Fluorescence from an Azobenzene-Containing Diblock Copolymer Micelle in Solution

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We report the observation of unusual fluorescence emission from an azobenzene-containing polymer micellar solution. An amphiphilic diblock copolymer composed of the hydrophilic quaternized poly(4-vinyl pyridine) (QP4VP) and a hydrophobic liquid crystalline polymethacrylate bearing azobenzene side groups (PAzoMA) is nonfluorescent in molecularly dissolved state in *N,N*-dimethyl formamide (DMF) but becomes fluorescent as a result of the micellization upon addition of water, which confines azobenzene groups into the core region of micellar aggregates. Experimental results suggest that the micellization-enhanced fluorescence was caused by a slowdown, due to the confinement effect, in the rate of the trans-to-cis photoisomerization that is the main nonradiative relaxation process for excited azobenzene groups in the trans form. Furthermore, it was found that the fluorescence intensity of aqueous micellar solution is sensitive to changes in pH (reversible fluorescence variation) and to illumination (irreversible fluorescence variation). The results indicate that a subtle change in the state of polymer micellar association may alter the confining state of azobenzene groups responsible for the fluorescence emission.

Introduction

Generally, the azobenzene chromophore is nonfluorescent in solution at room temperature.[1] However, a few exceptions were reported in the literature.[2−7.] Fluorescence emission with a maximum at ∼ 600 nm was observed for some azobenzenes confined in a bilayer structure,[2,3] which was attributed to excitonic states of aggregated azobenzene moieties. Fluorescence centered at ∼500 nm was also observed from some azobenzenes confined in nanoporous membranes at acidic pH,[4,5] which was believed to arise from protonated azobenzenes. A more recent study on small-molecule azobenzene compounds, whose trans−cis photoisomerization imparts an amphiphilic character to the molecules, found that they can display enhanced fluorescence emission in solution after a prolonged UV irradiation, as a result of light-driven molecular self-assembly into micellar aggregates.[6,7] Although the exact origin of enhanced fluorescence of azobenzene is far from being understood and seems to vary depending on the systems, a common feature that emerged from those rare cases is that fluorescent azobenzene molecules are confined inside a small (nanometer-scale) space where changes in the aggregation states of their dipoles are likely to occur. This apparently aggregation-allowed fluorescence of azobenzene is reminiscent of the aggregation-induced enhanced emission of other organic molecules.[8,9] Given the considerable interest on azobenzene-containing polymers,[10−12] it would be interesting to extend the search and exploitation of fluorescent azobenzenes to polymers.

In this paper, we report, to our knowledge, the first observation of fluorescence emission from an azobenzene-containing diblock copolymer micelle in solution. The studied block copolymer comprises a hydrophilic quaternized poly(4-vinyl pyridine) (QP4VP), which forms the corona of micelle, and a hydrophobic liquid crystalline polymethacrylate bearing pendent azobenzene mesogens (PAzoMA), which forms the core of micelle. We found that the micellization of the polymer in solution could induce fluorescence emission at ∼450 nm upon excitation of azobenzene groups at 360 nm. The enhanced fluorescence emission was accompanied by a significant slowdown in the rate of the trans-to-cis photoisomerization of azobenzene groups upon UV irradiation at similar wavelengths. This suggests that the confinement effect acting on excited trans azobenzene groups in the micelle may hamper their main nonradiative relaxation process and thus enable their fluorescence emission. Furthermore, we found that a subtle change of the aggregation state of the micelle, resulting from a pH change or UV/visible illumination, could reduce or even suppress the emissive process in a reversible (in response to pH change) or an irreversible fashion (in response to illumination).

