

## LETTERS

### Fluorescence Modulation via Isomer-Dependent Energy Transfer in an Azobenzene-Functionalized Poly(phenylenevinylene) Derivative

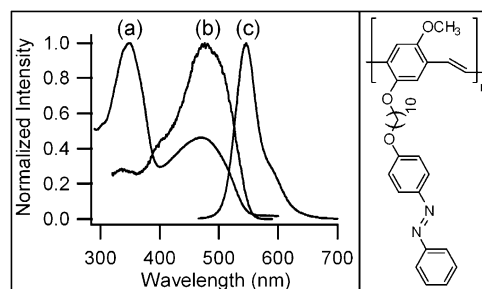
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Fluorescence studies of poly(2-methoxy-5-(4-(phenylazo)phenyl-4'-(1,10-dioxydecyl))-1,4-phenylenevinylene) (MPA-10-PPV), a PPV derivative with alkyl-tethered azobenzene side chains that was first synthesized by Yoshino and co-workers, are presented. The emission intensity of MPA-10-PPV in dilute solution is partially quenched by energy transfer from the PPV backbone to the azobenzene side chains, and the energy transfer is more efficient to the *cis* azobenzene isomer than to the *trans*. Because of this differential, the emission intensity can be reversibly modulated by controlling the isomeric form of the azobenzene side chain with light. The energy transfer process sensitizes the *cis* to *trans* azobenzene isomerization, and this additional isomerization pathway alters the composition of the azobenzene photostationary state in MPA-10-PPV.

Poly(*p*-phenylenevinylene) (PPV) derivatives are of interest for a variety of applications that exploit the strong light-emitting properties of these conjugated polymers.<sup>1,2</sup> We seek to develop a PPV-based molecular photoswitch to control polymer emission properties with light. Toward this end, we present fluorescence studies of poly(2-methoxy-5-(4-(phenylazo)phenyl-4'-(1,10-dioxydecyl))-1,4-phenylenevinylene) (MPA-10-PPV), a PPV derivative with alkyl-tethered azobenzene side chains that was first synthesized by Yoshino and co-workers.<sup>3–6</sup> The emission of MPA-10-PPV is dependent on the isomeric form of the side chain: the emission intensity is quenched by energy transfer from the PPV backbone to the azobenzene side chains, and the energy transfer is more efficient to the *cis* azobenzene isomer than to the *trans*. Thus, we can reversibly activate and deactivate the energy transfer, and hence backbone emission, by controlling the isomeric form of the azobenzene side chain with light. This work contributes a polymer-based system<sup>7,8</sup> to the growing number of organic, covalently linked bichromophoric systems

