

RSC Advances

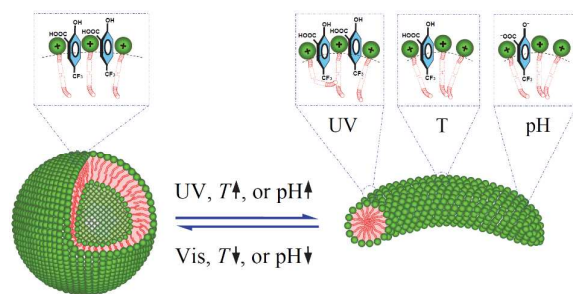


This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



temperature, light and pH induced morphological of $C_{10}AZOC_2IMB$ and 4FS binary systems

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Thermal, Light and pH Triple Stimulated Changes in Self-assembly of a Novel Small Molecular Weight Amphiphile Binary System

Kangle Jia, Yuming Cheng, Xiong Liu, Xuefeng Li* and Jinfeng Dong*

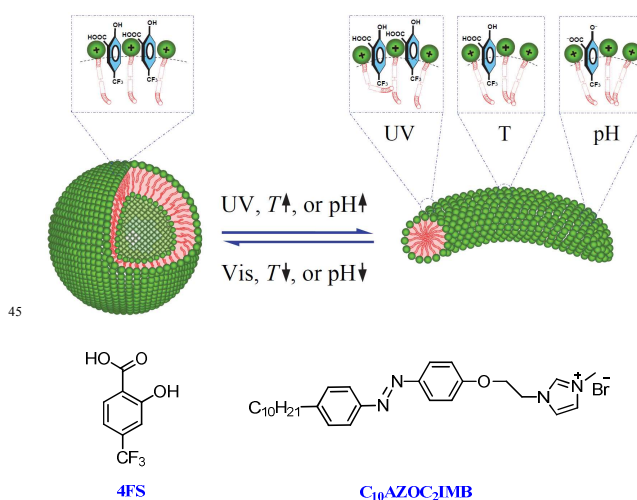
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Novel multiple stimuli-responsive fluids based on an azobenzene-contained surfactant 1-[2-(4-decylphenylazo-phenoxy)-ethyl]-3-methylimidazolium bromide ($C_{10}AZOC_2IMB$) 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^{1,2}. The use of chemical bond to insert stimuli groups in polymers or supra-molecules is attractive due to the feasibility in organic synthesis³. Light is used for bringing about photoreactions and structural isomerizations of molecules, leading to changes of matter^{5,7}. Heat and pH are available in fabrication of nanoscale objects such as polymers or molecular assemblies in solutions^{4,6}. However, there is no report claiming that low molecular weight amphiphiles are 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 ($C_{10}AZOC_2IMB$)/4-(trifluoromethyl) salicylic acid (4FS) binary system is shown in Scheme 1.

$C_{10}AZOC_2IMB$ was synthesized starting from 4-decylaniline in a 4 step procedure outlines. The identity was confirmed by ¹H NMR, ¹³C NMR and ESI-MS. The synthetic details and characterization data are provided in the ESI.



Scheme 1 Schematic representation for temperature, light and pH induced morphological of $C_{10}AZOC_2IMB$ and 4FS binary systems and chemical structure of $C_{10}AZOC_2IMB$ and 4FS.

The binary phase behavior of $C_{10}AZOC_2IMB$ 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 η_0 increases by a factor of about 500 at 85 °C (see ESI). Upon UV irradiation^a, the *trans*-azobenzene group in $C_{10}AZOC_2IMB$ 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

(Fig. 1c). This data presented here suggest a transition from vesicles to wormlike micelles induced by temperature, light and pH.

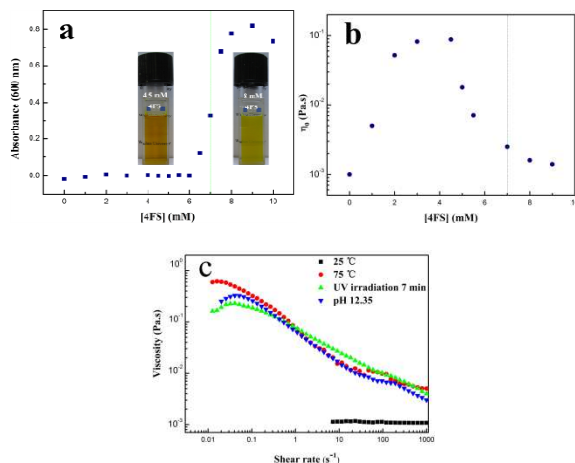


Fig. 1 Phase behavior at 25 °C of $C_{10}AZOC_2IMB/4FS$ mixtures at a fixed $C_{10}AZOC_2IMB$ concentration of 12.5 mM by varying the concentration of 4FS. *a* and *b* show the turbidity and the zero-shear viscosity, respectively. Samples containing 4.5 mM 4FS are highly viscous (left photograph in panel *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 $C_{10}AZOC_2IMB$ and 8 mM 4FS at 25 °C, 75 °C, after UV irradiation 7 min and pH 12.35.

