

A Supramolecular Off-On Fluorescent Switch and IMPLICATION Logic Gate for Detection of Cationic Surfactant

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Abstract A supramolecular system was used to detect cationic surfactant CTAB in aqueous solution through the fluorescence indicator displacement mechanism. The dynamic detection range and the detection limit of cationic surfactants can be adjusted by altering the initial concentration of receptor. Furthermore, a three-input IMPLICATION gate was achieved with SDS, CTAB and temperature as inputs.

Keywords Supramolecular sensor · Fluorescent switch · Cationic surfactant · IMPLICATION logic gate

Introduction

Cationic surfactants, whose relatively high toxicity caused by a slow biodegradation owing to their bactericidal nature, are commonly used as preservatives in various pharmaceutical and cosmetic products and result in a great environmental problem [1–3]. Apart from the efforts made in studying the degradation processes of these compounds to

reduce their environmental impact, developing new useful and convenient methods to determine these toxic products in environment and in water samples is another important aspect [4–7].

It's difficult to selectively and sensitively measure surfactants for the lacking of a specific binding site of these compounds. Many well-known methodologies in cationic surfactants determination, such as high-performance liquid chromatography (HPLC), capillary electrophoresis, flow injection analysis and two-phase titration, etc [8–14], suffer from time-consuming tedious procedures or lower sensitivity. There are some reports on the determination of cationic surfactants with colorimetric and/or fluorometric methods, which are proven to be fast and convenient with relatively high sensitivity [15–19]. Recently, several research groups employed supramolecular fluorescence assays to recognize relevant chemicals through competitive association; significant improvements were achieved by this method [20–24].

Boolean operations at the molecular level have received much attention over the past two decades [25–28]. Today, many logic gates with different functions have been reported [29–39]. IMPLICATION function in which one input implies the other is very important because it is equal to IF-THEN operation; but very few examples can realize this function even for two-input case [40, 41]. Herein, we present a highly selective “off-on” supramolecular fluorescent switch for cationic surfactants, in which we used compound **P1** as a fluorescent indicator and anionic surfactant SDS as a receptor due to its ability of forming a complex with cationic surfactants. At the same time, a three-input IMPLICATION logic gate was accomplished with SDS, CTAB and temperature as inputs.

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Experimental

Reagents

All the solvents and reagents were of analytic grade and used as received. Doubly distilled water was used.

Absorbance and Fluorescence Titration

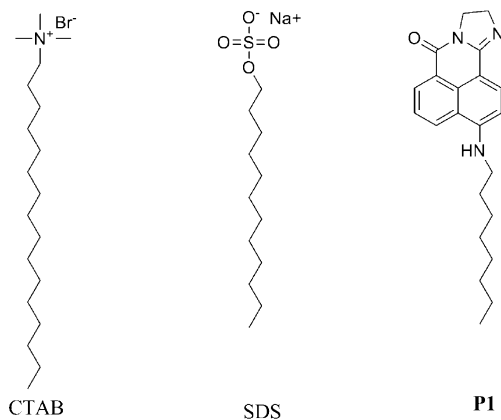
An accurately massed amount of **P1** was dissolved in 10 mL MeOH to obtain a stock solution. An aliquot stock solution was added to 20 mL water to obtain 6×10^{-6} M **P1** aqueous solution. Absorption measurements were performed with a Varian Cary 500 spectrophotometer (1 cm quartz cell) and fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell). All the experiments were performed at 25.0 ± 0.1 °C except for the temperature titration experiments. In temperature titration experiments, **P1**-SDS solutions were placed in a thermostat and equilibrated for 10 min at each temperature.

