# LANGMUIR

Article

Subscriber access provided by La Trobe University Library

### Photo-Responsive Self-Assembly of Surface Active Ionic Liquid

Aoli Wu, Fei Lu, Panpan Sun, Xinpei Gao, Lijuan Shi, and Li-Qiang Zheng Langmuir, Just Accepted Manuscript • DOI: 10.1021/acs.langmuir.6b01937 • Publication Date (Web): 22 Jul 2016 Downloaded from http://pubs.acs.org on July 22, 2016

#### **Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Langmuir is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

## Photo-Responsive Self-Assembly of Surface Active Ionic Liquid

Aoli Wu,<sup>†</sup> Fei Lu,<sup>†</sup> Panpan Sun,<sup>†</sup> Xinpei Gao,<sup>†</sup> Lijuan Shi,<sup>‡</sup> Liqiang Zheng<sup>\*†</sup>

<sup>†</sup>Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China

<sup>‡</sup>Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China

ABSTRACT: A novel photo-responsive surface active ionic liquid (SAIL) 1-(4-methyl azobenzene)-3-tetradecylimidazolium bromide ([ $C_{14}$ mimAzo]Br) with azobenzene located in the head group was designed. Reversible vesicle formation and rupture can be finely controlled by photo stimuli without any additives in the aqueous solution of the single-tailed ionic liquid. The photoisomerization of the azobenzene derivative was investigated by <sup>1</sup>H NMR and UV-vis spectroscopy. Density functional theory (DFT) calculations further demonstrate that *trans*-[ $C_{14}$ mimAzo]Br has less negative interaction energy, which is beneficial to aggregate formation in water. The incorporation of *trans*-azobenzene group increases the hydrophobicity of head group and reduces the electrostatic repulsion by delocalization of charge, which are beneficial to the formation of vesicles. However, the bend of *cis*-azobenzene makes the *cis*-isomers have no ability to accumulate tightly, which induces the rupture of

vesicles. Our work paves a convenient way to achieve controlled topologies and self-assembly of single SAIL.

#### **1. INTRODUCTION**

Amphiphiles with specific functional groups is crucial to achieve rich hierarchically complex architectures by controllable self-assembly. Systems with controllable responsivity are potential candidates in catalysis, drug delivery, biosensors, and diagnostics.<sup>1-4</sup> Amphiphilicity of the well-organized structures can be tuned by external stimulus such as temperature,<sup>5</sup> CO<sub>2</sub>,<sup>6</sup> redox reagent,<sup>7</sup> salinity,<sup>8</sup> enzyme<sup>9</sup> as well as combined stimuli.<sup>10,11</sup> In particular, light is easy to obtain and can be precisely manipulated in a clean environment without pollution to system, which makes it more competitive as an ideal external stimulus to modulate molecular self-assembly at nanoscale or macroscopic scale.<sup>12-14</sup> Photo-induced isomerization of the molecules might trigger the re-arrangement of the building blocks to bring about morphological transitions, which have been considered as promising photo-responsive materials.

The most common light-responsive systems contain phenylazosulfonate, stilbene, cinnamate or azobenzene.<sup>15,16</sup> Compounds containing azobenzene usually show higher medium sensitivity. Moerover, they are capable of undergoing reversible *trans-cis* transition under UV and visible light irradiation, and widely applied in drug delivery,<sup>17</sup> nanomaterials,<sup>18</sup> catalysis,<sup>19</sup> biochemical engineering<sup>20</sup> and commodity field.<sup>21</sup> Up to now, controlled self-assembly systems, such as solutions,<sup>22,23</sup> liquid crystals,<sup>24</sup> gels,<sup>25</sup> and solids<sup>26,27</sup> formed by amphiphiles with azobenzene groups, have been successfully constructed. Huang et al. have investigated a light-active

#### Langmuir

self-assembled system, consisting of azobenzene derivative sodium (4-phenylazo-phenoxy)-acetate (AzoNa) and conventional surfactant CTAB.<sup>28</sup> The mixture of AzoNa and CTAB can exhibit wormlike micelles, vesicles, lamellar structure and small micelles in aqueous solution depending on illumination time. Photo-responsive amphiphiles consisted of oligooxyethylene, alkyl chain and azobenzene which located in the hydrophobic tail have been designed by Hughes and coworkers.<sup>29</sup> The lyotropic liquid crystal phase can be significantly changed by photoisomerization. Because of the hydrophobicity, azobenzene is often used as an additive or as hydrophobic chain. The complex systems will always introduce inorganic salts, which is not conducive to understand the weak interactions responsible for aggregate formation. Putting the azobenzene in the hydrophilic head group may be an alternative pathway to tune their aggregation behavior, so as to provide a versatile platform to fabricate novel controllable self-assembly materials.

The self-assembled aggregates based on ionic liquids (ILs) have attracted increasing attentions during the last ten years due to their extraordinary properties, such as negligible vapor pressure, low melting point, large electrochemical window and thermal stability.<sup>30,31</sup> Ionic liquids with long alkyl chains are regarded as amphiphiles named as surface active ionic liquids (SAILs), which combine the properties of ILs and surfactants.<sup>32-35</sup> SAILs can self-assemble into a rich variety of hierarchically complex architectures with controllable functions depending on the structure of SAILs and the composition of solution.<sup>36-39</sup> Based on the designability of SAILs, it will be expected to achieve the functionalization of self-assembled aggregates by

tailoring the structures of SAILs.

Herein, we designed a photo-responsive SAIL 1-(4-methyl azobenzene)-3-tetradecylimidazolium bromide ( $[C_{14}mimAzo]Br$ ) with azobenzene located in the head group (Scheme 1). The incorporation of azobenzene group has a significant influence on the surface activity and aggregate structures. Before UV irradiation, two kinds of aggregates, micelles and vesicles, can be observed in  $[C_{14}mimAzo]Br$  aqueous solution with increasing concentration. After UV irradiation, *trans-cis* photoisomerization of azobenzene in the headgroup induces the rupture of vesicles. Significantly, the rapid and reversible responses of the single SAIL open a door to new fields for special applications.



