

# pH-Controlled “Off–On–Off” Switch Based on Cu<sup>2+</sup>-Mediated Pyrene Fluorescence in a PAA–SDS Micelle Aggregated Supramolecular System

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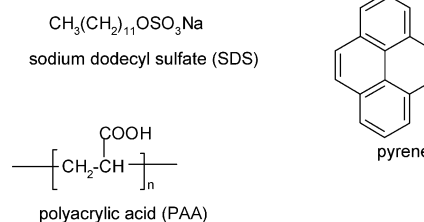
We report herein the fluorescence response of pyrene in the presence of sodium dodecyl sulfate (SDS) micelle and poly(acrylic acid) (PAA) with Cu<sup>2+</sup> as an ionic quencher. Pyrene present in the PAA–SDS complex is quenched by Cu<sup>2+</sup> at pH ~ 2 (“off” state). Quenched pyrene emission is recovered at pH ~ 8 (“on” state). Due to easy protonation and deprotonation of the PAA chain in aqueous solution, this pH-controlled micellar ternary system exhibits a highly reversible “off–on–off” switch of the pyrene emission.

## Introduction

Surfactants and water-soluble polymers are often present together in various formulations for several chemical, biological, and pharmaceutical applications. Polymer–surfactant aggregation and their interactions in solution have been studied extensively in the last few decades.<sup>1</sup> However, interactions between an anionic surfactant and polymer of the same charge have not explored much. The driving force for the interaction between an anionic surfactant and polymer of the same charge is governed by hydrophobic interactions and H-bonding. Interaction of SDS with PAA was reported for the first time by Maltesh and co-workers.<sup>2</sup> They explained the interaction of such systems as a combination of a hydrophobic interaction of the apolar tail of surfactants to the backbone of PAA and H-bonding between the acidic groups of the polymer and the polar head group of the surfactants.<sup>3</sup> The PAA–surfactant complex is highly pH-sensitive and stable only at very low pH. The surfactant concentration required to induce binding to the polymer is referred to as the critical aggregation concentration (cac), which is generally lower than the critical micelle concentration (cmc) in polymer-free solution, the difference being a measure of the strength of polymer–surfactant interaction. It has been established that fluorescence techniques can provide valuable information concerning the structure of aggregate systems in aqueous solutions.<sup>4</sup> The association of PAA with oppositely charged surfactants or with nonionic surfactants and multivalent metal ions in the presence of pyrene has been studied in the past.<sup>5–7</sup> However, the ternary systems containing a polyanion, a multivalent metal ion, and anionic surfactant in aqueous solution has not been investigated much.

Here, we report for the first time a highly reversible “off–on–off” pyrene emission based on the formation and deformation of ternary SDS–PAA–Cu<sup>2+</sup> supramolecular aggregates by tuning the pH of an aqueous system. In this paper, we have reported the effect of pH on the interactions between SDS micelles and PAA in the presence of Cu<sup>2+</sup> using the steady-state fluorescence probe method. The idea was to use Cu<sup>2+</sup> both

## SCHEME 1: Molecular Structure of SDS, Pyrene, and Polyacrylic Acid



as a quencher and as an important component for complex formation with polymer. Such a system has the potential for several applications in the field of nanotechnology, like metal nanoparticle synthesis for catalytical purposes.<sup>8</sup>

## Experimental Section

**Materials.** PAA (molecular weight 1800 Da), copper sulfate (CuSO<sub>4</sub>), and SDS (Scheme 1) were procured from Sigma–Aldrich Chemicals Co.. Pyrene was purchased from Fluka. Water was obtained from a Milli-Q purification system. All experiments were performed with freshly prepared solutions. In order to ensure equilibrium, measurements were conducted after 24 h of storage at room temperature.