Results and Discussion

CTAB Effect on the Spectra Properties of **P1**-SDS System

P1 (Scheme 1) is fluorescent with $\Phi_F \approx 0.135$ in water, while the addition of SDS ($[\text{SDS}] < 2.4$ mM, $\text{CMC} \approx 8.0$ mM [42]) to **P1** aqueous solution quenched the fluorescence rapidly ($\Phi_F \approx 0.012$ at $[\text{SDS}] = [\text{P1}] = 6$ μM , see Supplementary Materials Figure S1) with obvious color change from yellow to nearly colorless. The formation of surfactant-dye complex resulted in the above results [43].

The addition of CTAB ($\text{CMC} \approx 0.92$ mM [42]) to **P1**-SDS aqueous solution led to an enhancement in the fluorescence of **P1** centered at 526 nm without noticeable wavelength shift (Fig. 1a), and a regular increase in the absorbance at



Scheme 1 Molecular structures of CTAB, SDS and **P1**

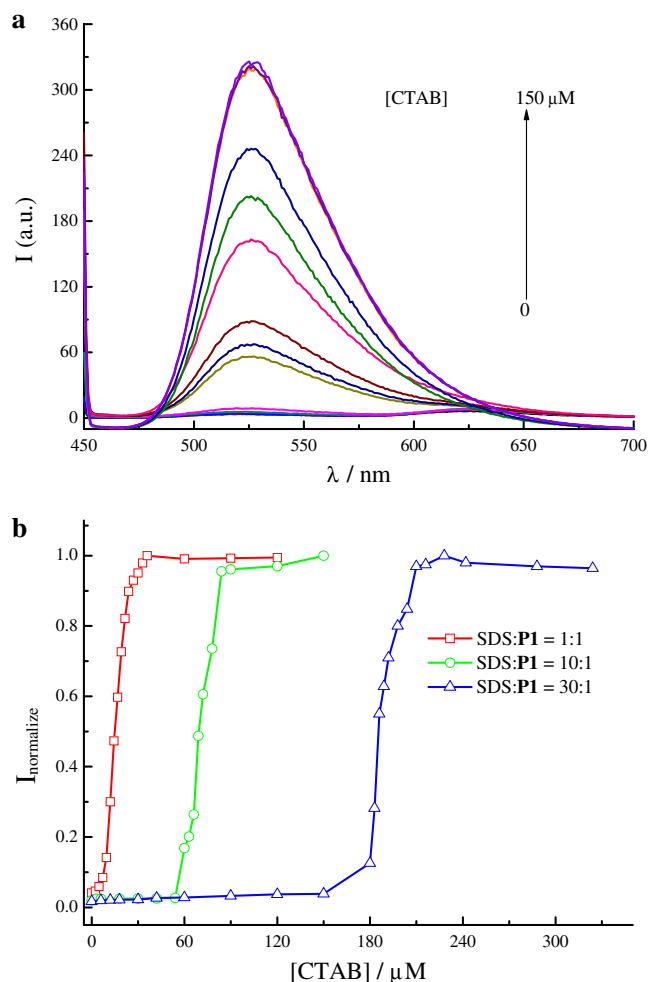


Fig. 1 CTAB effect on the fluorescence spectrum of **P1**-SDS aqueous solution (a, $[\text{SDS}] / [\text{P1}] = 10:1$) and the normalized CTAB titration curves at different ratios of $[\text{SDS}]$ to $[\text{P1}]$ (b) ($[\text{P1}] = 6$ μM , $\lambda_{\text{ex}} = 445$ nm)

470 nm (see Supplementary Materials Figure S2a). In neutral water, about 25-fold enhancement and clear color change from almost colorless to yellow were observed at 100 μM of CTAB, which showed an “off-on” fluorescent response towards CTAB. The green line (O) in Fig. 1b is the CTAB titration curve of Fig. 1a. It can be seen that the fluorescence intensity hardly changed at $[\text{CTAB}]$ less than 50 μM , and leveled off at $[\text{CTAB}]$ above 85 μM . When $[\text{CTAB}]$ was in the range of 57–85 μM , the emission intensity increased abruptly and almost linearly.

