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The environmental-sensitivity of a fluorescent ZTRS–Cd(II) complex was applied to discriminate different types of surfactants and determine their CMC values†

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We have, for the first time, reported a fluorescent probe (ZTRS–C_{18}–Cd(II) complex) which discriminated four types of surfactants. This recognition was realized depending on the transformation of ZTRS–Cd^{2+} binding patterns in different microenvironments formed in various types of surfactants.

Surfactants are widely used in daily life and industries. They are chemicals capable of lowering the surface tension (or interfacial tension) between two liquids or between a liquid and a solid, attributed to their hydrophobic tails and hydrophilic heads. According to the nature of the hydrophilic head, surfactants are classified into anionic, cationic, zwitterionic (amphoteric) and nonionic types.[1] All types of surfactants can act as wetting agents, emulsifiers, foaming agents, and dispersants with different efficiencies in different application fields.[2,3] The extensive use of surfactants and their unregulated disposal into environmental media such as soil, water and sediment cause them to be well-known environmental pollutants.[4] Surfactant toxicity has aroused a worldwide alert leading to studies of environmental impacts of surfactants and the development of biodegradable ones. These research fields require the development of new and improved sensing methods for surfactant determination. Compared to traditional detection methods, such as ion-selective electrodes, chromatography and mass spectrometry, fluorescence analysis has attracted extensive attention due to its high sensitivity and selectivity. So far, fluorescent compounds such as polydiacetylenes,[5,6] perylenes[7] and squaraines[8] have been applied in surfactant detection. To the best of our knowledge, most of the reported probes can only recognize either anionic[5,8–13] or cationic surfactants.[6,7,14,15] Very few probes have been reported to recognize zwitterionic or nonionic surfactants. Xu *et al.* reported a cross-responsive sensing array based on squaraines to discriminate anionic, cationic and nonionic types of surfactants.[16] However, the detection was based on mathematical analysis and it was hard to accomplish with the naked eye. Until now, there has been no one probe that can discriminate all types of surfactants.

In this work, we reported a probe to discriminate all types of surfactants and determine their CMC values. The design of such a kind of probe originated from the different environments formed by the hydrophilic heads of various types of surfactants and the environmental sensitivity of the fluorophore to respond to the interaction with different surfactants in four fluorescence channels (Fig. 1a). Solvatochromic dyes which change their emission wavelength in response to environmental variation would be good candidates to possess the functions required as mentioned above.[17,18] A typical solvatochromic dye contains a push–pull molecular structure undergoing intramolecular charge transfer (ICT). Emission of their highly polarized excited state shifts to the red in more polar solvents. Another key concept to design efficient solvatochromic dyes is excited-state intramolecular proton transfer (ESIPT), which responds to the microenvironment by changing the relative intensity of the two emissive tautomeric forms.[19] In our previous work, we reported a probe (**ZTRS**) which can bind Zn^{2+} and Cd^{2+} in different patterns. **ZTRS** consisted of a push–pull naphthalimide fluorophore and an amide-containing DPA chelator (Fig. 1b). The sensor bound Zn^{2+} in an imidic acid tautomeric form and emitted around 525 nm in a CH_3CN/50 mM HEPES mixture, while Cd^{2+} was bound in an amide tautomeric form and emitted around 450 nm. The fluorescence enhancement helped in distinguishing Cd^{2+} and Zn^{2+} from other metal ions. And the emission maxima shifted towards the opposite direction eliminated the interference from each other. In this work, further studies demonstrated that **ZTRS** was a new type of solvatochromic dye. As shown in Fig. 1b and c, in non- or weak polar solvents, **ZTRS** bound Cd^{2+} in an amide tautomer form and emitted around 450 nm, while in polar solvents **ZTRS** bound Cd^{2+} in an imidic acid tautomer form and emitted around 525 nm. The I_{450}/I_{525} ratio of the **ZTRS–Cd(II)** complex varied in different solvents (Fig. 1c). Plotting the I_{450}/I_{525} ratio against dielectric