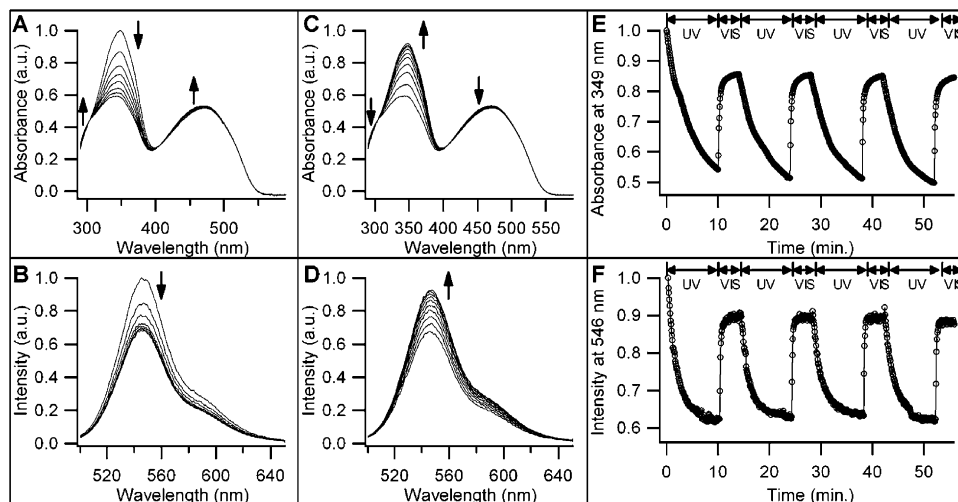


**Figure 1.** Static spectra of MPA-10-PPV in THF: (a) absorption; (b) fluorescence excitation for emission at 546 nm ( $\lambda_{\text{max}} = 478$  nm); (c) fluorescence emission upon 457 nm excitation ( $\lambda_{\text{max}} = 546$  nm). Side panel: MPA-10-PPV structure.

that undergo intramolecular nonradiative energy transfer to a photochromic acceptor.<sup>9–21</sup>

Absorption and fluorescence spectra of MPA-10-PPV in dilute THF solution are shown in Figure 1 along with the polymer structure. The azobenzene side chains are predominantly in the *trans* form at room temperature in solutions prepared and stored in the dark. The absorption spectrum

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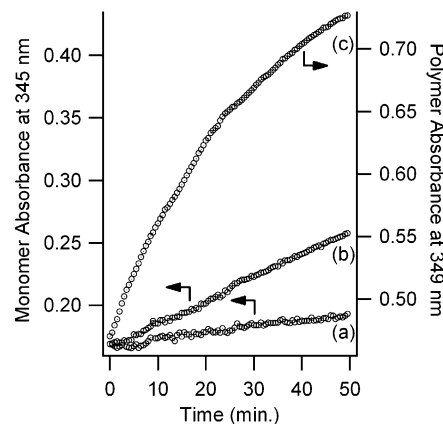


**Figure 2.** Spectral changes of MPA-10-PPV in dilute THF solution upon ultraviolet and visible irradiation. Absorption (A) and emission (B) spectra measured during ultraviolet irradiation with  $\Delta t = 1$  min between spectra. Irradiation source: Spectroline long wave UV pencil lamp (approximate intensity  $1 \text{ mW/cm}^2$  of 365 nm). Absorption (C) and emission (D) spectra measured during visible irradiation with  $\Delta t = 4$  min between spectra. Irradiation source: PTI 75 W xenon arc lamp equipped with 500 nm short pass cutoff and an Andover 400 nm long pass filter and transmitted via liquid light guide (approximate intensity  $= 2.6 \text{ mW/cm}^2$ ). Isosbestic points are observed at 304 and 410 nm in both (A) and (C). (E) Absorbance monitored at trans azobenzene  $\lambda_{\text{max}}$  (349 nm) and (F) emission monitored at  $\lambda_{\text{max}}$  (546 nm) during alternate cycles of ultraviolet and visible irradiation. For (E) and (F), UV cycles consist of 10 min irradiation with pencil lamp as described for (A) and (B); VIS cycles consist of 4 min irradiation with 488 nm line of Melles-Griot argon-ion laser transmitted via PTI liquid light guide (approximate intensity  $110 \text{ mW/cm}^2$ ).

features two peaks, an intense absorption at 349 nm corresponding to the  $\pi \rightarrow \pi^*$  transition of the trans azobenzene side chain and an additional peak at 470 nm due primarily to the conjugated polymer backbone with a contribution from the weak  $n \rightarrow \pi^*$  transition of the trans azobenzene. The excitation ( $\lambda_{\text{max}} = 478 \text{ nm}$ ) and emission ( $\lambda_{\text{max}} = 546 \text{ nm}$ ) spectra represent fluorescence from the polymer backbone as neither isomeric form of the azobenzene side chain emits under these conditions.