The Φ_F increased from 0.009 ($[\text{CTAB}] = 0$) to 0.156 ($[\text{CTAB}] = 100$ μM), the latter was larger than that of **P1** in aqueous solution. Similar change in absorbance was observed (see Supplementary Materials Figure S2b), and the dynamic detection window was 57–85 μM . Figure 1b also shows that both the detection limit and the detection range can be adjusted by altering the initial SDS concentrations: they increase with initial SDS concentration (the

dynamic detection windows are 3.5~26, 57~85 and 172~204 μM at SDS concentrations being 6, 60 and 180 μM , respectively); the detection limit is $\sim 3 \mu\text{M}$ in the case of 1:1 [SDS]/[P1] (S/N =3), which is comparable with those in literatures [8–14, 18]. In addition, the detection window can be enlarged if different ratios of [SDS]/[P1] are combined together.

We then studied CTAB effect on the UV-vis and emission spectra of P1. The results showed that a small amount of CTAB ([CTAB]<CMC) increased both the absorbance and fluorescence quantum yield of P1 (see Supplementary Materials Figure S3) indicating the formation of a more fluorescent complex of P1-CTAB. The association constant between CTAB and P1 was about $1.1 \times 10^4 \text{ M}^{-1}$, which was much smaller than that between SDS and P1 ($\sim 1.3 \times 10^6 \text{ M}^{-1}$).

It should be mentioned that the imine group (C=N) in P1 can be protonated with a pKa of about 7.0, which makes P1 positively charged in neutral water. The electrostatic and hydrophobic interactions between P1 and the negatively charged SDS lead to the formation of P1-SDS complex; as a result, the fluorescence of P1 is quenched by the intermolecular electron or energy transfer between SDS and P1.

There may exist electrostatic repulsion and hydrophobic interaction between cationic surfactant CTAB and P1. The former makes P1 far away from CTAB, while the latter drives them close to each other. The enhancement of the fluorescence intensity of P1 upon the addition of CTAB suggests that the hydrophobic interaction is much stronger than the electrostatic repulsion and thus makes P1 form complex with CTAB ([CTAB]<CMC) or locate into the less polar CTAB micelles ([CTAB]>CMC).

SDS and CTAB, bearing oppositely charged head groups, both have a long-chain alkyl substitute (Scheme 1). So, strong association between SDS and CTAB can be expected because of electrostatic and hydrophobic interactions. The results in Fig. 1 indicated that CTAB gradually displaced P1 to form CTAB-SDS mixed aggregates and set P1 free, which recovered the fluorescence and absorbance of P1. The detection limit was close to the initial SDS concentration, which can be used to qualitatively determine the unknown CTAB concentration by altering the initial [SDS]. The detection window of CTAB was in the range of 20~30 μM , which was of the same order of P1 concentration (6 μM) suggesting that the interaction between SDS and CTAB is comparable with that between SDS and P1. When SDS concentration was much higher than P1 concentration, the emission and absorption intensities of P1 kept unchanged until [CTAB] was almost equal to [SDS] added, which implied that CTAB first formed mixed aggregate with free SDS and then competed with P1 to set P1 free.

This supramolecular system shows a similar fluorescence response towards other similar cationic surfactants. The selectivity of SDS-P1 for this kind of surfactants over various detected cations was rather high [43]. Even chemically closely related cationic ions (e.g., short chain quaternary alkyl ammonium) and noionic surfactant Triton X-100 did not exert much influence on the spectral properties of P1-SDS complex [43].

Temperature Effect on the Spectral Properties of P1-SDS System

Temperature influences the spectral properties of P1 to some extent. Both the fluorescence intensity and the absorbance of P1 were enhanced slightly at higher temperature (compare the 2nd row with the 1st row in Fig. 3), which resulted from the increment of the solubility of P1. Whereas, temperature affects the spectral properties of P1-SDS aqueous solution significantly (Fig. 2). In the case of 10:1 [SDS]/[P1], the emission and absorption intensities hardly changed at temperatures below 50 $^{\circ}\text{C}$ or beyond 80 $^{\circ}\text{C}$, they increased steadily when temperature was raised from 50 to 80 $^{\circ}\text{C}$ (O, green line), indicating a gradual dissociation of SDS-P1 complex in this interval. These spectral changes were reversible at temperatures below 90 $^{\circ}\text{C}$. The temperature detection window shifted to the higher temperature region with increasing [SDS]/[P1] ratio (Fig. 2).