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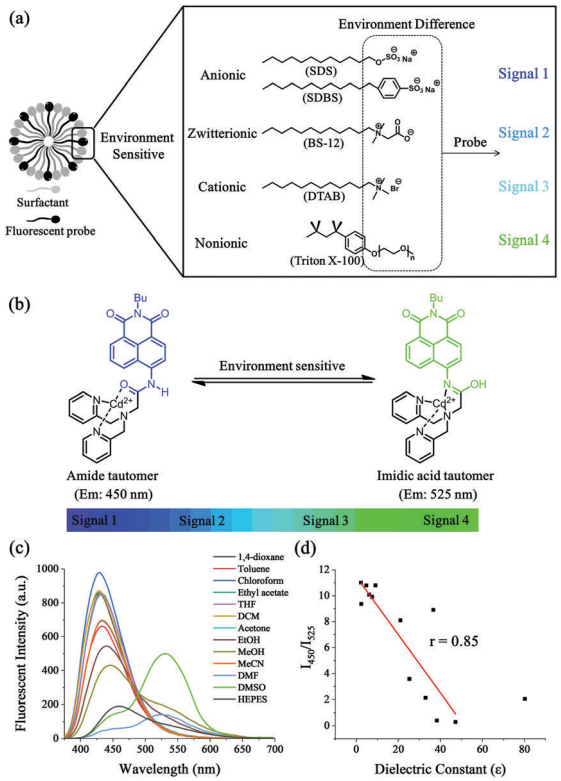

Fig. 1 (a) The design of a fluorescent probe to discriminate different types of surfactants. (b) The different binding modes of **ZTRS** with Cd^{2+} were environment-sensitive. (c) Fluorescence spectra of 10 μM **ZTRS–Cd(II)** in different solvents. (d) Relationship between the I_{450}/I_{525} ratios of the **ZTRS–Cd(II)** complex and dielectric constants.

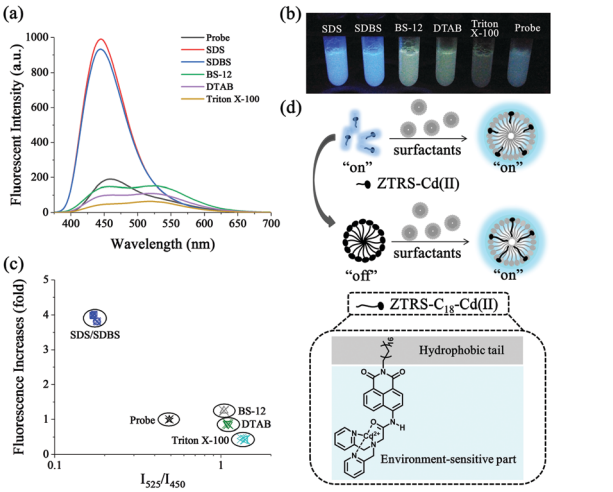

Fig. 2 (a) The fluorescence responses of 10 μM **ZTRS–Cd(II)** to various types of surfactants (20 mM) in buffer solutions (50 mM, pH 7.2). (b) Visible emissions of the samples mentioned above under UV irradiation. (c) Two-dimensional plot of the intensity increment and I_{525}/I_{450} for the discrimination of the four types of surfactants. (d) The action mode of the **ZTRS–C_{18}–Cd(II)** probe to display off–on fluorescence changes governed by the strategy of aggregation-caused quenching and disaggregation induced increase.

constants, we observed a negative correlation between these variates with a correlation coefficient of 0.85 (Fig. 1d). These results indicated that, like ESIPT dyes did, the **ZTRS–Cd(II)** complex responded to the microenvironment by changing the relative intensity of the two emissive tautomeric forms. These environment-sensitive properties of the **ZTRS–Cd(II)** complex inspired us to apply them to discriminate different types of surfactants. As shown in Fig. 1a, the micro-environments of the various types of surfactants were different, which induced the rational changes in the **ZTRS–Cd(II)** binding modes between imidic acid and amide tautomeric forms. Since the emission maxima correspond to specific binding modes (450 nm for the amide tautomer and 525 nm for the imidic acid tautomer), we could distinguish the different types of surfactants based on the intensity ratios of blue and green emissions.