The response of MPA-10-PPV in THF solution to ultraviolet (UV) and visible irradiation is shown in Figure 2. UV irradiation near the  $\lambda_{\text{max}}$  of the trans azobenzene induces trans  $\rightarrow$  cis photoisomerization in the azobenzene side chains of the polymer. This process manifests itself in the absorption spectra as a reduction in the trans azobenzene  $\pi \rightarrow \pi^*$  peak and a concomitant increase in the weaker cis  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  peaks (shown in Figure 2A as a function of irradiation time). Isosbestic points are observed at 304 and 410 nm, indicating that the observed process reflects conversion between only two species, the trans and cis forms of the side chain. As the azobenzene side chains isomerize, the intensity of emission from the polymer backbone decreases to  $66 \pm 3\%$  of initial intensity (Figure 2B). These changes are reversible: upon visible (400–500 nm) irradiation, the azobenzenes undergo cis  $\rightarrow$  trans back-isomerization and the emission intensity recovers nearly to its initial intensity (Figure 2C,D).<sup>22</sup>

The emission intensity of the polymer can be modulated by reversibly cycling the side chain isomeric state with UV and visible light (Figure 2E,F). Each cycle of UV irradiation induces trans  $\rightarrow$  cis isomerization in the side chain and a corresponding decrease in emission intensity whereas each visible (488 nm) irradiation cycle returns most of the side chains to trans and the emission intensity to ca. 90% of its initial value. The extent of recovery depends on both the wavelength and intensity of visible irradiation and ranges from 80 to 98% depending on the irradiation source employed. It should also be noted that fluorescence quenching and recovery saturate before the photostationary state (PSS) concentration of cis azobenzene is reached.<sup>23</sup> On the basis of preliminary studies of related polymers with substituted azobenzenes, we believe that this is



**Figure 3.** Absorbance monitored at trans azobenzene  $\lambda_{\text{max}}$  as a function of time during cis  $\rightarrow$  trans back isomerization. The cis isomers were generated by ultraviolet irradiation (not shown). Left axis: monomer absorbance in dilute THF solution during thermal (a) and photoinduced (b) back isomerization. Right axis: MPA-10-PPV in dilute THF solution during (c) photoinduced back isomerization. (b) and (c) were measured under identical irradiation conditions (400–500 nm from Xe lamp, approximate intensity  $2 \text{ mW/cm}^2$ ). Monomer and polymer solutions were normalized to initial absorbance at the  $\lambda_{\text{max}}$  of the trans isomer prior to any irradiation.

due to issues of accessibility and/or relative alignment between donor polymer backbone and acceptor azobenzenes that can be resolved by tuning the azobenzene structure.

We have eliminated trivial explanations for the reversible fluorescence modulation including inner filter effects and radiative energy transfer<sup>24</sup> and assign the observed effect to nonradiative energy transfer to the azobenzene side chains. Evidence for energy transfer as the cause of the fluorescence modulation is shown in Figure 3. The MPA-10-PPV monomer (1-(4-(10-(2,5-bis(bromomethyl)-4-methoxyphenoxy)decyloxy)-phenyl)-2-phenyldiazene) was employed as a model to assess the extent to which the azobenzene response to irradiation is a result of its covalent attachment to the polymer backbone. The monomer and polymer have identical azobenzene subunits, but the monomer lacks the conjugated polymer backbone that is

formed during polymerization. Two monomer samples and one polymer sample were irradiated with UV light to generate the PSS concentration of cis azobenzene, and the absorbance at the trans azobenzene  $\lambda_{\text{max}}$  was monitored during the cis  $\rightarrow$  trans back-isomerization.