Experimental Section

The azobenzene-containing amphiphilic diblock copolymer whose micelles emit fluorescence is quaternized poly(4-vinyl pyridine)-*b*-poly{6-[4-(4-ethoxyphenyl-azo)phenoxy]hexyl methacrylate}, referred to as QP4VP-*b*-PAzoMA hereafter (chemical structure shown below). As for most azobenzene block copolymers studied in recent years, it was prepared using atom transfer radical polymerization (ATRP).[13−16] Using a chlorine-terminated P4VP macroinitiator, a diblock copolymer of P4VP-*b*-PAzoMA was first obtained. Combining the GPC and ^{1}H NMR results (Supporting Information), the

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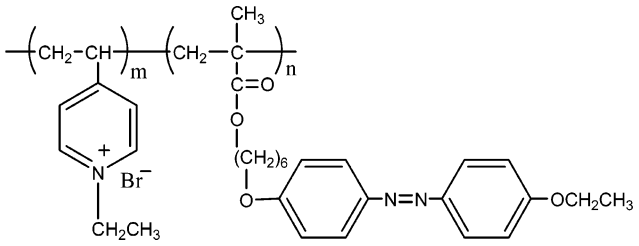
diblock copolymer composition was estimated to be $P4VP_{22}$-*b*-$PAzoMA_{13}$. Subsequently, a quaternization reaction using bromoethane was performed to convert the diblock copolymer into $QP4VP_{22}$-*b*-$PAzoMA_{13}$. Infrared spectra (Supporting Information) revealed a quaternization degree of ~ 95%. Note that the synthetic details will be reported elsewhere,[17] in a study of layer-by-layer (LBL) assembly of different polymer micelles.



The micelles of QP4VP-*b*-PAzoMA were obtained by means of two procedures. The first consisted in dissolving the block copolymer in *N*,*N*-dimethyl formamide (DMF) at a concentration of 0.8 mg mL^{-1}, which is a good solvent for the two blocks, followed by addition of water, which is a bad solvent for PAzoMA, to induce the formation of micelles from a critical amount of water. The second method was to dissolve the copolymer surfactant directly in water at a concentration above the critical micelle concentration (CMC) being determined as ~0.06 mg mL^{-1} using the well-known pyrene-probe method.[18]

Steady-state fluorescence emission and excitation spectra were recorded on a SPEX 1680 double-monochromator spectrophotometer. Fluorescence quantum yield (Φ_f) measurements, using 9,10-diphenylanthracene as reference ($\Phi_f = 1$), were performed at room temperature for a DMF solution with molecularly dissolved block copolymer and for its micellar solution upon addition of water. The polymer concentration was chosen to give an absorbance of about 0.05 for azobenzene moieties at 360 nm, The experiment was repeated three times. The fluorescence lifetime for the micellar solution was measured using a Timemaster model TM-3 apparatus from PTI. The source was a nitrogen laser equipped with a high-resolution dye laser (fwhm 1500ps), and the fluorescence lifetime was obtained from a deconvolution and distribution lifetime analysis.[19]

Regarding other characterizations, dynamic light scattering (DLS) measurements were carried out on a Zetasizer Nano ZS from Malvern Instruments, with a laser at 633 nm. Infrared and UV−vis spectra were obtained using a Bomem MB-100 FTIR spectrometer and a Hewlett-Packard 8452A diode array spectrophotometer, respectively. Polymer micelles dispersed in aqueous solution were examined using a Hitachi H-7500 transmission electron microscope (TEM) operating at 80 KV. Samples for TEM were prepared by casting one drop of the micellar solution on a carbon-coated copper grid, followed by drying. To induce the trans−cis photoisomerization of azobenzene moieties in the micellar solutions, a UV−vis spot-curing system (Novacure) equipped with various filters was utilized to produce UV (~360 nm, 15 mW cm^{-2}) and visible light (~440 nm, 20 mW cm^{-2}).

