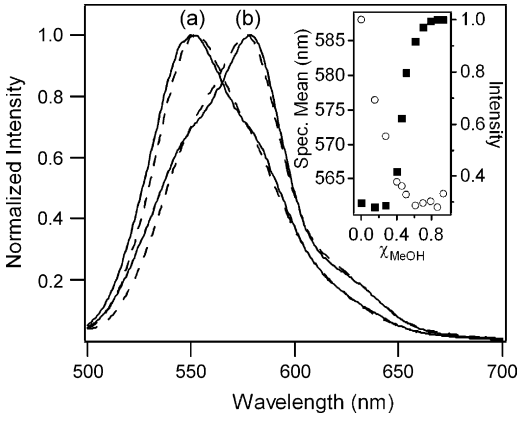

Fig. 2. Fluorescence spectra of HPA-10-PPV in DCM:methanol with $\chi_{MeOH} = 0.46$ in the all-*trans* form (trace b, solid line) and following irradiation to the pss form (trace a, solid line). The dashed line shows reconstructed spectra created according to Eq. (1) in the text.

The inset to Fig. 2 shows the evolution of the spectral mean and integrated intensity for *trans*-HPA-10-PPV as a function of methanol concentration. The spectral mean trajectory shows a steep rise over a fairly narrow range of cosolvent compositions while the integrated intensity declines from the first methanol addition and gradually levels off. The major changes in spectral position and intensity over a fairly narrow range of cosolvent compositions has been observed for MEH-PPV and interpreted as a reflection of dramatic conformational collapse [13]. We refer to the range of cosolvent concentrations over which this collapse occurs as the chain collapse region. Collison et al. have demonstrated that the fluorescence spectra of MEH-PPV in such mixed solvent systems can be accounted for by just two emitting forms of polymer chains: "isolated" chains with bluer emission and higher quantum yields and "well-packed" structures with redder emission and lower quantum yields [14].

Collison et al. provided additional support for their theory of two morphological chain species by successfully reconstructing experimental spectra with a linear combination of spectra from the conformational extremes [14]. We applied this approach to the reconstruction of the spectra shown in Fig. 2 using the spectra measured in 100% DCM and in 10:90 (v/v) DCM:methanol (equivalent to $\chi_{MeOH} = 0.93$) according to Eq. (1):

$$\text{Fit} = a_{100} \times (100\%\ \text{DCM spectrum}) + a_{10} \times (10\%\ \text{DCM spectrum}) \quad (1)$$

where a_{100} and a_{10} are the coefficients that control the magnitude of each spectrum's contribution to the reconstruction. The reconstructions appear as dashed lines in Fig. 2 and show fairly good agreement with the experimental spectra. An approximation of the relative proportions of extended and collapsed polymer chains that contribute to the observed spectrum can be obtained from the reconstruction coefficients. The *trans*-HPA-10-PPV spectrum (trace b) was reconstructed with $a_{100} = 0.23$ and $a_{10} = 0.77$, and values of $a_{100} = 0.58$ and $a_{10} = 0.42$ were used for pss-HPA-10-PPV (trace a). Thus, it appears that Fig. 2 spectra represent a phototriggered shift in the proportions of extended and collapsed polymer in solution: *trans* → *cis*-azobenzene isomerization induces an increase in the proportion of extended polymer chains that is reversed upon back-isomerization (spectra not shown).