Scheme 1. Chemical structure and *trans-cis* photoisomerization of [C<sub>14</sub>mimAzo]Br

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** Nitrosobenzene (98%), p-toluidine (99%), 1-bromotetradecane (98%), imidazole (99%), *N*-bromosuccinimide (99%) and benzoyl peroxide (98%) were purchased from J&K Scientific Ltd. Glacial acetic acid, ethanol, petroleum ether,

#### Langmuir

ethyl acetate, tetrahydrofuran, dichloromethane, tetrachloromethane, methanol and sodium hydroxide were purchased from Shanghai Chemical Co. All the above materials were used without further purification. Ultra-pure water was used throughout the whole experiment.

#### 2.2. Synthesis of [C<sub>14</sub>mimAzo]Br.

Synthesis of 1-tetradecylimidazole (1).<sup>40</sup>

Imidazole (2.16 g), NaOH (1.38 g) and ultra-pure water (1.38 mL) was added to a neck round bottom flask. 1-Bromotetradecane (8 g) was dissolved in THF and added dropwise into the above mixture. The system was refluxed for 3 days. After that, THF was removed by rotary evaporation. The crude product was extracted three times with  $CH_2Cl_2/H_2O$ . The organic layer was concentrated dried under vacuum to obtain white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.86-0.90 (t, 3H), 1.25-1.30 (m, 22H), 1.74-1.81 (m, 2H), 3.89-3.94 (m, 2H), 6.90 (s, 1H), 7.05 (s, 1H), 7.45 (s, 1H).

Synthesis of 4-methylazobenzene (2).<sup>41</sup>

Nitrosobenzene (3 g, 27.8 mmol) and p-toluidine (3 g, 27.8 mmol) were dissolved in 50 mL glacial acetic acid. The mixture was stirred in a round bottom flask under an atmosphere of nitrogen for 24 h at room temperature. After removing the solvent by a rotary evaporator, the resulting solid was recrystallized from EtOH/H<sub>2</sub>O for three times, followed by purification by column chromatography (petroleum ether and ethyl acetate). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 2.44 (s, 3H), 7.26-7.33 (m, 2H), 7.45-7.54 (m, 3H), 7.82-7.85 (m, 2H), 7.89-7.92 (m, 2H).

Synthesis of 4-(bromomethyl)azobenzene (3).<sup>41</sup>

4-Methylazobenzene (0.81 g), *N*-bromosuccinimide (NBS 0.73 g) and benzoyl peroxide (BPO 0.014 g) were dissolved in 24 mL CCl<sub>4</sub>. The mixture was refluxed for 24 h under a nitrogen atmosphere. After completion of the reaction, the solution was filtrated. The filtrate was removed by a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether and ethyl acetate). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 4.56 (s, 2H), 7.48-7.56 (m, 5H), 7.88-7.94 (m, 4H).

Synthesis of  $[C_{14}mimAzo]Br (4)$ .

4-(Bromomethyl)azobenzene (0.87 g) and 1-tetradecylimidazole (0.84 g) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred under a nitrogen atmosphere for 24 h at room temperature. The CH<sub>2</sub>Cl<sub>2</sub> was removed by rotary evaporated, and the product was purified by silica gel column chromatography (dichloromethane and methanol). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.86-0.89 (t, 3H), 1.24-1.32 (m, 22H), 1.91-1.94 (m, 2H), 4.27-4.31 (t, 2H), 5.78 (s, 1H), 7.21-7.29 (m, 2H), 7.50-7.52 (m, 3H), 7.67-7.69 (m, 2H), 7.90-7.93 (m, 4H).



Scheme 2. Preparation of [C<sub>14</sub>mimAzo]Br.

**2.3. Photoisomeric Experiments.** In order to achieve *trans-cis* transition, the samples in quartz tube were irradiated with a LUYOR-3109 UV light until it reached the maximum degree of conversion. This experiment was performed at 35 °C. After photoisomerization, all the samples were wrapped with aluminum foil to prevent the transformation from *cis* to *tans*.

#### 2.4. Characterizations.

*UV-vis Spectroscopy.* The UV-vis spectroscopy measurements of 0.1 mM aqueous solutions before and after different UV irradiation time were carried out on a UV-4100 spectrophotometer. The ultra-pure water was utilized as a blank in the experiments.

<sup>1</sup>*H NMR Measurements.* <sup>1</sup>*H NMR spectra were recorded on a Bruker AM-400* spectrometer equipped with a pulse field gradient module (Z axis). The samples were placed in a 5 mm BBO probe and dissolved in CDCl<sub>3</sub>.

*Surface Tension.* Surface tension measurements were determined by Model JYM-200B tensiometer (accuracy  $\pm$  0.1 mN/m) using the ring method. Temperature was controlled at 35  $\pm$  0.1 °C using a thermostatic bath. The platinum ring was washed with ultra-pure water and cleaned thoroughly by heating through flame till red hot. All measurements were repeated until the values were reproducible.

*Electrical Conductivity.* Electrical conductivity measurements were carried out on a low-frequency conductivity analyzer (model DDS-307. Shanghai Precision & Scientific Instrument Co., Ltd., accuracy  $\pm$  1%). The thermostatic bath was also used to control the temperature at 35  $\pm$  0.1 °C.

*Dynamic Light Scattering.* The size distributions of the aggregates at different conditions were employed using a dynamic light scattering (DLS; DynaPro NanoStar, Wyatt Instrument Co.) with an argon-ion laser operating at 658 nm. All samples were properly filtered through 0.45 µm filters prior to measurements.

*Cryo-TEM.* A pipette was used to load a small drop of sample on a copper grid, and a thin film was produced by blotting off the redundant liquid with two pieces of filter papers. This thin film was then quickly plunged into liquid ethane, which was cooled by liquid nitrogen. Observation of the sample was carried out at -183 °C.