Results and Discussion

When QP4VP-*b*-PAzoMA is molecularly dissolved in DMF, the solution is virtually nonfluorescent. Upon addition of water (pH 12) into the DMF solution, fluorescence emission begins to be detected as a result of the micellization that takes place because of water being a bad solvent for the hydrophobic azobenzene polymer block. Figure 1a shows the change in the fluorescence emission spectrum with increasing the amount of water for a solution with an initial polymer concentration in DMF of 0.8 mg mL^{-1} (excitation at 360 nm). The fluorescence centered at 450 nm becomes more important as more water is added, the intensity being enhanced by a factor of >220 when the amount of water is increased from 10% to 400% (v/v, with respect to DMF). The micellization of the polymer can easily be detected by measuring the change in turbidity of the solution upon addition of water; the inset of Figure 1a indicates the formation of micelles at ~10% of water. The TEM image in Figure 1b further confirms the formation of micellar aggregates. Under the used preparation conditions, it seems that core−shell micelles coexist with larger aggregates. Note that no enhanced fluorescence emission was observed upon simple dilution of the polymer in DMF. The fluorescence quantum yield of the initial DMF solution was found to be about 8×10^{-5}, which is consistent with the reported values for azobenzene derivatives ($10^{-7} \sim 10^{-5}$).[2,3] By contrast, the quantum yield of the micellar solution upon addition of 400% of water increased to about 3×10^{-2} with a lifetime of ~3.8 ns.

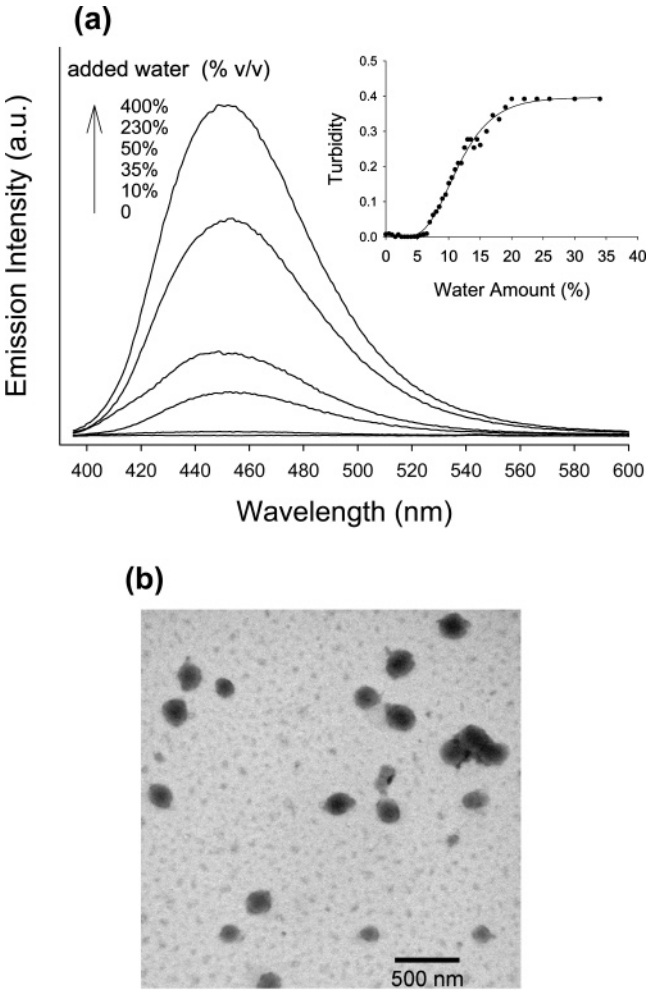


Figure 1. (a) Fluorescence emission spectra ($\lambda_{ex} = 360$ nm) upon addition of water into a DMF solution of QP4VP-*b*-PAzoMA (polymer concentration: 0.8 mg mL^{-1}), with the inset showing the change in turbidity as a function of the amount of added water. (b) TEM image of the micellar aggregates.

The highly efficient trans-to-cis photoisomerization of azobenzene is the main nonradiative relaxation process for excited azobenzene in the trans form, which quenches the fluorescence. In one of the early reports,[2] Shimomura et al. suggested that the fluorescence from azobenzene-containing bilayer membranes could originate from aggregated azobenzene moieties whose trans-to-cis photoisomerization was hindered to some extent by the confining environment. The micellization of our diblock co-

