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temperature, light and pH induced morphological of C_{10}AZOC_{2}IMB and 4FS binary systems
Thermal, Light and pH Triple Stimulated Changes in Self-assembly of a Novel Small Molecular Weight Amphiphile Binary System

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Novel multiple stimuli-responsive fluids based on an azobenzene-contained surfactant 1-[2-(4-decylphenylazo-phenoxy)-ethyl]-3-methylimidazolium bromide (C$_{10}$AZOC$_{2}$IMB) and a hydrotrope 4-(trifluoromethyl) salicylic acid (4FS) can be reversibly induced by temperature, light and pH from vesicles to wormlike micelles. UV-vis spectra, rheology, dynamic light scattering (DLS) and cryo-TEM measurements were utilized to prove the self-assembly transitions.

Developing multiple environmental stimuli-responsive materials has attracted much attention for the construction of soft functional materials. The use of chemical bond to insert stimuli groups in polymers or supra-molecules is attractive due to the feasibility in organic synthesis. Light is used for bringing about photoreactions and structural isomerizations of molecules, leading to changes of matter. Heat and pH are available in fabrication of nanoscale objects such as polymers or molecular assemblies in solutions. However, there is no report claiming that low molecular weight amphiphiles is capable of reacting to all three physical stimuli.

In the present study, we succeeded in developing a novel light, heat and pH responsive low molecular weight amphiphile binary system. Visible and UV light, heating up and cooling down, raising up and bringing down pH can all reversibly turn their aggregate morphology between vesicles and wormlike micelles. The sample solution exhibits a viscosity response with inputs of UV light, heating up and under alkaline conditions, which has potential as a molecular-based thickening fluids. The triple stimuli-responsive amphiphile (C$_{10}$AZOC$_{2}$IMB)/4FS binary system is shown in Scheme 1.

C$_{10}$AZOC$_{2}$IMB was synthesized starting from 4-decylaniline in a 4 step procedure outlines. The identity was confirmed by $^1$H NMR, $^{13}$C NMR and ESI-MS. The synthetic details and characterization data are provided in the ESI.

The binary phase behavior of C$_{10}$AZOC$_{2}$IMB and 4FS mixtures (see ESI) at 25 °C shows that at very low concentrations of 4FS (< 3 mM), the mixtures are clear with a very low viscosity, indicating that the aggregates were spherical or rodlike micelles (Fig. 1a). The viscosity increases as [4FS] was increased until a maximum. Further increase [4FS] results in the sharp decrease in viscosity and turbid appearance of solution. The viscosity of 12.5 mM/8 mM mixture was close to that of water (1 mPa.s) at 25 °C (Fig. 1b). It becomes viscous with the increase of temperature, and the zero-shear viscosity $\eta_0$ increases by a factor of about 500 at 85 °C (see ESI). Upon UV irradiation, the trans-azobenzene group in C$_{10}$AZOC$_{2}$IMB can be transformed into cis-azobenzene, subsequently the irradiated solution was then exposed to visible light, the cis-azobenzene can be reverted to trans-azobenzene reversibly (see ESI). After being UV irradiated for about 7 min, the viscosity of the samples reached the maximum (see ESI). Similar to temperature and light stimuli, when pH was increased from 2.09 to 12.35, 4FS molecule transformed into special molecular structure containing an ionized carboxylic acid moiety and an ionized hydroxyl moiety (see ESI), the low viscous solution become high viscoelastic fluid...
This data presented here suggest a transition from vesicles to wormlike micelles induced by temperature, light and pH.

![Fig. 1 Phase behavior at 25 °C of C_{10}AZOC:IMB/4FS mixtures at a fixed C_{10}AZOC:IMB concentration of 12.5 mM by varying the concentration of 4FS. a and b show the turbidity and the zero-shear viscosity, respectively. Samples containing 4.5 mM 4FS are highly viscous (left photograph in panel a) and samples containing 8 mM 4FS become turbid with a low viscosity (right photograph in panel a). c shows steady state rheology of 12.5 mM C_{10}AZOC:IMB and 8 mM 4FS at 25 °C, 75 °C, after UV irradiation 7 min and pH 12.35.](image)

The stimuli-responsive reversibility of the system was characterized by rheological response well. Fig. 2 showed that the rheological properties of such triple stimuli-responsive fluids can be almost reversibly controlled. The viscosity can be switched between \( \sim 10^9 \) and \( \sim 10^3 \) Pa's according to the different stimuli conditions and the sample can be tuned between high viscous fluid and waterlike fluid reversibly.