To assess the responses of **ZTRS–Cd(II)** complexes to the four types of surfactants (including anionic, zwitterionic, cationic and nonionic), we chose five most commonly used surfactants SDS, SDBS, BS-12, DTAB and Triton X-100 as examples (Fig. 1a). We set the concentrations of all surfactants at 20 mM to form micelles. The fluorescence spectrum of **ZTRS–Cd(II)** exhibited an emission band with a maximum at 458 nm (Φ = 0.084), which indicated that **ZTRS–Cd(II)** existed in an amide tautomeric form in pH 7.2 buffer solutions (Table S1, ESI†). In SDS and SDBS solutions (anionic surfactants), the fluorescence intensities of the **ZTRS–Cd(II)** complexes increased about 4 fold and the maximum emission slightly blue-shifted to 450 nm (Fig. 2a), which indicated the binding mode of the amide tautomer. Notably, the fluorescence spectra of **ZTRS–Cd(II)** in the other three types of surfactants displayed two emission peaks around 450 nm and 525 nm, respectively. These results suggested that **ZTRS–Cd(II)** existed as a mixture of amide tautomeric and imidic acid tautomeric complexes in cationic, zwitterionic and nonionic surfactants (Table S1, ESI†). And these three types of surfactants quenched fluorescence to different extents. Considering that **ZTRS–Cd(II)** is an ICT fluorophore, the fluorescence enhancement and blue-shifting emission in the anionic surfactants should be ascribed to the decrease in environmental polarity, while the fluorescence decrease and red-shifting emission in the cationic, zwitterionic or nonionic surfactants should be ascribed to the increase in environmental polarity. We used changes in fluorescence intensity and the intensity ratios of emission at 525 nm to that at 450 nm (I_{525}/I_{450}) as fingerprints to identify the different types of surfactants. As shown in Fig. 2c, anionic surfactants SDS and SDBS lead to blue-shifting emissions and large increases in fluorescence intensity, which put them far away from the probe itself and in the upper left part of the 2D map. For BS-12 (zwitterionic surfactant), DTAB (cationic surfactant) and Triton X-100 (nonionic surfactant), the differences in fluorescence intensity and I_{525}/I_{450} also lead them to be separately located on the right side of the probe.

Even though we can discriminate the four types of surfactants by the two-dimensional array, the fluorescence changes of **ZTRS–Cd(II)** were insufficient to distinguish different surfactants with the naked eye (Fig. 2b). In particular, the strong fluorescence background from the free probe interfered with the surfactant recognition. In terms of sensitivity and selectivity, obvious fluorescence changes (large off–on signals

or emission shifts) induced by the analytes were desired. To improve the off–on signal, we introduced a C18 alkyl chain into the probe to get the **ZTRS–C_{18}–Cd(II)** compound which was expected to aggregate and exhibited aggregation-caused fluorescence quenching (ACQ)[20] (Fig. 2d). The compatibility of the C18 chain with the hydrophobic tails of the surfactants will enhance the distribution of the probes in the micelles and then strengthen the interaction between the probe's environment-sensitive part and the hydrophilic heads of the surfactants.