Azobenzene photoisomerization has been used to trigger conformational or structural change in a number of azobenzene-functionalized macromolecular systems [21] in solution [22–25] including polystyrene [26], polypeptide [27–29], diblock copolymer [30], and radical copolymer [31] derivatives, to give just a few examples. In many cases the difference between *trans*- and *cis*-azobenzene properties is responsible for the macromolecular conformational change. While *trans*-azobenzene is fairly hydrophobic and has a dipole moment of 0.5 D or less, *cis*-azobenzene is more hydrophilic and more polar, with a dipole moment of 3.1 D [23]. These differences mean that *trans* → *cis*-isomerization can alter the balance of polymer–polymer and polymer–solvent interactions [23], leading to effects that range from changes in polymer coil dimensions [26] to reversible dissolution–precipitation of polypeptides [28]. Tong et al. studied vesicles formed by diblock copolymers with a hydrophobic azobenzene-functionalized methacrylate block and a hydrophilic *tert*-butyl acrylate-*co*-acrylic acid block [30]. Vesicles that are stable with azobenzenes in the *trans* form dissociate upon *trans* → *cis*-isomerization and reform upon back-isomerization. These dramatic effects were attributed to a decrease in the hydrophobicity of the azobenzene-methacrylate block due to the increase in dipole moment upon *trans* → *cis*-azobenzene isomerization. These literature precedents suggest that the conformational change that causes the fluorescence shifts in HPA-10-PPV is induced by a change in solvation that occurs in response to the change in azobenzene properties upon isomerization.

If the solvation hypothesis is correct, changing the length of the tether between the azobenzene and the polymer backbone should not change the observed phototriggered effects, as the number of azobenzenes would remain constant. We compared the fluorescence behavior of HPA-10-PPV with HPA-4-PPV, a polymer with 4 methylene units in its azobenzene tether in contrast with the 10 methylene units in HPA-10-PPV (Scheme 1). Due to the limited solubility of HPA-4-PPV, the comparison was performed with chloroform rather than DCM as the primary solvent. Fig. 3A shows the trajectory of the spectral mean of HPA-10-PPV as a function of the mole fraction of methanol added to the chloroform solution with separate traces for *trans* (open circles) and *cis* (closed squares) forms of the polymer. At low methanol concentrations ($\chi_{MeOH} < 0.4$), *trans* → *cis*-azobenzene isomerization does not induce any changes in the spectral means. As the methanol concentration increases ($0.45 < \chi_{MeOH} < 0.70$), the spectral mean of the *trans* form undergoes the expected red shift and differences between the spectral means of the *trans* and pss forms become significant. The phototriggered spectral changes are quantified by the blue shift, which is the difference between *cis* and *trans* spectral means in energy units. The inset to Fig. 3A shows that the largest phototriggered spectral differences coincide with the chain collapse region. It is important to note that the same differences between spectra of *trans*- and pss-HPA-10-PPV are observed whether each individually prepared solution is photoisomerized to the pss or whether methanol is added incrementally to a solution of *trans* or pss polymer prepared in 100% chloroform. Fig. 3B shows the spectral mean and blue shift trajectories

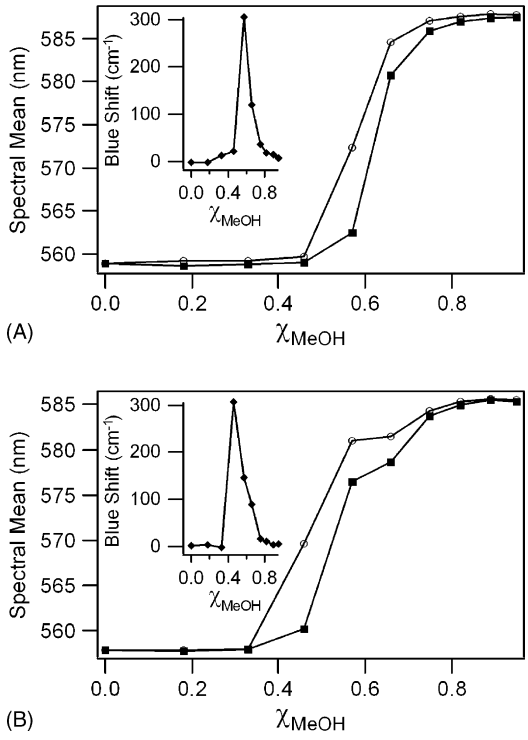

Fig. 3. Spectral mean trajectories as a function of methanol mole fraction in DCM:methanol solution for all-trans (open circles) and pss (closed squares) polymer: (A) HPA-10-PPV and (B) HPA-4-PPV. Inset: blue shift as a function of methanol mole fraction.

for HPA-4-PPV. Although the polymer collapses at slightly lower methanol concentrations than HPA-10-PPV, the behavior of the two polymers is otherwise essentially the same, with both exhibiting blue shifts of the same magnitude.