Trace a in Figure 3 shows the slow thermal return of the monomer from cis to trans in the dark and trace b shows that this process is only slightly faster via the photoinduced pathway with weak visible (400–500 nm) irradiation of the cis azobenzene. The polymer sample (c) was irradiated with the same intensity and wavelength range of visible light as the monomer and yet shows a much faster and more extensive recovery of its trans population (relative polymer:monomer first-order rate constants = 13:1). If cis  $\rightarrow$  trans back-isomerization in the polymer upon visible irradiation were due entirely to direct excitation of the cis isomer, traces (b) and (c) would be expected to be nearly identical because both monomer and polymer contain the same azobenzene moiety. The substantial difference in azobenzene back-isomerization rates in the monomer and polymer upon visible irradiation indicates that the conjugated PPV backbone, found only in the polymer, is transferring energy to the cis azobenzene side chain and sensitizing the cis  $\rightarrow$  trans back-isomerization. Energy transfer to both azobenzene isomers but sensitization of only the cis  $\rightarrow$  trans isomerization has been observed previously.<sup>15,25</sup> The sensitization also affects the rate of forward trans  $\rightarrow$  cis isomerization under UV irradiation with the result that this process is faster in the polymer than in the monomer (relative first-order rate constants = 1.4:1). The observed rate constant in the polymer case is the sum of the rate constants for the direct trans  $\rightarrow$  cis, direct cis  $\rightarrow$  trans,<sup>26</sup> and sensitized cis  $\rightarrow$  trans isomerizations whereas only the direct trans  $\rightarrow$  cis and cis  $\rightarrow$  trans rate constants contribute to the observed forward rate constant for the monomer.

Bichromophoric systems from the literature in which a fluorescent donor undergoes intramolecular energy transfer to an azobenzene acceptor typically involve energy transfer to both isomeric forms of the azobenzene but with different efficiencies.<sup>15,16,25</sup> This observation is not surprising given the substantial overlap of the cis and trans azobenzene absorption spectra. In our system, the extent of energy transfer to the trans isomer can be estimated by comparing emission intensities in the dark for MPA-10-PPV and a control polymer poly(5-(decyloxy)-2-methoxy-1,4-phenylenevinylene) (DM-10-PPV), which is structurally identical to MPA-10-PPV except without the azobenzene in the side chain. The emission of DM-10-PPV is 3.5 times as intense as MPA-10-PPV (with trans side chains) at the same concentration, indicating that MPA-10-PPV emission is at all times quenched by energy transfer to the azobenzene side chain. Fluorescence modulation is possible because the energy transfer process is more efficient to the cis isomer than to the trans, a result that is expected because of the greater spectral overlap between the cis absorption and polymer backbone emission.

In addition to modulating the fluorescence, the energy transfer process in MPA-10-PPV alters the isomeric composition of the photostationary state. The approximate % trans isomer at the PSS under UV irradiation is just  $17 \pm 7\%$  in the monomer but  $53 \pm 5\%$  in the polymer.<sup>27</sup> Although steric crowding might limit conversion of trans to cis to a certain extent in the polymer, we believe that the major factor in the high residual trans population at PSS in the polymer is the energy transfer process, which is active even upon UV irradiation. As is apparent in the MPA-10-PPV excitation spectrum (Figure 1), the polymer can be excited by UV irradiation, activating energy transfer to cis azobenzenes and sensitizing their return to trans. Thus, energy

transfer activates a competing cis  $\rightarrow$  trans pathway while direct trans  $\rightarrow$  cis photoisomerization is occurring. This additional pathway limits the concentration of cis that can be achieved in the polymer as compared to the monomer. Sensitization of the trans  $\rightarrow$  cis pathway by energy transfer is also theoretically possible but has not been observed in previous donor-azobenzene acceptor systems.<sup>15,25</sup>

The mechanism of nonradiative energy transfer in MPA-10-PPV is not yet known and could be a dipole–dipole (Förster) or exchange (Dexter) mechanism or a combination of mechanisms. If Förster transfer is assumed for the purpose of estimating the average energy transfer efficiency, then the efficiency,  $E$ , can be calculated according to

$$E = (1 - F_{\text{DA}}/F_{\text{D}}) \quad (1)$$

where  $F_{\text{DA}}$  and  $F_{\text{D}}$  are the donor fluorescence in the presence and absence of the acceptor, respectively.<sup>28</sup> Using DM-10-PPV for the  $F_{\text{D}}$  value, this relationship yields an energy transfer efficiency of 72% for the trans azobenzene. The maximum cis concentration obtained in these experiments is 47%, but the efficiency of energy transfer to the cis can be estimated by extrapolating the amount of quenching observed at low cis concentrations to 100% cis. This calculation yields  $E = 90\%$  for energy transfer to the cis azobenzene and assumes that the quenching does not saturate due to steric inaccessibility of the acceptors or other factors.