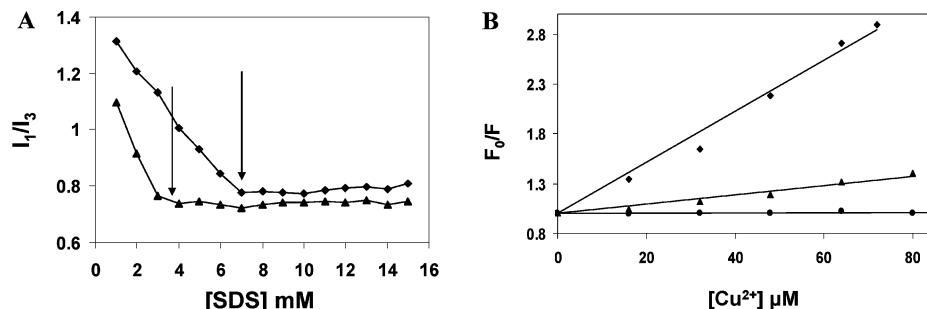
**Fluorescence Studies.** All fluorescence studies were performed using a Shimadzu RF-5301PC spectrofluorophotometer. Stock solutions of pyrene (1 × 10<sup>−3</sup> M) were prepared in ethanol, and the final concentration of pyrene was fixed at 9 × 10<sup>−8</sup> M for all studies. The excitation wavelength was set at 340 nm. The first vibronic band (I<sub>1</sub>) and the third (I<sub>3</sub>) vibronic band of the emission spectrum of pyrene were monitored at 373 and 384 nm, respectively. The excitation and emission slit widths were set at 3 and 5 nm, respectively.

**pH Measurement.** pH measurements were performed by means of a control dynamic pH meter.

## Results and Discussion

In the micellar medium, there are two factors that affect the mutual counter of the probe and the quencher molecules. These

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**Figure 1.** (A) Changes in the  $I_1/I_3$  intensity ratio of the pyrene emission as a function of SDS concentration in the presence of PAA at pH  $\sim 2$  ( $\blacktriangle$ ) and  $\sim 8$  ( $\blacksquare$ ). (B) Stern–Volmer plots for the pyrene fluorescence quenching upon addition of  $\text{Cu}^{2+}$  ions in the presence of SDS only ( $\blacksquare$ ), in PAA + SDS at pH  $\sim 2$  ( $\blacktriangle$ ), and in PAA + SDS at pH  $\sim 8$  ( $\bullet$ ).

**TABLE 1: Parameters Obtained from Fluorescence and Fluorescence Quenching Experiments**

	pH	cac (mM)	cmc (mM)	cac/cmc	$K_{SV}$ ( $\times 10^3 \text{ M}^{-1}$ )
SDS	$\sim 7$	—	7	—	25.6
SDS–PAA	$\sim 2$	4	—	0.57	4.7
SDS–PAA	$\sim 8$	7	—	1	0.09

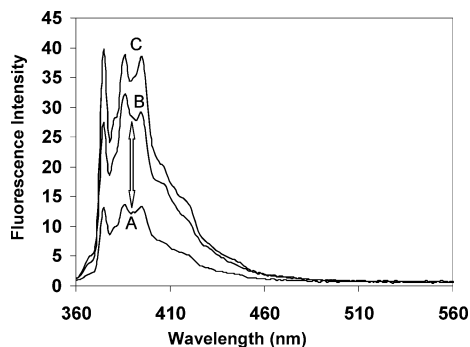
are (i) the partitioning of the fluorescent probe and the quenchers between the micellar and the aqueous phases and (ii) the dynamic distribution of the quenchers and fluorescent probe during the quenching process. The fluorescence value of pyrene ( $I_1/I_3$ ) is very sensitive to the polarity of the microenvironment.<sup>9</sup> When surfactant molecules aggregate, pyrene is solubilized in the hydrophobic part of the aggregates, and  $I_1/I_3$  decreases. Figure 1A shows the dependence of the  $I_1/I_3$  on the SDS surfactant concentration in the presence of PAA at two different pH, and the cmc and cac are listed in Table 1. The decrease in  $I_1/I_3$  reflects low polarity of the pyrene microenvironment. An empirical scale of solvent polarity based on the  $I_1/I_3$  ratio has been developed by Dong et al.<sup>10</sup> As shown in Figure 1A,  $I_1/I_3$  decreases as the surfactant concentration increases and pyrene is preferentially transferred from the aqueous environment to the less polar micellar environment. The average microenvironmental polarity decreases rapidly above the cmc and reaches a lower limit as the surfactant concentration increases. Thus, one may detect the hydrophobic microdomain formation in the micelle solution with or without polymer at varying pHs by using the variation of the  $I_1/I_3$  ratio of the emission spectrum of pyrene. Here, we have studied pyrene emission in the SDS micelle with or without PAA under two different pH conditions (pH  $\sim 2$  and  $\sim 8$ ). In the case of the only SDS solution, (concentration  $< 1$  mM), the ratio  $I_1/I_3$  values are in a higher range compared to the same in a higher concentration, indicating that pyrene senses a pure aqueous microenvironment where the SDS concentration is lower than 1 mM. Above this concentration regime, the  $I_1/I_3$  ratio starts decreasing, and after  $\sim 7$  mM, it remains constant, indicating the formation of the micelle. A similar trend was observed (Figure 1A) when SDS–PAA mixture was studied at pH  $\sim 8$ , suggesting that SDS micelle formation at higher pH is not affected at all in the presence of PAA and indicating absolutely no interaction between SDS and charged PAA. However, for a similar study in the case of SDS and PAA at pH  $\sim 2$ , the  $I_1/I_3$  value decreases on the order of 0.8 for 4 mM SDS, after which it remains constant, indicating hydrophobic microdomain formation due to polymer–surfactant aggregation formation. The strength of the interaction between the polymer and surfactant can also be characterized by the semiquantitative cac/cmc ratio.<sup>11</sup> A smaller cac/cmc ratio indicates a stronger interaction. It is shown in Table 1 that the