It should be mentioned that the Φ_F at higher temperature (even at 90 $^{\circ}\text{C}$) was lower than that of P1 without SDS. Further increase the temperature resulted in an irreversible decrease in the emission and absorption intensities. This means that the SDS-P1 complex can't be dissociated

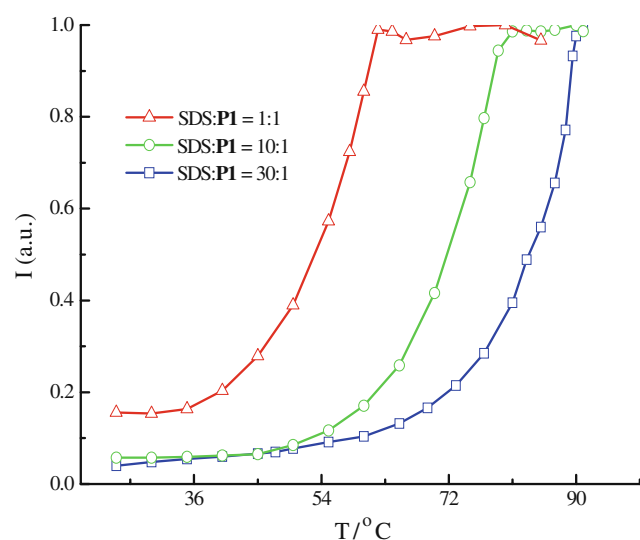


Fig. 2 Temperature effect on the fluorescence intensity of P1 at different ratios of [SDS] to [P1] ([P1]=6 μM , λ_{ex} =445 nm)

completely, i.e., free **P1** concentration is always less than the total **P1** concentration even at very high temperature (Eq. 4); in addition, the higher temperature may promote the decomposition of **P1**.

When [CTAB] or temperature is high enough, both the maxima of absorbance and Φ_F of SDS-**P1** aqueous solution decreased with increasing initial SDS concentration (see Supplementary Materials Table S1), denoting that free **P1** concentration is dependent on [SDS] added at certain total **P1** (Eqs. 4 and 10). These results can also be verified by the following Equations.

The free **P1** concentration can be expressed as following Equations, where K_{as1} and K_{as2} are the associating constants of SDS and **P1**, SDS and CTAB, respectively; K_{as3} is the competitive ability of CTAB vs. **P1** with SDS; $[P1]_T$ and $[P1]_F$ represent the total and free **P1** concentrations, respectively.



There has

$$[\text{SDS} \cdot \text{P1}] = [P1]_T - [P1]_F \quad (2)$$

$$K_{as1} = \frac{[\text{SDS} \cdot \text{P1}]}{[\text{SDS}][P1]_F} = \frac{[P1]_T - [P1]_F}{[\text{SDS}][P1]_F} \quad (3)$$

$$[P1]_F = \frac{[P1]_T}{K_{as1}[\text{SDS}] + 1} \quad (4)$$

From Eq. (4), it is known that under the conditions of fixed temperature and total **P1** concentration, the free **P1** concentration as well as the fluorescence intensity is lower at higher [SDS].