The fact that both HPA-10-PPV and HPA-4-PPV exhibit nearly identical phototriggered fluorescence changes in chloroform:methanol solutions lends some support to the idea that a change in solvation due to the change in azobenzene properties is responsible for the observed effects. To further investigate solvation in this system, we studied mixtures of DCM with 11 additional cosolvents, 6 protic and 5 aprotic (Table 1). To be included in the study, each cosolvent had to be miscible in DCM, a poor solvent for HPA-10-PPV, non-absorbing in the wavelength region under study, and not known to undergo any ultraviolet-induced photochemistry. All of the cosolvents studied induce polymer chain collapse and yield S-shaped spectral mean curves analogous to those shown in Fig. 3A. As was observed with methanol as cosolvent, no spectral changes occur as a result of azobenzene isomerization at low and high cosolvent concentrations. Phototriggered spectral changes are observed in all cosolvent mixtures at intermediate cosolvent concentrations that coincide with the chain collapse region. The largest blue shift for each cosolvent mixture is typically observed at a cosolvent concentration that gives a *trans*-HPA-10-PPV spectrum with a spectral mean in the 570–580 nm range, i.e., in the middle of the chain collapse region. While the cosolvents have these common effects on the fluorescence of HPA-10-PPV, the magnitude of the phototriggered changes varies greatly.

Table 1
Blue shifts and summary of solvent parameters

	Solvent	BS (cm^{-1})[a]	χ_{cosolv}[b]	π^*	β	α
1	Methanol	281 ± 40	0.46	0.60	0.66	0.98
2	Ethanol	291 ± 14	0.42	0.54	0.75	0.86
3	1-Propanol	307 ± 30	0.46	0.52	0.90	0.84
4	2-Propanol	199 ± 16	0.46	0.48	0.84	0.76
5	1-Butanol	240 ± 20	0.51	0.47	0.84	0.84
6	2-Butanol	291 ± 16	0.51	0.40	0.80	0.69
7	Acetic acid	220 ± 39	0.53	0.64	0.45	1.12
8	Cyclohexane	49 ± 6	0.70	0.00	0.00	0.00
9	Ethyl ether	91 ± 23	0.48	0.24	0.47	0.00
10	Acetonitrile	128 ± 15	0.29	0.66	0.40	0.19
11	DMF	122 ± 26	0.36	0.88	0.69	0.00
12	DMSO	113 ± 33	0.26	1.00	0.76	0.00
–	DCM	–	–	0.82	0.10	0.13

[a] Maximum blue shifts for each solvent mixture are average values based on 3 to 11 measurements for each mixture.
[b] Mole fraction of cosolvent at which the largest blue shift is observed. Solvent parameters are for the pure solvent and were obtained from Ref. [33].

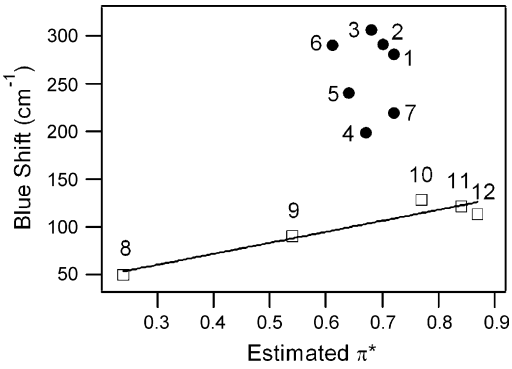

Fig. 4. Maximum blue shift observed for HPA-10-PPV in protic (closed circles) and aprotic (open squares) DCM:cosolvent mixtures plotted as a function of π^*, calculated for each mixture as described in the text. The numbers correspond to the cosolvents in Table 1. The line shows the fit through the aprotic solvents according to Eq. (3).