#### 3. RESULTS AND DISCUSSION

#### **3.1.** Photoisomerization of [C<sub>14</sub>mimAzo]Br.

The synthesized SAIL may undergo *trans-cis* transition depending on the wavelength of incident light. The photoisomerization in Scheme 1 suggests that the area of the head group will be significantly altered by the isomerization of the N=N double bond, leading to the change of critical packing parameter.<sup>16</sup> At the same time, *trans*-azobenzene has no dipole moment while the dipole moment of the *cis*-compound is 3.0 D.<sup>42</sup> That is, the hydrophilic-lipophile balance of [C<sub>14</sub>mimAzo]Br can be adjusted by UV and visible light.

The *trans-cis* transition of  $[C_{14}mimAzo]Br$  can be confirmed by UV-vis spectroscopy. Figure 1a shows the absorbance spectra of 0.1 mM  $[C_{14}mimAzo]Br$  aqueous solution irradiated by UV light for different times. Before UV irradiation, the strong absorption band at 320 nm is ascribed to the  $\pi$ - $\pi$ \* transition of *trans*- $[C_{14}mimAzo]Br$ . UV stimulus give rise to a remarkable decrease in intensity and an obvious blue shift of

the absorption peak at 320 nm. Concomitantly, a slight increase of a band located at about 425 nm is observed, which can be ascribed to the  $n-\pi^*$  bands of the *cis*-isomer. After irradiation for 5 minutes, the *trans-cis* photoisomerization has been completely finished and longer irradiation time causes no change in the UV-vis spectra. The *trans*-[C<sub>14</sub>mimAzo]Br can be obtained again when the irradiated sample is then treated with visible light. The *trans/cis* photoisomerization of the synthesized SAIL can be repeated many times without decomposition of the components (Figure 1b). It is anticipated that [C<sub>14</sub>mimAzo]Br can be used in photo-responsive molecular self-assembly.



**Figure 1.** (a) UV-vis absorption spectra of an aqueous  $[C_{14}mimAzo]Br$  solution (0.1 mM) at different times of UV-light irradiation; (b) the absorbance at 320 nm of  $[C_{14}mimAzo]Br$  solution by alternate irradiation at UV and visible light, respectively.

<sup>1</sup>H NMR technique is also used to confirm the *trans-cis* photoisomerization. As shown in the <sup>1</sup>H NMR spectra (Figure 2), discernible proton signals undergo obvious changes upon UV irradiation. Because of the significant shielding effect caused by the  $\pi$ - $\pi$  conjugation of the azobenzene group and magnetically anisotropic effect caused by the change of polarity, UV irradiation results in an upfield shift of attached protons

on *cis*-[C<sub>14</sub>mimAzo]Br compared with the *trans*-isomer.<sup>43,44</sup> As calculated from the <sup>1</sup>H NMR spectrum of aromatic protons, almost all of the compounds are *trans*-isomer before UV irradiation (Figure 2a). After UV lamp treatment over 30 minutes, the percentage of *trans*-isomer is reduced to 39% while the *cis*-form is increased to 61% (Figure 2b). Complete conversion cannot be achieved even irradiated by UV light for longer time.



**Figure 2.** <sup>1</sup>H NMR spectra of  $[C_{14}mimAzo]Br$  in CDCl<sub>3</sub> (a) before and (b) after UV-light irradiation

# **3.2.** Photo-responsible variation in surface properties and micellization parameters

The aggregation behaviors of  $[C_{14}mimAzo]Br$  before and after UV irradiation are investigated by surface tension and conductivity measurements at 35 °C. Figure 3 shows the surface tension ( $\gamma$ ) curves as a function of the  $[C_{14}mimAzo]Br$ concentration. The appearance of break point indicates certain kinds of self-assembled aggregates begin to be formed in the solution at the concentration of the transition

point. It is intriguing to find that there are two plateaus in the plots of  $[C_{14}mimAzo]Br$  before UV irradiation. This phenomenon is also described in other literatures.<sup>45-48</sup> The two critical aggregate concentrations denoted as cac<sub>1</sub> and cac<sub>2</sub> suggest that two kinds of self-assembled aggregates are formed with increasing concentrations. Interestingly, the dual-platform in the  $\gamma$ -*C* curve disappears after UV irradiation. This phenomenon indicates the presence of only one kind of aggregates.



**Figure 3.** Plots of the surface tension of  $[C_{14}mimAzo]Br$  aqueous solution as a function of  $[C_{14}mimAzo]Br$  concentration at 35 °C

The cac values of the two isomeric  $[C_{14}mimAzo]Br$  are further investigated by conductivity measurement. Electrical conductivity curves of  $[C_{14}mimAzo]Br$  aqueous solution with different concentrations at 35 °C are depicted in Figure 4. For the *trans*- $[C_{14}mimAzo]Br$ , the conductivity profiles fit into three straight lines with different slops originating from different aggregates. After irradiated by UV light, the

conductivity profiles of the same solution exhibit only two straight lines. The result obtained by this technology is consistent with the surface tension method.



**Figure 4.** Plot of conductivity against the concentration of  $[C_{14}mimAzo]Br$  aqueous solutions at 35 °C (a) before and (b) after UV irradiation

The values of A and  $\Gamma$  can reflect the arrangement of SAIL molecule at the air/liquid interface. By utilizing the Gibbs adsorption isotherm to the surface tension versus concentration plot, the amount of adsorbed molecules ( $\Gamma$ ) at the air/solution interface and the interfacial area (A) occupied by a SAIL molecule are calculated as follows:<sup>49,50</sup>

$$\Gamma = -\frac{1}{nRT} \left( \frac{\partial \gamma}{\partial lnC} \right)_{T} (mmol/m^2)$$
(1)

$$A = \frac{1}{N_A \cdot \Gamma} \left( \times 10^{23} \text{\AA}^2 \right) \tag{2}$$

where R represents the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>), T (K) is the absolute temperature of the test,  $\gamma$  is the surface tension (mN·m<sup>-1</sup>), C refers to the surfactant concentration (mol·L<sup>-1</sup>),  $\partial \gamma / \partial \ln C$  is the slope of the  $\gamma$  versus lnC curve when the concentration is near cac, and N<sub>A</sub> is Avogadro's number (6.022×10<sup>23</sup> mol<sup>-1</sup>). Before UV irradiation, almost all of the molecules are *trans*-isomer. The prefactor n is 1. While after UV light treatment, the coexist of the *trans*- and *cis*-isomers indicates that