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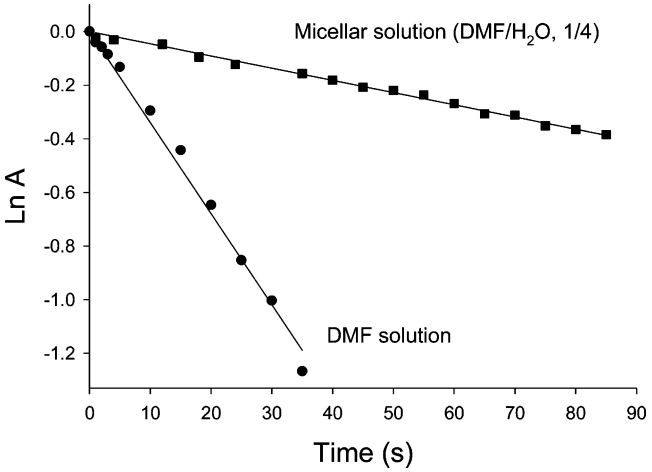

Figure 2. Plots of the first-order trans-to-cis photoisomerization upon UV irradiation (2 mW cm^{-2}) for the DMF solution of QP4VP-*b*-PAzoMA and its micellar solution after addition of 400% of water (polymer concentration: 0.16 mg mL^{-1}), showing different rates for the trans-to-cis photoisomerization of azobenzene moieties. See text for details.

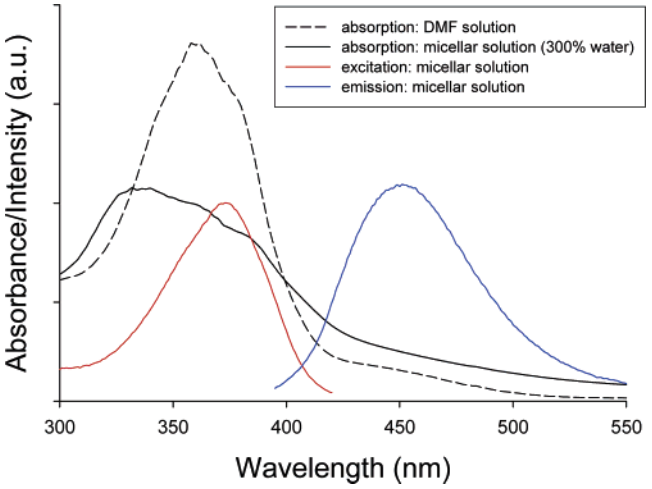

Figure 3. UV−vis spectra of a DMF solution of QP4VP-*b*-PAzoMA (polymer concentration: 0.8 mg mL^{-1}) and its micellar solution after addition of 300% of water as well as the fluorescence emission (λ_{ex} = 360 nm) and excitation (λ_{em} = 450 nm) spectra of the micellar solution.

polymer, which brings dissolved azobenzene polymer chains into a compact core of micelle, confines the pendent azobenzene moieties inside a nanometer-scale space. This is likely to result in a change in the stacking of azobenzene moieties, and the severe confinement may restrict their photoisomerization process. We thus performed careful measurements of the rate of trans-to-cis photoisomerization for two solutions in Figure 1: the nonfluorescent DMF solution and the fluorescent micellar solution with 400% of water added (2 mL solution, low 360 nm UV irradiation intensity of ~2 mW cm^{-2}). The polymer concentration in the DMF solution was adjusted to be the same as the micellar solution (0.16 mg mL^{-1}). The photoisomerization process was monitored by measuring the change in absorption of trans azobenzene at 360 nm ($\pi-\pi^*$ transition, see UV−vis spectra in Figure 3). The data were fitted with the first-order kinetic equation of $\ln A = -kt$, in which $A = (A_\infty - A_t)/(A_\infty - A_0)$, with A_0, A_t, and A_∞ being the absorbance before UV irradiation, after UV irradiation for time t, and at the photostationary state, respectively.[20] Figure 2 compares the plots of ln A vs UV irradiation time for the two solutions. It is seen that the rate of photoisomerization for the fluorescent micellar solution is slowed down considerably (rate constant $k \sim 4.6 \times 10^{-3}$ s^{-1}) as compared to the nonfluorescent DMF solution ($k \sim 3.4 \times 10^{-2}$ s^{-1}). This result clearly shows the role of a hindered trans-to-cis photoisomerization in enhancing the fluorescence emission. It seems that, being confined inside the core of micelle, the reduced efficiency for the nonradiative relaxation process (i.e., the trans-to-cis photoisomerization) allows a number of excited trans azobenzene moieties to return to their ground state through the radiative process leading to the fluorescence.