![Fig. 2 Zero-shear viscosity of 12.5 mM C_{10}AZOC:IMB and 8 mM 4FS during the repeated cycles of temperature variation (a), pH variation (b) and repeated UV irradiation for 7 min at 365 nm and visible light irradiation for 3 h at 450 nm (c).](image)

Cryo-TEM results also reveal that the microstructures changes from vesicles to wormlike micelles under the triple stimuli. Note that vesicles with different diameters were formed in its original state. When the temperature is increased to 50 °C, long and entangled wormlike micelles are observed in Fig. 3c. The elongated threadlike micelles are interconnecting with each other, resulting in a high viscosity liquid. After being UV irradiated for about 7 min on this original solution at room temperature, the various different diameters vesicles disappear and long and branched micelles are visible in Fig. 3d. Fig. 3e shows the morphology of the aggregates under ambient conditions when the mixtures solution pH was adjusted from 2.09 to 12.35, thread-like micelles were also observed.

UV-vis measurements were performed to elucidate the mechanism of the vesicle-micelle transitions. It is well established that the morphology of aggregates is closely related to the molecular packing parameter \( p \) proposed by Israelachivili:\(^8\) 

\[
p = \frac{v}{l a_0},
\]

where \( l \) and \( v \) are the effective maximum length and volume of the hydrophobic tail, respectively, and \( a_0 \) is the effective surface area of per surfactant molecule constituting the aggregate. When vesicles of C_{10}AZOC:IMB/4FS mixtures were under high temperatures, UV irradiation and alkaline conditions, the 4FS intercalating into the palisade layer of aggregates partly desorbs from the vesicles. Such desorption would increase the effective headgroup area and reduce the tail volume, thereby drive the vesicles to aggregates of higher curvature specifically to wormlike micelles. It is confirmed by the UV-vis spectra as shown in Fig. 4. When the temperature increases to 85 °C on this samples, the absorption peak shifted from 337 to 347 nm, which is almost the same wavelength as that of pure C_{10}AZOC:IMB (Fig. 4a). Upon UV irradiation for 10 s, the trans-C_{10}AZOC:IMB
totally transform to cis-C10AZOC2IMB corresponding the absorption shifts from 347 nm to 311 nm, and also results in blue-shift slightly of absorption peak of 4FS (Fig. 4b). This result proves that the association of C10AZOC2IMB and 4FS are weakened after UV irradiation, which results in the changes of the molecular packing parameter. In Fig. 4c, the 4FS solution shows a maximal absorbance λmax in 302 nm in the absence of C10AZOC2IMB, whereas the addition of C10AZOC2IMB makes the λmax shift to 311 nm and a broad shoulder can be easily noted. According to previous reports, the red shift of absorbance was attributed to the strong cation–π interaction between the aromatic ring of 4FS and the C10AZOC2IMB head group. As pH increases, 4FS transforms into ds-4FS (disodium 4-(trifluoromethyl) salicylic acid) and almost no red shift can be observed with the addition of C10AZOC2IMB (Fig. 4d). This means that the binding ability of hydrotrope to the C10AZOC2IMB head group was weakened at higher pH condition, leading to the structural transition from vesicles to wormlike micelles.

Fig. 4 UV-vis spectra of pure 0.032 mM 4FS, pure 0.05 mM C10AZOC2IMB at 25 °C and their mixture systems at 25 °C and 85 °C (a) and pure 0.1 mM 4FS, pure 0.025 mM C10AZOC2IMB and their binary systems before and after UV irradiation, respectively (b) and 0.1 mM 4FS in the presence and absence of 0.025 mM C10AZOC2IMB (c) and 0.1 mM ds-4FS in the presence and absence of 0.025 mM C10AZOC2IMB (d).

In conclusion, we have designed novel multiple stimulus-responsive fluids based on an azobenzene-contained surfactant C10AZOC2IMB and a hydrotrope 4FS successfully. And demonstrated that the 4-(trifluoromethyl)salicylic acid (4FS) can induce C10AZOC2IMB to form either wormlike micelles or vesicles depending on the solution composition. UV-vis spectra, rheology, DLS and cryo-TEM measurements were utilized and proved the self-assembly transition from vesicles to long and entangled wormlike micelles induced by temperature, light and pH. The vesicle to micelle transitions cause the solutions to switch from low-viscosity, Newtonian fluids to viscoelastic, shear-thinning fluids. The proposed mechanism was proved by UV-vis spectra. To the best of our knowledge, there is no report of reversible control of the vesicle to wormlike micelle transition by all the three external stimuli based on simple chemicals. This may be a promising strategy for fabricating stimuli-responsive materials, which find wide applications in the development of functional materials for drug delivery, crude oil recovery, analytical chemistry and military equipment.

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Notes and references