#### Langmuir

there are two kinds of molecules in solution. So, the value of n is taken as 2.<sup>51,52</sup>

The cac values obtained by surface tension and conductivity methods and micellization parameters are listed in Table 1, together with the data for 1-tetradecyl-3-methylimidazolium bromide (C<sub>14</sub>mimBr) obtained from reference.<sup>53</sup> As shown in Table 1, the cac<sub>1</sub> for *trans*-[C<sub>14</sub>mimAzo]Br is only 0.028 mM, which is much lower than C<sub>14</sub>mimBr, indicating that the incorporation of hydrophobic azobenzene group favors the micellization. The main reason is that the electrostatic repulsion among the imidazolium cations can be significantly reduced due to the delocalization of charge and the  $\pi$ - $\pi$  stacking interaction between azobenzene. The hydrophilicity of the *cis*-isomer<sup>28,54</sup> and the curved structure are not conducive to the molecule aggregation. Consequently, the cac value of *cis*-[C<sub>14</sub>mimAzo]Br is higher than the *trans*-form.

It is well demonstrated that the size of hydrophilic head group plays an important role in the values of A and  $\Gamma$ .<sup>53</sup> Both of the two forms of isomers have significantly larger  $\Gamma$  value and smaller A value than C<sub>14</sub>mimBr indicating a tighter arrangement of synthesized SAIL. This result is due to the decreased electrostatic repulsion among imidazolium cations and enhanced  $\pi$ - $\pi$  stacking interaction caused by two phenyl rings. Furthermore, the photoisomerization of azobenzene significantly alter the micellization parameters and aggregation behavior of [C<sub>14</sub>mimAzo]Br in aqueous solution. From Table 1, it can be found that, 0.15 mM aqueous solution of *cis*-[C<sub>14</sub>mimAzo]Br has a significantly smaller  $\Gamma$  value and a correspondingly larger A than *trans*-[C<sub>14</sub>mimAzo]Br. It is likely that, the bend of azobenzene increases the area

of head group. The change of hydrophobicity and polarity can also influence the surface properties and micellization parameters.<sup>46</sup>

Table 1. Surface properties and micellization parameters of [C<sub>14</sub>mimAzo]Br and

SAIL		cac (mM)			Г	٨	
		surface	conductivity	$\gamma_{\rm cmc}$ (mN·m <sup>-1</sup> )	$(\text{mmol}\cdot\text{m}^{-2})$	$(\text{Å}^2)$	Р
		tension					
trans-	$cac_1$	0.028	0.032	44.11	0.0036	43.22	0.46
[C14mimAzo]Br	$cac_2$	0.070	0.085	36.85	0.0062	26.98	0.78
cis-[C14mimAzo]Br		0.090	0.100	37.50	0.0029	79.45	0.26
C <sub>14</sub> mimBr		2.8	2.6	39.2	0.00196	84.7	/

C<sub>14</sub>mimBr in aqueous solution

#### 3.3. Photo-responsible variation in the self-assembly of [C<sub>14</sub>mimAzo]Br

DLS is utilized to observe the variation of aggregate size of the aqueous  $[C_{14}mimAzo]Br$  solution upon UV irradiation. The size distributions under different irradiation conditions are shown in Figure 5. Aggregate size of 30 nm was observed when the concentration of *trans*- $[C_{14}mimAzo]Br$  is 0.05 mM. When the concentration of *trans*- $[C_{14}mimAzo]Br$  is 0.05 mM. When the concentration of *trans*- $[C_{14}mimAzo]Br$  increases to 0.15 mM, the size of the aggregates increases significantly to 250 nm. This great change in aggregate sizes can be proposed to a transformation from micelles to vesicles. After UV lamp treatment, the aggregate size of 0.15 mM solution decreases to 25 nm which indicates a manifest structural transition. Of great interest, aggregate size at about 150 nm can be obtained again followed by visible light exposure. This phenomenon indicates that transformation between different aggregates is reversible.



**Figure 5.** Size distributions of [C<sub>14</sub>mimAzo]Br aqueous solutions.

Cryo-TEM was applied to confirm the above proposal. As shown in Figure 6a, spherical micelles are formed in 0.05 mM aqueous solution. When the concentration is increased to 0.15 mM, unilamellar and mutilamellar vesicles with diameters from about 50 to 500 nm can be observed in Figure 6b. As marked in the chart, the vesicles with a mean thickness of 3.2 nm are obtained. After UV irradiation to this system, vesicles are ruptured and then transformed into spherical micelles (Figure 6c). More importantly, vesicles can be re-formed after visible light irradiation (Figure 6d). This is consistent with the DLS results above. It can be concluded that the [C<sub>14</sub>mimAzo]Br system experiences a phase transition from vesicles to micelles after UV and visible light irradiation. This phenomenon indicates that both of concentration and UV treatment play important roles in controlling the size and morphology of aggregates.



**Figure 6.** Cryo-TEM images of 0.05 mM [ $C_{14}$ mimAzo]Br solution before UV irradiation (a), 0.15 mM before (b) and after (c) UV irradiation and 0.15 mM after UV irradiation followed by visible light exposure (d).