When CTAB is added to **P1**-SDS mixed system, there have:



$$K_{as2} = \frac{[\text{SDS} \cdot \text{CTAB}]}{[\text{CTAB}][\text{SDS}]} \quad (6)$$



$$K_{as3} = \frac{[\text{SDS} \cdot \text{CTAB}][P1]_F}{[\text{CTAB}][\text{SDS} \cdot \text{P1}]} \quad (8)$$

$$[P1]_F = \frac{K_{as3}[\text{CTAB}][\text{SDS} \cdot \text{P1}]}{[\text{SDS} \cdot \text{CTAB}]} \quad (9)$$

Neglect the association between CTAB and **P1**, and combine Eqs. (2), (6) and (9) together, then the free **P1** concentration can be expressed as Eq. (10), from which, it is known that $[P1]_F$ is the reciprocal ratio of [SDS].

$$[P1]_F = \frac{K_{as3}[P1]_T}{K_{as2}[\text{SDS}] + K_{as3}} \quad (10)$$

IMPLICATION Logic Gate of Three-Input System

From the above results, it can be seen that the presence of SDS quenched, while CTAB and higher temperature enhanced the Φ_F of **P1**. Then we demonstrate the IMPLICATION logic operation with SDS, CTAB and temperature as inputs, A_{470} (see Supplementary Materials Figure S4) and the fluorescence intensity at 525 nm as outputs, respectively. Figure 3 shows the fluorescence characteristics of **P1** in aqueous solution under eight different conditions. As shown in Fig. 3, **P1** is fluorescent in water, but its fluorescence was quenched by SDS due to the formation of unfluorescent SDS-**P1** complex (the 5th row). Both CTAB and higher temperature dissociated the SDS-**P1** complex and recovered the emission and absorption intensities of **P1**. CTAB can form more fluorescent complex with **P1** (see Supplementary Materials Figure S3), while higher temperature makes **P1** more soluble in water. So, the outputs were high when CTAB concentration and/or temperature were kept high. The outputs are low (0) only when three inputs SDS, CTAB and temperature are kept 1, 0 and 0, respectively; they are high (1) under the other seven conditions.

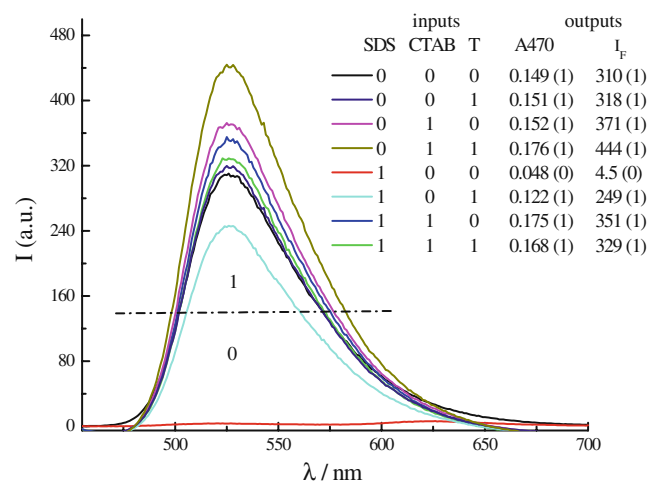


Fig. 3 Fluorescence spectra of **P1** in water under the eight experimental conditions required to demonstrate three-input IMPLICATION logic ([SDS] is 0 (low, 0) or 10 μM (high, 1), [CTAB] is 0 (low, 0) or 20 μM (high, 1) and the temperature is 25 $^{\circ}\text{C}$ (low, 0) or 75 $^{\circ}\text{C}$ (high, 1); $[P1]=6 \mu\text{M}$, $\lambda_{ex}=445 \text{ nm}$)

Conclusions

In summary, a multiple functional supramolecular system **P1**/SDS was employed as a sensor to detect cationic surfactant CTAB. The dynamic detection window can be adjusted by altering the initial [SDS]/[**P1**] ratio. The detection limit is comparable with those in the literatures and can be further improved by elaborately selecting [SDS]/[**P1**]. Moreover, **P1** can also execute three-input IMPLICATION function with SDS, CTAB and temperature as inputs. The results presented here may provide a new strategy for designing and constructing supramolecular devices with multiple functions.

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