The results of the cosolvent study can be summarized as follows: protic cosolvents induce phototriggered spectral changes analogous to those depicted in Fig. 2 with methanol cosolvent while aprotic cosolvents yield changes of a much smaller magnitude. Table 1 lists the average blue shift for each cosolvent along with the cosolvent concentration at which it is observed and several solvent parameters. The protic cosolvents (solvents 1–7) all yield phototriggered fluorescence changes that qualitatively and, in many cases, quantitatively match those observed in DCM:methanol. The cosolvent concentration at which the largest blue shift is observed is nearly the same for all protic cosolvents ($\chi_{cosolv} = 0.4$–0.5) while the magnitude of the shifts varies from a low of 199 cm^{-1} for 2-propanol to a high of 307 cm^{-1} for 1-propanol. Aprotic cosolvents (solvents 8–12) show a much larger variation in the concentration required to induce the largest blue shift, with mole fractions ranging from 0.26 for DMSO to 0.70 for cyclohexane. This result is not surprising as the aprotic cosolvents have a wider range of solvent properties than the protic cosolvents. The magnitude of the largest blue shift observed in aprotic cosolvent mixtures varies from 49 cm^{-1} for cyclohexane to 128 cm^{-1} for acetonitrile, which is significantly lower than the shifts observed with protic cosolvents.

A number of solvent parameters vary substantially across the series of cosolvents and could potentially correlate with the magnitude of the observed shifts. We explored correlations using the linear solvation energy relationship (LSER) developed by Kamlet et al. for dealing with interacting solvent effects [32]. The general LSER equation involves parameters that account for solvent polarity/polarizability (π^*), hydrogen bond acceptor ability (β), and hydrogen bond donor ability (α), as shown in Eq. (2), where π^*, β, and α are weighted by regression coefficient s, a, and b, respectively, and BS is the blue shift:

$$BS = BS_0 + S\pi^* + a\alpha + b\beta \quad (2)$$

For the mixed solvent systems studied herein, values for all parameters were calculated as a linear combination of values for the two component solvents (e.g., $\alpha_{est} = \chi_{cosolv} \times \alpha_{cosolv} + \chi_{dcm} \times \alpha_{dcm}$). This calculation ignores nonideality of the mixtures and possible preferential solvation effects but provides a useful estimation for the examination of general trends.

We explored one-, two-, and three-parameter correlations based on Eq. (2) to determine if the magnitude of the blue shift correlates with solvent parameters. For the protic cosolvent mixtures, the magnitude of the shifts does not correlate with any single parameter or combination of parameters. Given that all protic cosolvents induce shifts larger than all aprotic solvents, the ability to donate hydrogen bonds must play a role in inducing polymer conformational change upon azobenzene isomerization. However, the magnitude of the observed shifts does not correlate with hydrogen bond donor ability as quantified by the α parameter, which ranges from a low of 0.69 for 2-butanol to a high of 1.12 for acetic acid for the protic cosolvents studied here [33]. For aprotic cosolvent mixtures, the magnitude of the blue shift was found to correlate with solvent polarity/polarizability (π^*) as shown in Eq. (3) [34]:

$$BS = 25\,cm^{-1} + (115\,cm^{-1})\pi^*, \quad r = 0.954 \quad (3)$$

Fig. 4 shows the largest blue shift observed for each solvent mixture plotted against the estimated π^* value for that mixture. The trend of increasing blue shift with increasing polarity/polarizability in the aprotic cosolvents (open squares) is evident. The protic cosolvents (closed circles) clearly do not shown any trend with respect to π^*.