As expected, **ZTRS–C_{18}–Cd(II)** aggregated in aqueous solution. The results of dynamic light scattering (DLS) and transmission electron microscopy (TEM) experiments showed that the formed particles were rodlike with an average length of 80 nm (Fig. 3a and b). Compared with **ZTRS–Cd(II)**, the fluorescence intensity of **ZTRS–C_{18}–Cd(II)** significantly decreased due to the aggregation effect (Φ = 0.008). Notably, the emission peak of **ZTRS–C_{18}–Cd(II)** red-shifted to 505 nm (Fig. 3c). The aggregation enhanced the interaction between the complexes. And the repulsion between positive charges may be attributed to the binding transformation from the amide to imidic acid tautomer (Table S1, ESI†). The addition of the anionic surfactants dispersed the **ZTRS–C_{18}–Cd(II)** aggregation (Fig. 3c) and induced large fluorescence enhancements (48 fold in SDS and 38 fold in SDBS, respectively). Besides, the interaction between the anionic surfactants and **ZTRS–C_{18}–Cd(II)** blue-shifted the fluorescence emission from 505 nm to 450 nm, which indicated that the binding mode of **ZTRS–C_{18}–Cd(II)** was restored to the amide tautomer form in the anionic surfactants. The addition of the other three types of surfactants also induced obvious fluorescence enhancements (15 fold in BS-12, 12 fold in DTAB and 6 fold in Triton X-100). More importantly, the emission peak appeared around 525 nm for the imidic acid tautomeric complexes. The fluorescence spectra of **ZTRS–C_{18}–Cd(II)** in DTAB and Triton X-100 solutions displayed only one emission peak around 525 nm and 505 nm, respectively. These results indicated that **ZTRS–C_{18}–Cd(II)** existed mainly in an imidic acid tautomer in the cationic or nonionic surfactants. The cationic surfactants provided a stronger polar environment, so the fluorescence wavelength was further red-shifted to 525 nm. The fluorescence of **ZTRS–C_{18}–Cd(II)** in BS-12 solutions showed broad emission with two emission maxima with nearly equal intensities centered around 450 nm and 525 nm. This implied that both tautomeric forms co-existed in zwitterionic surfactants. Depending on the changes in fluorescence intensity and the emission ratio (I_{450}/I_{525}), **ZTRS–C_{18}–Cd(II)** could be used to distinguish different types of surfactants easily even with the naked eye (Fig. 3d and e). To exclude interference, common ions including Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, NO_3^-, and PO_4^{3-} were also added to the **ZTRS–C_{18}–Cd(II)** solutions. As shown in Fig. 3c, only surfactants caused obvious emission changes.

The critical micelle concentration (CMC) is an important value for surfactants, indicating the formation of thermodynamically stable micelles above this value.[21] It has been proved that fluorescence can also be used to study this self-assembly process and determine the CMC values.[22–24] To evaluate our probe's ability to monitor the process of micelle formation, fluorescence titration experiments of **ZTRS–C_{18}–Cd(II)** with various concentrations of the four types of surfactants were conducted (Fig. S1–S5, ESI†). The fluorescence intensities gradually increased with increasing concentrations of both SDS and SDBS. Besides, the emission maxima also gradually shifted to around 450 nm. The fluorescence intensity enhancement and I_{450}/I_{525} values were further plotted as functions of surfactant concentrations in order to estimate the CMC values of SDS and SDBS (Fig. 4a and b). Taking the data of SDS as an example, there was a smooth transition between the concentrations of 6 mM and 10 mM and a linear behavior with different slopes above and below this transition. But a linear relationship could be hardly observed at very low concentrations (from 0 mM to 2 mM), which was in accord with previous reports of a nonlinear relation between the physical properties and concentration at very low and very high concentrations.[25] Therefore, to guarantee the linear behavior in both the pre- and postmicellar regions in measuring the CMC, it would be convenient to exclude these data.[25] According to this guidance, the intersection of the two straight lines of the fluorescence intensity titration curves indicated that the CMC value of SDS was 7.4 mM. At the same time, the measured CMC value of SDS through the I_{450}/I_{525} ratio was found to be 6.8 mM. Similarly, the CMC values of SDBS, BS-12, DTAB and Triton X-100 were also obtained based on titration experiments of both fluorescence intensity and I_{450}/I_{525} or I_{525}/I_{450} changes (Fig. 4b–f and Fig. S6–S10, ESI†). As shown in Table 1, most of the CMC values[26–30] determined here were in accordance with the reported values except for Triton X-100. This might be attributed to the weak interaction between Triton X-100 and **ZTRS–C_{18}–Cd(II)**. From the above data, addition of **ZTRS–C_{18}–Cd(II)** into 20 mM Triton X-100 solution only induced a 6 fold fluorescence increase with the emission maxima nearly unchanged. The unobvious