#### 3.4. Mechanism of photo-responsive aggregates transformation

Density functional theory (DFT) calculation can be used to understand the interaction of SAIL with water and further comprehend the aggregates transformation mechanism. Gaussian 09 package with the hybrid B3LYP functional and the 6-31G (d,p) basis set were performed. Figure 7 shows the optimized structures of the two binary complex systems (*trans*- and *cis*-[C<sub>14</sub>mimAzo]Br with water). Their interaction energies (E<sub>int</sub>) The are listed in Table 2. calculated interaction energy of the *trans*- $[C_{14}mimAzo]Br/H_2O$  complex is smaller than that of *cis*- $[C_{14}mimAzo]Br/H_2O$ , indicating that the *trans*-[C<sub>14</sub>mimAzo]Br is more readily to form aggregates in water.<sup>55,56</sup> This result is in agreement with the surface tension result. The length of

single *trans/cis*-[C<sub>14</sub>mimAzo]Br molecule are also evaluated as 21.2 Å and 21.1 Å





**Figure 7.** B3LYP/6-31G(d,p)-optimized structures: (a) *trans*-[C<sub>14</sub>mimAzo]Br, (b) *cis*-[C<sub>14</sub>mimAzo]Br. Color code for atoms: dark gray, carbon; light gray, hydrogen; blue, nitrogen; red, oxygen.

Table 2. Interaction energy (-E<sub>int</sub>) of SAIL with H<sub>2</sub>O

complex system	trans-[C14mimAzo]Br	cis-[C14mimAzo]Br
interaction energy (-E <sub>int</sub> /kJ·mol)	167.832	173.292

To propose the mechanism of phase transition, critical packing parameter (P) values are calculated according to the surface tension-concentration curve, and the results are also displayed in Table 1. The calculation of P is described as P=V/AL, where V represents the effective hydrophobic chain volume, A represents the effective head group area, and L is the alkyl chain length of SAIL. The values of L and V can be estimated as follows:<sup>57</sup>

$$L = 1.5 + 1.265N$$
(3)

$$V_{\rm L}({\rm \AA}^3) = 27.4 + 26.9 {\rm N} \tag{4}$$

where N is the number of carbon atoms in the hydrophobic chain. The calculation of P for the prediction of the aggregates is still valid to the novel SAIL systems. According to the molecular packing parameter theory, the self-assembly structures of the SAILs are predicted as micelles, vesicles and micelles respectively according to obtained values (Table 1). The results are in agreement with above test.

The reasons for the vesicle formation and rupture of the synthesized SAIL at different conditions can be explained as follows. Before UV irradiation, all the molecules are trans-isomer, and the formation of micelles can be observed. The incorporation of azobenzene group, on one hand, could increase the steric hindrance between molecules due to the large size of the head group. On the other hand, the charge delocalization caused by azobenzene could reduce the electron density and induce the molecules to pack more compactly and then reduce the adverse effects of steric hindrance to aggregation. More importantly, the hydrophobicity of the trans-azobenzene makes the configuration of the head group more appropriate to fit the critical packing parameter required for micelle formation.<sup>58</sup> Our group has a similar result about a long-chain N-aryl imidazolium bromide incorporated by a 2,4,6-trimethylphenyl group.<sup>59</sup> Due to the stronger hydrophobic interaction between the alkyl chains and lower polarity of the azobenzene group, the expressions of molecules give the chance of vesicle formation.<sup>46</sup> The thickness of vesicle is smaller than a bi-molecular length of  $[C_{14}minAzo]Br (4,2 nm)$ , which indicates an overlap among the hydrophobic chains during the formation of vesicles according to the well-established theory of vesicle formation.<sup>14</sup> The azobenzene is hid in the

membrane of the vesicle to avoid exposing in water while the imidazole contact with water. When a part of the *trans*-forms are transformed into more hydrophilic *cis*-forms under UV light, the curvature of the head group increases the A value threefold. Therefore, the obtained P value indicates that this is not conducive to the formation of vesicles. The steric hindrance caused by the bend of azobenzene makes the *cis*-isomers have no ability to accumulate tightly by weak  $\pi$ - $\pi$  staking interaction. Therefore, it is anticipated that the variation of structure will cause a significant reorganization of the SAIL aggregates. Based on the analysis above, the possible accumulation mode of molecules and the transition between different aggregates are described in Scheme 3.



Scheme 3. Schematic illustration of the proposed packing structures of aggregates formed by  $[C_{14}mimAzo]Br$  and the aggregates transition under different conditions.

#### 4. CONCLUSIONS

In conclusion, photo-controllable self-assembly based on SAIL with azobenzene located in the head group was achieved. The cac obtained for  $[C_{14}mimAzo]Br$  is much lower than that for  $C_{14}mimBr$ , suggesting that the delocalization of charge caused by azobenzene group reduces the electron density of head-group and facilitates the

formation of vesicles. The *trans-cis* transition of the azobenzene can be manipulated by external light signal without any pollution to the system. The change in geometry and dipole moment of head-group in  $[C_{14}mimAzo]Br$  influence the critical packing parameters and hydrophilic-hydrophobic balance and leads to reversible transition between vesicles and micelles in the absence of additives. We believe that this work can help to achieve the controllability of self-assembled structures by external stimulus, which is benefit for the application of responsive materials.

#### AUTHOR INFORMATION

#### **Corresponding Author**

E-mail: lqzheng@sdu.edu.cn. Phone: +86-531-88366062. Fax: +86-531-88564750.

#### Notes

Any additional relevant notes should be placed here

#### ACKNOWLEDGEMENTS

The authors are grateful to the National Basic Research Program (2013CB834505), the National Natural Science Foundation of China (no. 21573132), and the National Natural Science Foundation of China (no. 21403151) for financial support.

#### REFERENCES

 Ma, Y.; Zhou, M.; Walter, S.; Liang, J.; Chen, Z.; Wu, L. Selective Adhesion and Controlled Activity of Yeast Cells on Honeycomb-Patterned Polymer Films *via* a Microemulsion Approach. *Chem. Commun.* 2014, *50*, 15882-15885.