Figure 3 shows the UV−vis absorption spectra of the block copolymer in DMF before micellization and after micellization upon addition of 300% of water. The micellization is accompanied by a blue shift of the absorption maximum of trans azobenzene from ~360 to 330 nm, which indicates an increase in population for azobenzene groups in the H-aggregated state.[21] Also shown are the fluorescence emission (excitation at 360 nm) and excitation (emission detected at 450 nm) spectra for this micellar solution. It appears that the fluorescence is mainly contributed by azobenzene groups absorbing at longer wavelengths (> 350 nm), i.e., azobenzene groups in nonaggregated and J-aggregated states. This is consistent with the fluorescence observed from azobenzenes confined in bilayer membranes[2] and with the fact that H-aggregates of most dyes are nonflurescent.[22]

We found that the fluorescence intensity of aqueous micellar solutions was sensitive to stimuli such as pH change and illumination, as a result of an alteration of the micellar association. The results in Figure 4 were obtained with an aqueous solution prepared by removing DMF through dialysis against water. Figure 4a shows the plot of normalized fluorescence at 450 nm as a function of pH (polymer concentration 0.1 mg mL^{-1}). Strong fluorescence is observed at high (basic) pH but decreases drastically at low (acidic) pH, being reduced by a factor of about 15 passing from pH = 12 to 4. As shown by the inset in Figure 4a, the change of fluorescence intensity in response to the change in pH is reversible. By adjusting the pH with 1.0 M HCl and NaOH solutions, reversible switching of fluorescence emission was obtained for several cycles of pH changes. Alteration of the polymer micelles at the two pHs was observed through DLS measurements, as shown in Figure 4b. The pH change resulted in a significant variation of the average size of the micellar aggregates, decreasing from ~159 nm at pH = 12 to 149 nm at pH = 4. This result suggests that a subtle change in the packing of azobenzene groups in the core region may occur and alter drastically the fluorescent association state of the chromophore. It is possible that the pH sensitivity of QP4VP-*b*-PAzoMA micelles originated from a small amount (~5%) of unquaternized 4VP groups in the QP4VP block (Supporting Information). At acidic pH = 4, the protonation of the residual 4VP groups could shift the hydrophilic/hydrophobic balance and modify the association state of PAzoMA chains. Since the 4VP groups can be deprotonted at basic pH, the polymer micelle may recover its association state at pH = 12, which accounts for the reversibility in Figure 4a. A couple of more notes need to be made here. First, the fact that fluorescence is reduced at pH = 4 excludes the possibility that the fluorescence of the polymer micellar solution originated from azobenzene groups protonated at acidic pH like azobenzenes confined in nanoporous membranes.[4,5] Second, even