cac/cmc for the SDS and PAA mixture at pH  $\sim 2$  is almost half of the value obtained at pH  $\sim 8$ , suggesting a higher probability of SDS–PAA interaction at lower pH. The steady-state fluorescence quenching experiment using the  $\text{Cu}^{2+}$  ion as the quencher is an established technique to assess the accessibility of a fluorophore toward the quencher molecule in a micellar environment.<sup>9</sup> A relative measure of the quenching efficiency ( $K_{SV}$ ) reflects the accessibility of one to the other. Thus, this experiment can throw light on the approachability of the quencher to the fluorophore, that is, the compactness of the micellar head groups. The SDS concentration was maintained around its cmc, that is, 10 mM. In this condition, the excimer emission was only feeble; thus, quenching of the pyrene monomer emission with a surfactant system by the heavy metal ion ( $\text{Cu}^{2+}$ ) was monitored. The Stern–Volmer plots according to eq 1 in the micellar environments are

$$F_0/F = 1 + K_{SV}[Q] \quad (1)$$

$F_0$  and  $F$  being the fluorescence intensities of the pyrene monomer in the absence and presence of different concentrations of the quencher.  $K_{SV}$  and  $[Q]$  are the Stern–Volmer constant and quencher concentration, respectively.  $\text{Cu}^{2+}$  has quenched the fluorescence of pyrene in the aqueous as well as in the SDS micelle. The plot of  $F_0/F$  versus quencher concentration is linear in the pure SDS micelle and SDS–PAA system (Figure 1B), indicating dynamic (collisional) quenching.

Electrostatic interaction between the anionic micelle SDS and  $\text{Cu}^{2+}$  could bring the metal ion in close proximity of pyrene, which prefers to stay in the micellar hydrophobic part. At low pH, when  $\text{Cu}^{2+}$  was introduced to the PAA–SDS mixture, the probability of  $\text{Cu}^{2+}$  binding with SDS micelle was less (compared to that of the free SDS micelle) but could quench the pyrene emission significantly. This could be due to formation of ternary PAA–SDS– $\text{Cu}^{2+}$  supramolecular aggregates at lower pH, where  $\text{Cu}^{2+}$  was associated with the anionic SDS micelle which was also wrapped by a polymer chain due to PAA–SDS interaction. As shown in Figure 2, the fluorescence intensity of  $\text{Cu}^{2+}$ -quenched pyrene can be recovered by increasing the pH of the medium. The  $K_{SV}$  value (listed in Table 1) at pH  $\sim 8$  is estimated to be much lower ( $\sim 50$  fold) than that of the same system at pH  $\sim 2$ . In fact, no quenching of pyrene fluorescence was observed at pH  $\sim 8$ . This is only possible if  $\text{Cu}^{2+}$  is taken away from the close vicinity of pyrene which is present in the SDS micellar nanocage. The probability of SDS–PAA complex deformation and anionic PAA formation increases at pH  $\sim 8$ . Due to electrostatic repulsion between the anionic SDS micelle and anionic PAA, and higher chances of  $\text{Cu}^{2+}$  complexation with anionic PAA,  $\text{Cu}^{2+}$  moves away from the SDS micelle.