The above estimation yields a rough idea of the average energy transfer efficiencies to the two isomers but neglects a number of complicating factors in this system including multiple acceptors per donor, heterogeneity in the number of acceptors per donor, a distribution of donor–acceptor distances, and heterogeneous PPV photophysics. PPV-type conjugated polymer chains function as multichromophoric molecules in which each individual chromophore within a chain is made up of a number of repeating subunits and intramolecular energy transfer between chromophores can occur.<sup>29–31</sup> Because there is one azobenzene per subunit, there are potentially many acceptors for each donor chromophore and likely a distribution in this number as well as in donor–acceptor distances. When the energy transfer efficiency to the trans azobenzene is calculated via the Förster radius ( $R_0$ , ca. 32 Å) and a reasonable donor–acceptor distance ( $r$ ) according to eq 2,<sup>28</sup>  $E$  is much higher (>90%) than when calculated by eq 1 above (75%).<sup>32</sup>

$$E = R_0^6/(R_0^6 + r^6) \quad (2)$$

This difference may indicate that quenching by the azobenzene acceptors is, in fact, extremely efficient but that a fraction of donor chromophores remain unquenched at all times. These complexities will be further explored in future work, and experiments on the single molecule level may ultimately reveal a distribution of photophysical behavior that is presently observed as an ensemble average.

In conclusion, we have observed reversible modulation of MPA-10-PPV fluorescence via more efficient energy transfer to the cis than the trans isomer of the azobenzene side chain. Future work includes studies of the energy transfer mechanism and kinetics, exploration of the solid-phase behavior of MPA-10-PPV, and development of a more digital (on/off) photoswitch.