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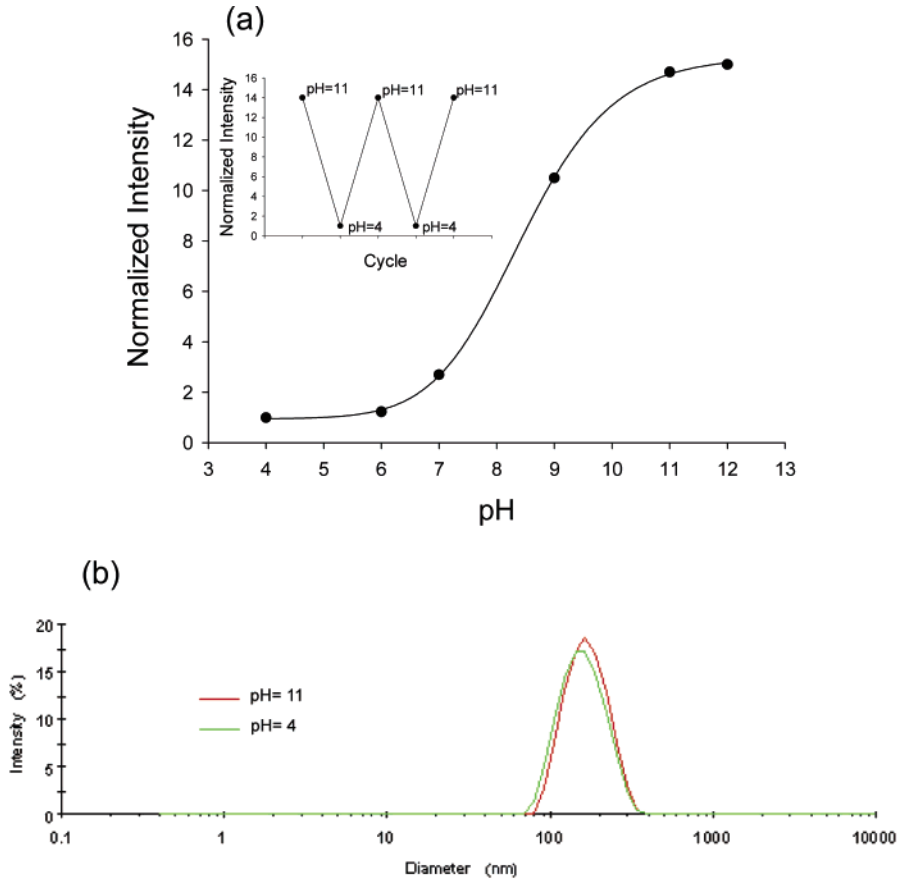

Figure 4. (a) Change in normalized fluorescence intensity measured at 450 nm ($\lambda_{ex} = 360$ nm) as a function of pH of the aqueous micellar solution (polymer concentration: 0.1 mg mL^{-1}), the inset shows the reversibility for the change in fluorescence. (b) DLS curves for the distribution of sizes of micellar aggregates in solutions at pH = 12 (red line) and pH = 4 (green line).

though pyridine and pyridinium solvents are known to be able to quench the fluorescence of some chromophores through H-bonding or charge-transfer induced formation of complexes,[23] quaternized 4VP and the residual unquaternized 4VP groups on the QP4VP block are unlikely to cause the drop in fluorescence of the micellar solution at pH = 4. At this acidic pH, only pyridinium groups exist, whereas azobenzene moieties contain no electron donating groups for possible charge transfer. Moreover, the QP4VP blocks form the micelle corona that basically is segregated from the micelle core region confining the PAzoMA blocks.

We wanted to know if the reduced fluorescence at pH = 4 was also related to a change in the rate of the trans-to-cis photoisomerization of azobenzene. Using the same UV irradiation conditions as in Figure 2, the first-order kinetic plots were obtained for the two aqueous micellar solutions at pH = 12 (strong fluorescence) and pH = 4 (less fluorescence). The results in Figure 5 show that this indeed is the case. The strongly fluorescent solution at pH = 12 displays the lower rate of photoisomerization ($k \sim 1.7 \times 10^{-3}$ s^{-1}) as compared to the weakly fluorescent solution at pH = 4 ($k \sim 5.1 \times 10^{-3}$ s^{-1}). This result provides additional support to the assumption that the activation of the emissive process of excited trans azobenzene might be caused by a less efficient nonradiative relaxation process.

The fluorescence of the diblock copolymer micellar solution was found to be also sensitive to pre-illumination using UV and visible light for the trans-to-cis and the reverse cis-to-trans