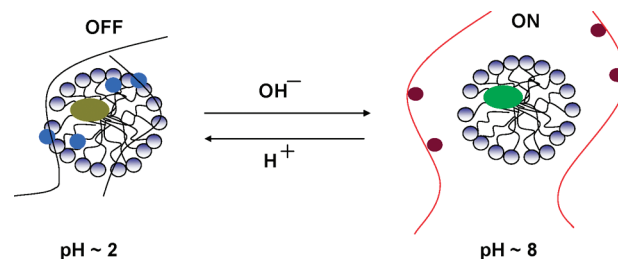
**Figure 2.** Emission spectra of pyrene in SDS (conc. 10 mM) (C), pyrene in SDS in the presence of PAA (conc. 0.5 mM) and  $\text{Cu}^{2+}$  at pH  $\sim 2$  (A), and pyrene in SDS in the presence of PAA (conc. 0.5 mM) and  $\text{Cu}^{2+}$  at pH  $\sim 8$  (B).

Hence, quenching in this case becomes ineffective. As shown in Figure 2, the fluorescence intensity of  $\text{Cu}^{2+}$ -quenched pyrene at pH  $\sim 2$  (off state) can be recovered by changing the pH of the medium to  $\sim 8$  (on state). This pyrene fluorescence intensity “quenching and recovery”, that is, the off and on states by changing the pH of the medium to “lower and higher”, respectively, is highly reversible and reproducible. The complete recovery of pyrene fluorescence (comparable with the no “ $\text{Cu}^{2+}$ ” system) has not been achieved; this could be due to the fraction of  $\text{Cu}^{2+}$  that remains in the SDS-bound form and thus does not strip away by the anionic PAA chain at pH  $\sim 8$ .

The system described above is remarkable from a number of different perspectives. The key component is the pyrene present in the hydrophobic environment of the anionic micelle SDS in ternary PAA–SDS– $\text{Cu}^{2+}$  supramolecular aggregates, quenched by  $\text{Cu}^{2+}$ , which leads to some critical effects. First is the quenching sensitivity at pH  $\sim 2$ , which proves the close proximity of pyrene and bound  $\text{Cu}^{2+}$  present in ternary PAA–SDS– $\text{Cu}^{2+}$  supramolecular aggregates. Second, once the quenching reagent (here,  $\text{Cu}^{2+}$ ) has been swept away at pH  $\sim 8$  by the uncoiled anionic PAA polymer chain, the deformation of the SDS–PAA complex and relatively strong complex formation of PAA– $\text{Cu}^{2+}$  lead to fluorescence recovery.

On the basis of all of these results, we propose that at pH  $\sim 2$ , the pyrene fluorescence intensity is quenched (off state) due to the close proximity of  $\text{Cu}^{2+}$  to pyrene in the PAA–SDS– $\text{Cu}^{2+}$  ternary system. At pH  $\sim 8$ , ternary complexes become destabilized due to lack of interaction between PAA and SDS. PAA becomes anionically charged (carboxylate

## SCHEME 2: Proposed Pyrene Fluorescence “Off–On–Off” Switching Mechanism<sup>a</sup>



<sup>a</sup> Given are the locations of quenched pyrene in the off state (dark yellow), fluorescent pyrene in the on state (green), and free  $\text{Cu}^{2+}$  (blue) and PAA-complexed  $\text{Cu}^{2+}$  (violet). Lines represent uncharged PAA chain (black) and charged PAA chain (red).

anion generation) and uncoiled, thus moves away from SDS due to electrostatic repulsion. At this pH, pyrene fluorescence is reversed back (on state) as the PAA backbone forms a relatively strong complex with  $\text{Cu}^{2+}$  and sweeps the quencher ( $\text{Cu}^{2+}$ ) away from pyrene, which always prefers to be present in a micellar nanocage (Scheme 2).

In conclusion, on the basis of ternary PAA–SDS– $\text{Cu}^{2+}$  supramolecular aggregate formation (at lower pH), PAA–SDS complex deformation and the  $\text{Cu}^{2+}$  complexing property of PAA by its free carboxylic group (at higher pH), we have developed a novel pH-controlled “off–on–off” switch, which is highly reversible in nature.

## References and Notes

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