#### Langmuir

- Qin, S.; Geng, Y.; Discher, D. E.; Yang, S. Temperature-Controlled Assembly and Release from Polymer Vesicles of Poly(ethylene oxide)-*block*-poly(*N*-isopropylacrylamide). *Adv. Mater.* 2006, *18*, 2905-2909.
- (3) Sun, Y.; Yang, Y.; Chen, D.; Wang, G.; Zhou, Y.; Wang, C.; Stoddart, J. F. Mechanized Silica Nanoparticles Based on Pillar[5]arenes for On-Command Cargo Release. *Small* **2013**, *9*, 3224-3229.
- (4) Chen, S.; Ruan, Y.; Brown, J. D.; Gallucci, J.; Maslak, V.; Hadad, C. M.; Badjić, J. D. Assembly of Amphiphilic Baskets into Stimuli-Responsive Vesicles. Developing a Strategy for the Detection of Organophosphorus Chemical Nerve Agents. J. Am. Chem. Soc. 2013, 135, 14964-14967.
- (5) Li, M.; Bresson, B.; Cousin, F.; Fretigny, C.; Tran, Y. Submicrometric Films of Surface-Attached Polymer Network with Temperature-Responsive Properties. *Langmuir* 2015, , 11516-11524.
- (6) Zhang, Y.; Feng, Y.; Wang, Y.; Li, X. CO<sub>2</sub>-Switchable Viscoelastic Fluids Based on a Pseudogemini Surfactant. *Langmuir* 2013, 29, 4187-4192.
- (7) Nakahata, M.; Takashima, Y.; Yamaguchi, H.; Harada, A. Redox-Responsive Self-Healing Materials Formed from Host-Guest Polymers. *Nat. Commun.* 2011, 2, 511-516.
- (8) Yan, Y.; Xiong, W.; Li, X.; Lu, T.; Huang, J.; Li, Z.; Fu, H. Molecular Packing Parameter in Bolaamphiphile Solutions: Adjustment of Aggregate Morphology by Modifying the Solution Conditions. *J. Phys. Chem. B* 2007, *111*, 2225-2230.
- (9) Guo, D.; Zhang, T.; Wang, Y.; Liu, Y. Enzyme-Responsive Supramolecular

Polymers by Complexation of Bis(p-sulfonatocalixarenes) with Suberyl Dicholine-Based Pseudorotaxane. *Chem. Commun.* **2013**, *49*, 6779-6781.

- (10) Wang, D.; Long, P.; Dong, R.; Hao, J. Self-Assembly in the Mixtures of Surfactant and Dye Molecule Controlled *via* Temperature and β-Cyclodextrin Recognition. *Langmuir* 2012, 28, 14155-14163.
- (11) Yang, R.; Peng, S.; Wan, W.; Hughes, T. C. Azobenzene Based Multistimuli Responsive Supramolecular Hydrogels. *J. Mater. Chem. C* **2014**, *2*, 9122-9131.
- (12) Xia, D.; Yu, G.; Li, J.; Huang, F. Photo-Responsive Self-Assembly Based on a Water-Soluble Pillar[6]arene and an Azobenzene-Containing Amphiphile in Water. *Chem. Commun.* 2014, *50*, 3606-3608.
- (13) Xing, P.; Chen, H.; Ma, M.; Xu, X.; Hao, A.; Zhao, Y. Light and Cucurbit[7]uril Complexation Dual-Responsiveness of a Cyanostilbene-Based Self-Assembled System. *Nanoscale* **2016**, *8*, 1892-1896.
- (14) Wang, C.; Chen, Q.; Xu, H.; Wang, Z.; Zhang, X.: Photoresponsive Supramolecular Amphiphiles for Controlled Self-Assembly of Nanofibers and Vesicles. *Adv. Mater.* 2010, *22*, 2553-2555.
- (15) Eastoe, J.; Vesperinas, A. Self-Assembly of Light-Sensitive Surfactants. *Soft Matter* 2005, *1*, 338-347.
- (16) Faure, D.; Gravier, J.; Labrot, T.; Desbat, B.; Oda, R.; Bassani, D. M. Photoinduced Morphism of Gemini Surfactant Aggregates. *Chem. Commun.* 2005, 1167-1169.
- (17) Luo, G.; Chen, W.; Jia, H.; Sun, Y.; Cheng, H.; Zhuo, R.; Zhang, X. An

#### Langmuir

2		
3 4		Indicator-Gu
5 6 7		Silica/Gold 1
8 9	(18)	Lysyakova, I
10 11 12		S. Light
13 14		Nanoparticle
15 16 17		Chem. C 201
18 19	(19)	Wang, J.; Hu
20 21 22		Generated in
23 24		from Nitroar
25 26 27	(20)	Diguet, A.;
28 29		UV-Induced
30 31 32		Photosensitiv
33 34	(21)	Chevallier, E
35 36 37		of Foam Des
38 39		Langmuir 20
40 41 42	(22)	Bi, Y.; Wei,
43 44		Photorespon
45 46 47		Liquid/Azob
48 49	(23)	Eastoe, J.; Z
50 51 52		Phases. Soft
53 54	(24)	Fang, G.; Sł
55 56		Photo-Rever
57 58 59		
60		

idicator-Guided Photo-Controlled Drug Delivery System Based on Mesoporous ilica/Gold Nanocomposites. *Nano Res.* **2015**, *8*, 1893-1905.