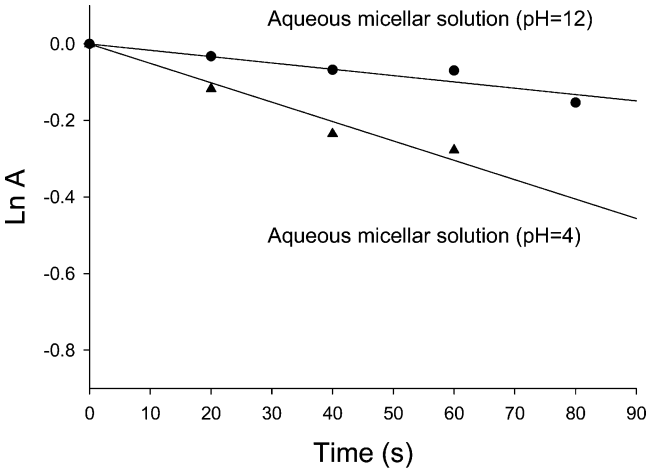

Figure 5. Plots of the first-order trans-to-cis photoisomerization upon UV irradiation (2 mW cm^{-2}) for two aqueous micellar solutions at pH = 4 and pH = 12 (polymer concentration: 0.2 mg mL^{-1}), showing different rates for the trans-to-cis photoisomerization of azobenzene moieties. See text for details.

isomerization of azobenzene moieties. Some recent studies found that the morphology (association state) of micellar aggregates of azobenzene-containing diblock copolymers[24] and H-bonded polymers[25] could be affected by the photoisomerization of azobenzene groups. In case the trans-to-cis photoisomerization results in a significant increase in the dipole moment of pendent

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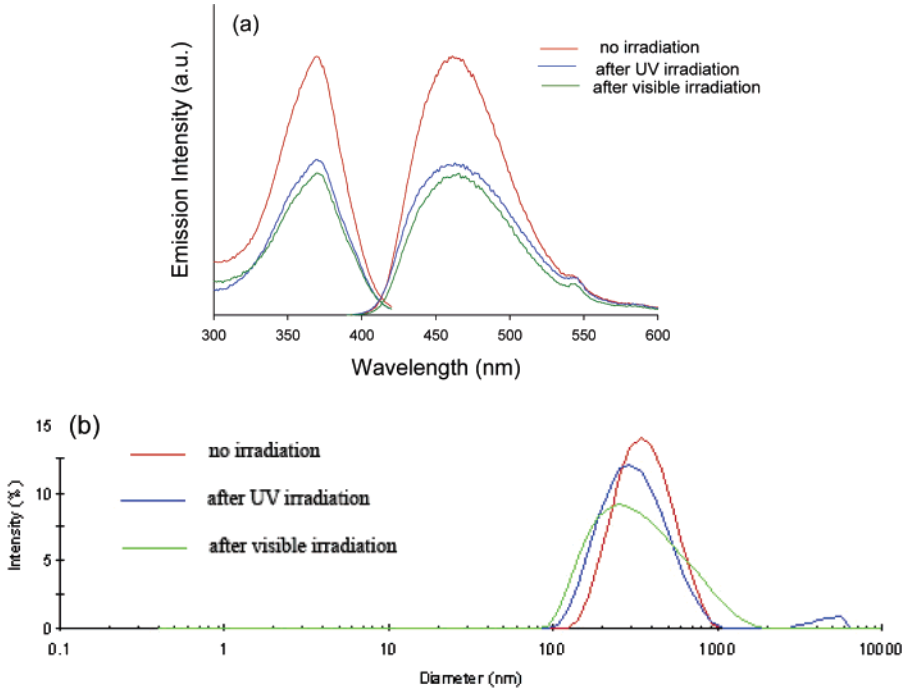

Figure 6. (a) Fluorescence emission (λ_{ex} = 360 nm) and excitation (λ_{em} = 450 nm) spectra for an aqueous micellar solution before and after illumination using UV and visible light. (b) DLS curves for the distribution of sizes of micellar aggregates in the aqueous micellar solution before illumination (red line), after UV irradiation (blue line) and after subsequent visible irradiation (green line). See text for details.