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**Supporting Information Available:** Additional spectral characterization of polymer precursors and experimental and synthetic details are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430.
- (2) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A. D.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
- (3) Matsui, T.; Nagata, T.; Ozaki, M.; Fujii, A.; Onoda, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 599.
- (4) Yoshino, K.; Nagata, T.; Nakayama, K.; Fujii, A.; Ozaki, M.; Onoda, M. *Mol. Mater.* **2000**, *12*, 143.
- (5) A structurally similar polymer was synthesized by Wang and co-workers: Wang, G.; Li, M.; Yu, M.; Guo, C.; Chen, X.; Li, G.; Zhou, E. *Liq. Cryst.* **2000**, *27*, 867.
- (6) Wang, G.; Li, M.; Chen, X.; Wu, F.; Tian, W.; Shen, J. *Macromol. Rapid Commun.* **1999**, *20*, 591.
- (7) Myles, A. J.; Gorodetsky, B.; Branda, N. R. *Adv. Mater.* **2004**, *16*, 922.
- (8) Gorodetsky, B.; Sud, D.; Norsten, T. B.; Myles, A. J.; Branda, N. R. *J. Porphyrins Phthalocyanines* **2003**, *7*, 313.
- (9) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *J. Org. Chem.* **2003**, *68*, 5681.
- (10) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 818.
- (11) Jin, M.; Lu, R.; Bao, C. Y.; Xu, T. H.; Zhao, Y. Y. *Opt. Mater.* **2004**, *26*, 85.
- (12) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759.
- (13) Giordano, L.; Jovin, T. M.; Irie, M.; Jares-Erijman, E. A. *J. Am. Chem. Soc.* **2002**, *124*, 7481.
- (14) Song, L.; Jares-Erijman, E. A.; Jovin, T. M. *J. Photochem. Photobiol. A: Chem.* **2002**, *150*, 177.
- (15) Ceroni, P.; Laghi, I.; Maestri, M.; Balzani, V.; Gestermann, S.; Gorka, M.; Vögtle, F. *New J. Chem.* **2002**, *26*, 66.
- (16) Asakawa, M.; Ashton, P. R.; Balzani, V.; Brown, C. L.; Credi, A.; Matthews, O. A.; Newton, S. P.; Raymo, F. M.; Shipway, A. N.; Spencer, N.; Quick, A.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1999**, *5*, 860.
- (17) Bahr, J. L.; Kodis, G.; de la Garza, L.; Lin, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2001**, *123*, 7124.
- (18) Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784.
- (19) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913.
- (20) Kawaia, T.; Sasaki, T.; Irie, M. *Chem. Commun.* **2001**, 711.
- (21) Ferri, V.; Scoconi, M.; Bignozzi, C. A.; Tyson, D. S.; Castellano, F. N.; Doyle, H.; Redmond, G. *Nano Lett.* **2004**, *4*, 835.
- (22) Emission intensity recovery also occurs during thermal back-isomerization of the side chains in the dark although this process is slow ( $k \sim 7 \times 10^{-4} \text{ min}^{-1}$ , data not shown).
- (23) The fluorescence kinetics are clearly faster than those measured by absorption during UV irradiation. Energy transfer to the trans azobenzene contributes to the observed fluorescence kinetics but not to absorption because the energy transfer alters the emission intensity but not the trans azobenzene population, which is monitored in the absorbance experiment. A more quantitative exploration of the kinetics is underway.
- (24) All experiments were conducted in dilute solution with absorbance less than 0.1 to minimize absorption of fluorometer excitation or polymer emission by the azobenzene side chains. Additionally, the observed fluorescence modulation effects were found to be independent of cuvette path length, a result that would not be expected if inner filter effects were operating. Poly(5-(decyloxy)-2-methoxy-1,4-phenylenevinylene) (DM-10-PPV), a control polymer without the azobenzene in the side chain, was mixed with decyloxyazobenzene in THF in proportions that simulated the MPA-10-PPV absorption spectrum. This control sample was submitted to the same irradiation conditions as for MPA-10-PPV; upon UV irradiation, the free decyloxyazobenzene underwent trans to cis isomerization and the polymer emission did not decrease (data not shown). Collectively, these controls demonstrate that the observed modulation is not due to inner filter effects or radiative energy transfer.
- (25) Vögtle, F. G.; Marius; Hesse, R.; Ceroni, P.; Maestri, M.; Balzani, V. *Photochem. Photobiol. Sci.* **2002**, *1*, 45.
- (26) The direct cis to trans back-isomerization under UV irradiation makes only a minor contribution to the observed kinetics. This discussion also excludes the contribution of the thermal cis to trans back-isomerization, which is slow at room temperature (see Note 22).
- (27) Because the absorbance of the cis azobenzene is negligible at the  $\lambda_{\text{max}}$  of the trans  $\pi-\pi^*$  band, the concentration of trans isomer at a given time can be estimated by dividing the absorbance at the trans  $\lambda_{\text{max}}$  at time  $t$  by the absorbance in the dark, when the sample is roughly assumed to be 100% trans.
- (28) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum: New York, 1999; p 370.
- (29) Yip, W.-T.; Hu, D.; Vanden Bout, D. A.; Barbara, P. F. *J. Phys. Chem. A* **1998**, *102*, 7564.
- (30) Hu, D.; Yu, J.; Barbara, P. F. *J. Am. Chem. Soc.* **1999**, *121*, 6936.
- (31) Huser, T.; Yan, M.; Rothberg, L. J. *Proc. Natl. Acad. Sci.* **2000**, *97*, 11187.
- (32) It is not possible to generate a sample with 100% cis azobenzene in this system to obtain the spectral data required to determine  $R_0$ , so the energy transfer efficiency to the cis isomer was not calculated by eq 2. However, it would be higher than to the trans isomer due to the increased value of the overlap integral for the cis versus the trans azobenzene.