- Lysyakova, L.; Lomadze, N.; Neher, D.; Maximova, K.; Kabashin, A. V.; Santer,
   S. Light-Tunable Plasmonic Nanoarchitectures Using Gold Nanoparticle-Azobenzene-Containing Cationic Surfactant Complexes. J. Phys. Chem. C 2015, 119, 3762-3770.
- (19) Wang, J.; Hu, L.; Cao, X.; Lu, J.; Li, X.; Gu, H. Catalysis by Pd Nanoclusters Generated in *situ* of High-Efficiency Synthesis of Aromatic Azo Compounds from Nitroaromatics under H<sub>2</sub> Atmosphere. *RSC Adv.* **2013**, *3*, 4899-4902.
- (20) Diguet, A.; Yanagisawa, M.; Liu, Y.; Brun, E.; Abadie, S.; Rudiuk, S.; Baigl, D.
  UV-Induced Bursting of Cell-Sized Multicomponent Lipid Vesicles in a Photosensitive Surfactant Solution. J. Am. Chem. Soc. 2012, 134, 4898-4904.
- (21) Chevallier, E.; Monteux, C.; Lequeux, F.; Tribet, C. Photofoams: Remote Control of Foam Destabilization by Exposure to Light Using an Azobenzene Surfactant. *Langmuir* 2012, 28, 2308-2312.
- (22) Bi, Y.; Wei, H.; Hu, Q.; Xu, W.; Gong, Y.; Yu, L. Wormlike Micelles with Photoresponsive Viscoelastic Behavior Formed by Surface Active Ionic Liquid/Azobenzene Derivative Mixed Solution. *Langmuir* 2015, *31*, 3789-3798.
- (23) Eastoe, J.; Zou, A.; Espidel, Y.; Glatter, O.; Grillo, I. Photo-Labile Lamellar Phases. *Soft Matter* **2008**, *4*, 1215-1218.
- (24) Fang, G.; Shi, Y.; Maclennan, J. E.; Clark, N. A.; Farrow, M. J.; Walba, D. M. Photo-Reversible Liquid Crystal Alignment Using Azobenzene-Based

Self-Assembled Monolayers: Comparison of the Bare Monolayer and Liquid Crystal Reorientation Dynamics. *Langmuir* **2010**, *26*, 17482-17488.

- (25) Zakrevskyy, Y.; Richter, M.; Zakrevska, S.; Lomadze, N.; von Klitzing, R.; Santer, S. Light-Controlled Reversible Manipulation of Microgel Particle Size Using Azobenzene-Containing Surfactant. *Adv. Funct. Mater.* 2012, *22*, 5000-5009.
- (26) Chakraborty, S.; Rajput, L.; Desiraju, G. R. Designing Ternary Co-Crystals with Stacking Interactions and Weak Hydrogen Bonds. 4,4'-Bis-hydroxyazobenzene. *Cryst. Growth Des.* **2014**, *14*, 2571-2577.
- (27) Chevallier, E.; Monteux, C.; Lequeux, F.; Tribet, C. Photofoams: Remote Control of Foam Destabilization by Exposure to Light Using an Azobenzene Surfactant. *Langmuir* 2012, 28, 2308-2312.
- (28) Lin, Y.; Cheng, X.; Qiao, Y.; Yu, C.; Li, Z.; Yan, Y.; Huang, J. Creation of Photo-Modulated Multi-State and Multi-Scale Molecular Assemblies *via* Binary-State Molecular Switch. *Soft Matter* 2010, *6*, 902-908.
- (29) Peng, S.; Guo, Q.; Hartley, P. G.; Hughes, T. C. Azobenzene Moiety Variation Directing Self-Assembly and Photoresponsive Behavior of Azo-Surfactants. J. Mater. Chem. C 2014, 2, 8303-8312.
- (30) Giernoth, R. Task-Specific Ionic Liquids. Angew. Chem. Int. Ed. 2010, 49, 2834-2839.
- (31) Dandpat, S. S.; Sarkar, M. Investigating the Molecular and Aggregated States of
  - a Drug Molecule Rutaecarpine Using Spectroscopy, Microscopy,

Crystallography and Computational Studies. *Phys. Chem. Chem. Phys.* 2015, *17*, 13992-14002.

- (32) Singh, G.; Singh, G.; Kang, T. S. Micellization Behavior of Surface Active Ionic Liquids Having Aromatic Counterions in Aqueous Media. J. Phys. Chem. B 2016, 120, 1092-1105.
- (33) Brown, P.; Butts, C. P.; Eastoe, J.; Fermin, D.; Grillo, I.; Lee, H.-C.; Parker, D.;
  Plana, D.; Richardson, R. M. Anionic Surfactant Ionic Liquids with
  1-Butyl-3-methyl-imidazolium Cations: Characterization and Application. *Langmuir* 2012, 28, 2502-2509.
- (34) Mandal, S.; Kuchlyan, J.; Ghosh, S.; Banerjee, C.; Kundu, N.; Banik, D.; Sarkar,
  N. Vesicles Formed in Aqueous Mixtures of Cholesterol and Imidazolium Surface Active Ionic Liquid: a Comparison with Common Cationic Surfactant by Water Dynamics. J. Phys. Chem. B 2014, 118, 5913-5923.
- (35) Cognigni, A.; Gaertner, P.; Zirbs, R.; Peterlik, H.; Prochazka, K.; Schröder, C.;
  Bica, K. Surface-Active Ionic Liquids in Micellar Catalysis: Impact of Anion Selection on Reaction Rates in Nucleophilic Substitutions. *Phys. Chem. Chem. Phys.* 2016, 18, 13375-13384.
- (36) Xu, W.; Yin, Q.; Gao, Y.; Yu, L. Solvent and Substituent Effects on the Aggregation Behavior of Surface-Active Ionic Liquids with Aromatic Counterions and the Dispersion of Carbon Nanotubes in their Hexagonal Liquid Crystalline Phase. *Langmuir* **2015**, *31*, 12644-12652.
- (37) Mahajan, S.; Sharma, R.; Mahajan, R. K. An Investigation of Drug Binding

Ability of a Surface Active Ionic Liquid: Micellization, Electrochemical, and Spectroscopic Studies. *Langmuir* **2012**, *28*, 17238-17246.