azobenzene moieties, the change in the hydrophilic/hydrophobic balance can even lead to the dissociation of micelles or vesicles.[24] Therefore, it was no surprise that the fluorescence of the micellar solution of QP4VP-b-PAzoMA could be changed upon illumination. Figure 6a shows the fluorescence emission and excitation spectra for an aqueous micellar solution at pH = 12 (polymer concentration 0.07 mg mL^{-1}) before UV irradiation (initial solution), after UV irradiation, and after subsequent visible irradiation. The fluorescence intensity drops after the trans-to-cis photoisomerization upon UV irradiation. However, the change in fluorescence is irreversible. After the subsequent visible irradiation that brings azobenzene groups back to the trans isomer due to the reverse cis-to-trans photoisomerization, the fluorescence continues to decrease. It can also be noticed that the excitation spectra differ only in the intensity, showing that in all cases the fluorescence arises from azobenzene moieties absorbing at >350 nm. The change in micellar association state upon illumination was confirmed by DLS measurements. Figure 6b shows that the UV and visible irradiation resulted in a continuous decrease in the average size of the micellar aggregates and a broadening of the distribution of sizes. We mention that the larger average size of the micellar aggregates (as compared to Figure 4b) may be caused by different preparation conditions used. The aqueous micellar solution used for this series of experiments was prepared by directly dissolving the diblock copolymer surfactant in water at pH = 12, instead of using the dialysis to remove DMF from a micellar solution of DMF/water.

The fluorescence emission from our azobenzene-containing block copolymer micelles has a similar feature to other reported systems,[2−7] namely, confinement of azobenzene groups in a nanometer-scale space. Understandably, a severe confinement may hinder the trans-to-cis photoisomerization. This is what happened in our azobenzene diblock copolymer micellar solution based on the measurements of the rate of photoisomerization. A significant slowdown in the rate of the nonradiative photoisomerization process appears to be required for activating the emissive process. This, however, may not be the only important condition. The great sensitivity of fluorescence to stimuli (pH change and illumination) that can alter the state of micellar association implies that azobenzene groups need to be arranged in a particular state to fluoresce. Any changes of experimental conditions and variables that distract azobenzene groups from this particular state may quench the fluorescence emission. We have also prepared two other samples of QP4VP-*b*-PAzoMA containing respectively a shorter and longer PAzoMA block than the used sample but failed to observe the enhanced fluorescence emission from their micellar solutions. Similar to the effects of external stimuli, a shorter or longer hydrophobic PAzoMA block means a shift of the hydrophilic/hydrophobic balance that can affect the association state of azobenzene groups. DLS measurements indeed found different sizes for their micelles in aqueous solution (data not shown). At this point, we are unable to answer the question of what is the association state of azobenzenes leading to fluorescence. More studies are needed to elucidate it and to understand the roles of parameters such as the interaction between solvent molecules and confined azobenzene groups.

Although appearing intriguing, it should be emphasized that the whole of the results ruled out the possibility that the observed fluorescence originated from a fluorescent impurity in the material. Many observations, such as the fluorescence enhancement related to the micellization, the coincidence of the excitation spectrum with the absorption spectrum of trans azobenzene groups in the nonaggregated and J-aggregated state, and the sensitivity of fluorescence to the trans−cis photoisomerization of azobenzene groups, pointed to azobenzene as being responsible for the fluorescence emission. We hope this first report on the finding of enhanced fluorescence from azobenzene-containing block copolymer micellar solution may spark more interest in searching for and studying the fluorescence from azobenzene polymers.

Conclusion

Unusual fluorescence emission from an azobenzene-containing block copolymer micellar solution was observed. The micelli-

zation, which brings azobenzene polymer chains into nanodomains defined by the core regions of micelles, appears to exert a severe confinement on the azobenzene moieties to slowdown significantly their trans-to-cis photoisomerization upon absorption of UV light at around 360 nm. The reduced efficiency of the main nonradiative relaxation process could allow a number of excited trans azobenzene moieties to return to the ground state through the fluorescence emissive process. The fluorescence intensity from the polymer micellar solution was found to be sensitive to stimuli such as pH change and illumination that can alter the morphology or association state of the micelles and, consequently, the stacking (interaction) state of azobenzene moieties. It is of interest to conduct future studies on different azobenzene polymers that provide a severe confining environment to restrict the photoisomerization process, and to elucidate the role of other possible variables important to enhanced fluorescence of azobenzenes.

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Supporting Information Available: ^{1}H NMR, GPC, and infrared spectra of diblock copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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