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 $\sim 10^0$ 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.

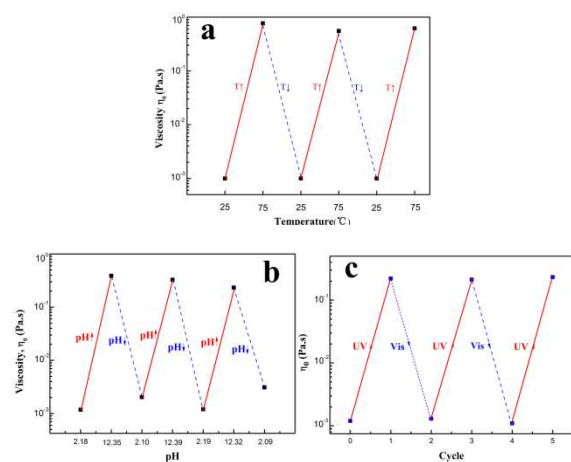


Fig. 2 Zero-shear viscosity of 12.5 mM $C_{10}AZOC_2IMB$ and 8 mM 4FS during the repeated cycles of temperature variation (*a*), pH variation (*b*) and repeated UV irradiation for 7 min at 365 nm and visible light irradiation for 3 h at 450 nm (*c*).

Cryo-TEM result of the sample, prepared from an aqueous solution of $C_{10}AZOC_2IMB$ with a concentration of 12.5mM, shows that rodlike and wormlike micelles are formed at the addition of 4.5 mM 4FS (Fig. 3a); whereas spherical vesicles with

a diameter from tens of nanometers to hundreds of nanometers are formed in the presence of 8 mM 4FS (Fig. 3b). The cryo-TEM results are indicative of a phase transition from wormlike micelles to vesicles in $C_{10}AZOC_2IMB-4FS$ mixtures with increasing 4FS concentration, which is consistent with the turbidity, viscosity results well.

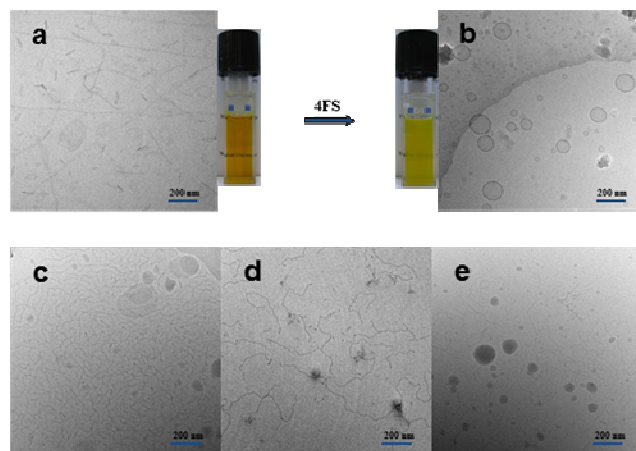


Fig. 3 Cryo-TEM photographs and morphological of 12.5 mM $C_{10}AZOC_2IMB$ solution containing 4.5 mM (*a*), 8 mM (*b*) 4FS at 25 °C, respectively. And cryo-TEM micrographs of 12.5 mM $C_{10}AZOC_2IMB$ and 8 mM 4FS at (*c*) 50 °C, (*d*) after UV irradiation 7 min and (*e*) pH 12.35, respectively.

Cryo-TEM results also reveal that the microstructures changes from vesicles to worm-like 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 thread-like micelles are inter-connecting 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 $p = v/a_0l$, 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 $C_{10}AZOC_2IMB/4FS$ 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 $C_{10}AZOC_2IMB$ (Fig. 4a). Upon UV irradiation for 10 s, the *trans*- $C_{10}AZOC_2IMB$

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 λ_{\max} in 302 nm in the absence of C₁₀AZOC₂IMB, whereas the addition of C₁₀AZOC₂IMB makes the λ_{\max} shift to 311 nm and a broad shoulder can be easily noted. According to previous reports^{4d}, 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.