- (38) Singh, T.; Drechsler, M.; Müeller, A. H. E.; Mukhopadhyay, I.; Kumar, A. Micellar Transitions in the Aqueous Solutions of a Surfactant-Like Ionic Liquid:
  1-Butyl-3-methylimidazolium Octylsulfate. *Phys. Chem. Chem. Phys.* 2010, *12*, 11728-11735.
- (39) Rao, V. G.; Mandal, S.; Ghosh, S.; Banerjee, C.; Sarkar, N. Ionic Liquid-in-Oil Microemulsions Composed of Double Chain Surface Active Ionic Liquid as a Surfactant: Temperature Dependent Solvent and Rotational Relaxation Dynamics of Coumarin-153 in [Py][TF2N]/[C4mim][AOT]/Benzene Microemulsions. J. Phys. Chem. B 2012, 116, 8210-8221.
- (40) Choi, U. H.; Lee, M.; Wang, S.; Liu, W.; Winey, K. I.; Gibson, H. W.; Colby, R. H. Ionic Conduction and Dielectric Response of Poly(imidazolium acrylate) Ionomers. *Macromolecules* 2012, *45*, 3974-3985.
- (41) Peng, L.; You, M.; Wu, C.; Han, D.; Öçsoy, I.; Chen, T.; Chen, Z.; Tan, W.
  Reversible Phase Transfer of Nanopar Ticles Based on Photoswitchable
  Host-Guest Chemistry. ACS Nano. 2014, 8, 2555-2561.
- (42) Dugave, C.; Demange, L. Cis-Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* 2003, *103*, 2475-2532.
- (43) Dong, B.; Gao, Y.; Su, Y.; Zheng, L.; Xu, J.; Inoue, T. Self-Aggregation Behavior of Fluorescent Carbazole-Tailed Imidazolium Ionic Liquids in Aqueous Solutions. J. Phys. Chem. B 2010, 114, 340-348.

Page 27 of 29

- (44) Yan, H.; Long, Y.; Song, K.; Tung, C.-H.; Zheng, L. Photo-Induced Transformation from Wormlike to Spherical Micelles Based on Pyrrolidinium Ionic Liquids. *Soft Matter* 2014, *10*, 115-121.
- (45) Wu, J.; Li, N.; Zheng, L.; Li, X.; Gao, Y.; Inoue, T. Aggregation Behavior of Polyoxyethylene (20) Sorbitan Monolaurate (Tween 20) in Imidazolium Based Ionic Liquids. *Langmuir* 2008, 24, 9314-9322.
- (46) Wang, H.; Zhang, L.; Wang, J.; Li, Z.; Zhang, S. The First Evidence for Unilamellar Vesicle Formation of Ionic Liquids in Aqueous Solutions. *Chem. Commun.* 2013, 49, 5222-5224.
- (47) Yin, T.; Wu, J.; Wang, S.; Shen, W. Structural Rearrangement in the Aqueous Solution of Surface Active Ionic Liquid 1-Buty-3-methylimidazolium Bis(2-ethylhexyl) Sulfosuccinate. *Soft Matter* 2015, *11*, 4717-4722.
- (48) Wang, G.; Li, P.; Du, Z.; Wang, W.; Li, G. Surface Activity and Aggregation Behavior of Siloxane-Based Ionic Liquids in Aqueous Solution. *Langmuir* 2015, 31, 8235-8242.
- (49) Nave, S.; Eastoe, J. What is so Special About Aerosol-OT? 1. Aqueous Systems. Langmuir 2000, 16, 8733-8740.
- (50) Eastoe, J.; Downer, A.; Paul, A.; Steytler, D. C.; Rumsey, E.; Penfold, J.; Heenan,
  R. K. Fluoro-Surfactants at Air/Water and Water/CO<sub>2</sub> Interfaces. *Phys. Chem. Chem. Phys.* 2000, 2, 5235-5242.
- (51) Brown, P.; Butts, C.; Dyer, R.; Eastoe, J.; Grillo, I.; Guittard, F.; Rogers, S.; Heenan, R. Anionic Surfactants and Surfactant Ionic Liquids with Quaternary

Ammonium Counterions. Langmuir 2011, 27, 4563-4571.

- (52) Li, Z. X.; Lu, J. R.; Thomas, R. K. Neutron Reflectivity Studies of the Adsorption of Aerosol-OT at the Air/Water Interface: the Surface Excess. *Langmuir* **1997**, *13*, 3681-3685.
- (53) Dong, B.; Zhao, X.; Zheng, L.; Zhang, J.; Li, N.; Inoue, T. Aggregation Behavior of Long-Chain Imidazolium Ionic Liquids in Aqueous Solution: Micellization and Characterization of Micelle Microenvironment. *Colloids Surf.*, A 2008, 317, 666-672.
- (54) Lee, C. T.; Jr.; Smith, K. A.; Hatton, T. A. Photoreversible Viscosity Changes and Gelation in Mixtures of Hydrophobically Modified Polyelectrolytes and Photosensitive Surfactants. *Macromolecules* 2004, *37*, 5397-5405.
- (55) Pan, A.; Mati, S. S.; Naskar, B.; Bhattacharya, S. C.; Moulik, S. P. Self-Aggregation of MEGA-9 (*N*-Nonanoyl-*N*-methyl-D-glucamine) in Aqueous Medium: Physicochemistry of Interfacial and Solution Behaviors with Special Reference to Formation Energetics and Micelle Microenvironment. *J. Phys. Chem. B* 2013, *117*, 7578-7592
- (56) Cheng, N.; Yu, P.; Wang, T.; Sheng, X.; Bi, Y.; Gong, Y.; Yu, L. Self-Aggregation of New Alkylcarboxylate-Based Anionic Surface Active Ionic Liquids: Experimental and Theoretical Investigations. J. Phys. Chem. B 2014, 118, 2758-2768.
- (57) Tanford, C. Micelle Shape and Size. J. Phys. Chem. 1972, 76, 3020-3024.
- (58) Li, N.; Zhang, S.; Zheng, L.; Inoue, T. Aggregation Behavior of a Fluorinated

#### Langmuir

Surfactant in 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquid. *Langmuir* **2009**, *25*, 10473-10482.

(59) Shi, L.; Li, N.; Yan, H.; Gao, Y.; Zheng, L. Aggregation Behavior of Long-Chain N-Aryl Imidazolium Bromide in Aqueous Solution. *Langmuir* 2011, 27, 1618-1625.

#### Table of Contents Graphic