The difference in phototriggered fluorescence effects observed when the cosolvent is protic versus aprotic is highlighted by comparison of 1-propanol and DMSO as cosolvents. The fluorescence spectrum of *trans*-HPA-10-PPV at the cosolvent concentration that yields the largest phototriggered blue shift is nearly identical for these two cosolvents. *Trans*-HPA-10-PPV in DCM with $\chi_{PrOH} = 0.46$ shows a spectrum that can be reconstructed (Eq. (1)) with $a_{100} = 0.35$ and $a_{10} = 0.65$. Likewise, the fluorescence spectrum of *trans*-HPA-10-PPV in DCM with $\chi_{dmso} = 0.26$ is reconstructed with nearly identical values of $a_{100} = 0.32$ and $a_{10} = 0.68$. These spectra appear to reflect similar populations of extended and collapsed chains, but the

extent to which these populations change upon *trans* → *cis*-azobenzene isomerization is very different in the two solvent mixtures. The spectrum of pss-HPA-10-PPV is reconstructed with $a_{100} = 0.85$ and $a_{10} = 0.15$ for 1-propanol cosolvent and $a_{100} = 0.48$ and $a_{10} = 0.52$ for DMSO as cosolvent. These reconstructions indicate that the equilibrium shifts dramatically in favor of extended chains in the DCM:1-propanol solution while the shift in DCM:DMSO solution is rather minor by comparison.

Collectively, the results described above demonstrate that all cosolvent mixtures can induce a change in the HPA-10-PPV fluorescence spectrum at cosolvent concentrations in the chain collapse region. Spectral reconstructions indicate that these changes reflect a shift in the population of extended and collapsed polymer chains, with *trans* → *cis*-azobenzene isomerization inducing some fraction of the collapsed chains to become extended. These effects can be explained by a change in polymer–solvent interactions that occurs upon azobenzene isomerization. As the concentration of poor solvent is increased, nonpolar *trans*-azobenzene will favor azobenzene–azobenzene and polymer–azobenzene interactions over solvent interactions. Association between *trans*-azobenzenes could involve organized aggregates, as has been observed in some azobenzene amphiphiles [35], although no evidence for a specific type of azobenzene aggregate was observed for HPA-10-PPV. Azobenzene photoisomerization produces *cis* isomers that are not only geometrically unable to organize but are also more polar. These changes make a polymer with *cis*-azobenzene side chains much more amenable to solvent interactions, particularly in polar solvent mixtures. This change in polymer–solvent interactions is responsible for the increase in the population of extended chains observed upon *trans* → *cis*-azobenzene isomerization. The observation that protic cosolvents promote a larger increase in polymer–solvent interactions than aprotic cosolvents could have its origins in hydrogen bonding to *cis*-azobenzene, which would further increase polymer–solvent interactions.

4. Conclusions

We have investigated phototriggered changes in the shape of the fluorescence spectrum of HPA-10-PPV, an azobenzene-functionalized conjugated polymer, in binary mixtures of dichloromethane and seven protic and five aprotic cosolvents. *Trans* → *cis*-azobenzene isomerization induces a "blue shift," as measured by a reduction in λ_{max} or spectral mean, in all of the solvent mixtures. Spectral reconstructions indicate that the fluorescence spectra can be accounted for by two species, extended and collapsed chains, and that the blue shifts reflect an increase in the proportion of extended chains triggered by the azobenzene photoisomerization. We attribute this population shift to increased polymer–solvent interactions promoted by *cis*-azobenzene's increased polarity versus nonpolar, hydrophobic *trans*-azobenzene. The largest blue shifts are observed for protic cosolvents although the magnitude of the shifts is not correlated with any single solvent parameter or combinations of parameters. In aprotic cosolvent mixtures, the blue shifts are of a smaller magnitude but are correlated with solvent polarity/polarizability. These conclusions suggest that phototriggered fluorescence changes in future polymers could be increased by tuning azobenzene structure to maximize the difference between *trans*- and *cis*-azobenzene dipole moment and related properties.

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