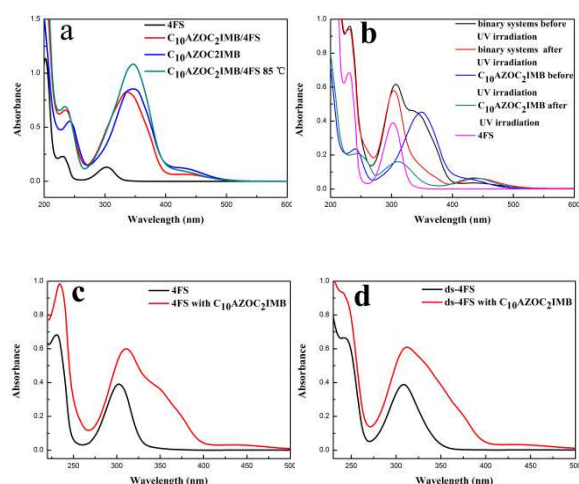


Fig. 4 UV-vis spectra of pure 0.032 mM 4FS, pure 0.05 mM C₁₀AZOC₂IMB at 25 °C and their mixture systems at 25 °C and 85 °C (a) and pure 0.1 mM 4FS, pure 0.025 mM C₁₀AZOC₂IMB and their binary systems before and after UV irradiation, respectively (b) and 0.1 mM 4FS in the presence and absence of 0.025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

This work was supported by the National Natural Science Foundation of China (NSFC 20973129 and 21273165).

Notes and references

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China, Fax: 00 8627 68754067; Tel: 00 8627 68754067; E-mail:lixuefeng@whu.edu.cn (Xuefeng Li), jfdong@whu.edu.cn (Jinfeng Dong).

^a Experimental temperatures were kept at 25 °C using a thermostat water bath when the sample were irradiated by UV or visible light lamp, and the distance between the sample and light source was fixed at 15 cm.

[†] Electronic Supplementary Information (ESI) available: C₁₀AZOC₂IMB synthesis, characterization, phase behavior, zero-shear viscosity, UV-vis spectra, species distribution.

- (a) A. M. Le, Ny. C. T and L. Jr, *J. Am. Chem. Soc.*, 2006, **128**, 6400; (b) X. -Guo, F. C and S. Jr, *Acc. Chem. Res.*, 2003, **36**, 335; (c) H. M and M. V, *J. Mater. Eng. Perform.*, 2014, **23**, 1182; (d) Y.-X. Liu, P. G. Jessop, M. Cunningham, C. A. Eckert and C. L. Liotta, *Science*, 2006, **313**, 958.
- (a) Y.-Y. Lin, Y.-D. Zhang, Y. Qiao, J.-B. Huang and B.-C. Xu, *J. Colloid Interface Sci.*, 2011, **362**, 430; (b) Y.-J. Song, R. M. Garcia, R. M. Dorin, H.-R. Wang, Y. Qiu, E. N. Coker, W. A. Steen, J. E. Miller and J. A. Shelnett, *Nano Lett.*, 2007, **7**, 3650; (c) J. L. Zakin, B. Lu and H. W. Bewersdorff, *Rev. Chem. Eng.*, 1998, **14**, 253; (d) Y.-M. Zhang, Y.-J. Feng, J.-Y. Wang, S. He, Z.-R. Guo, Z.-L. Chu and C. A. Dreiss, *Chem. Commun.*, 2013, **49**, 4902.
- J.-M. Zhuang, M. R. Gordon, J. Ventura, L.-Y. Li and S. Thayumanavan, *Chem. Soc. Rev.*, 2013, **42**, 7421.
- (a) Y. Yang, J.-F. Dong and X.-F. Li, *J. Colloid Interface Sci.*, 2012, **380**, 83; (b) Y. Yang, J.-F. Dong, B. Cai, Z. Jiang, L. Cheng and X.-F. Li, *Soft Matter*, 2013, **9**, 1458; (c) T. S. Davies, A. M. Ketner and S. R. Raghavan, *J. Am. Chem. Soc.*, 2006, **128**, 6669; (d) Y.-Y. Lin, X. Han, J.-B. Huang, H.-L. Fu and C.-L. Yu, *J. Colloid Interface Sci.*, 2009, **330**, 449.
- (a) H. Sakai, Y. Orihara, H. Kodashima, A. Matsumura, T. Ohkubo, K. Tsuchiya and M. Abe, *J. Am. Chem. Soc.*, 2005, **127**, 13454; (b) A. M. Ketner, R. Kumar, T. S. Davies, P. W. Elder and S. R. Raghavan, *J. Am. Chem. Soc.*, 2007, **129**, 1553; (c) J. Eastoe and A. Vesperinas, *Soft Matter*, 2005, **1**, 338; (d) Y.-C. Lu, T.-F. Zhou, Q. Fan, J.-F. Dong and X.-F. Li, *J. Colloid Interface Sci.*, 2013, **412**, 107.
- Z. Jiang, X.-F. Li, G.-Y. Yang, L. Cheng, B. Cai, Y. Yang and J.-F. Dong, *Langmuir*, 2012, **28**, 7174.
- C. Wang, Q. Chen, F. Sun, D.-Q. Zhang, G.-X. Zhang, Y.-Y. Huang, R. Zhao and D.-B. Zhu, *J. Am. Chem. Soc.*, 2010, **132**, 3092.
- J. N. Israelachvili, *Intermolecular and surfaces Forces*, Academic Press, London, 2nd edn, 1992.