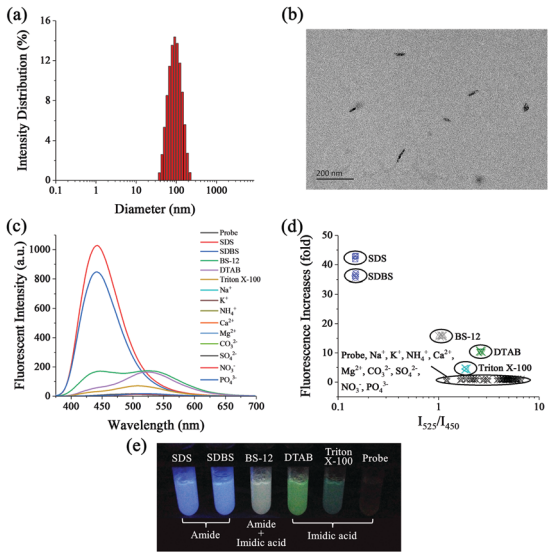

Fig. 3 (a) DLS analysis of the particle-size distribution of the self-assembled **ZTRS–C_{18}–Cd(II)** (10 μM) in HEPES (50 mM, pH 7.2). (b) TEM image of the self-assembled **ZTRS–C_{18}–Cd(II)**. (c) Fluorescence spectra of 10 μM **ZTRS–C_{18}–Cd(II)** in the presence of 20 mM various analytes (50 mM, pH 7.2). (d) Fluorescence increase and I_{525}/I_{450} for a two-dimensional plot. (e) Visible emissions of samples under UV irradiation.

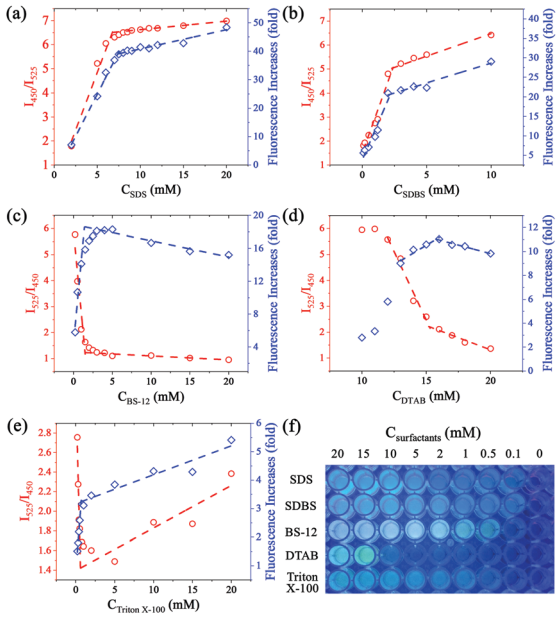

Fig. 4 The ratiometric fluorescence changes (red) and fluorescence intensity enhancement (blue) as functions to determine the CMC values of (a) SDS; (b) SDBS; (c) BS-12; (d) DTAB and (e) Triton X-100. (f) Visible emissions of **ZTRS–C_{18}–Cd(II)** in different concentrations of surfactants under UV irradiation.

Table 1 CMC values of surfactants

	CMC (mM)		
Surfactants	I_{450}/I_{525} (or I_{525}/I_{450})	Fluorescence enhancement	Literature reported
SDS	6.8	7.4	8.0–8.2
SDBS	2.4	2.2	1.4–1.6
BS-12	1.5	1.5	1.4–2.0
DTAB	14.9	15.8	14.6–16.0
Triton X-100	0.6	0.7	0.24–0.27

changes made it hard to determine the break point providing the CMC value. Besides, the CMC value obtained by the way of fluorescence enhancement was more closer to reported values than those based on I_{450}/I_{525} ratios in the anionic surfactants (SDS and SDBS), which might be attributed to the unobvious double emission maxima in the titration process. In addition, HEPES buffer solution might influence the micelle formation and induce slight changes in the CMC values. It is worth mentioning that the CMC values of the surfactants can be estimated directly through fluorescence intensity and color changes under a 365 nm UV lamp (Fig. 4f).

In summary, we have developed an environment sensitive fluorescent probe (**ZTRS–C_{18}–Cd(II)**) to distinguish different types of surfactants based on the environmental-dependence of the different binding patterns of **ZTRS** with Cd^{2+}. The CMC values of these surfactants could also be determined through the fluorescence intensity titration or the ratio changes of I_{450}/I_{525} (or I_{525}/I_{450}). It is worth noting that the detection of surfactants and determination of their CMC values could be achieved with the naked eye under UV irradiation, which facilitate its application. This work also provided a new strategy to design cell microenvironment probes with the **ZTRS–Cd(II)** complex.

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Conflicts of interest

There are no conflicts to declare.

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