Light Induced Micelle to Vesicle Transition in Aqueous Solution of a Surface Active Ionic Liquid

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Chemicals

The purities and the suppliers of the chemicals used in the synthesis of ionic liquids are listed in Table S1.

**Table S1** Purities and suppliers of chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-butylaniline</td>
<td>Aladdin</td>
<td>0.99</td>
</tr>
<tr>
<td>Sodium nitrite</td>
<td>Sinopharm Chemical</td>
<td>0.99</td>
</tr>
<tr>
<td>Phenol</td>
<td>Aladdin</td>
<td>0.99</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Sinopharm Chemical</td>
<td>0.98</td>
</tr>
<tr>
<td>1,6-dibromohexane</td>
<td>Aladdin</td>
<td>0.98</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>Aladdin</td>
<td>0.35</td>
</tr>
<tr>
<td>Sodium trifluoroacetate</td>
<td>Aladdin</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*a* all chemicals are used as received; *b* mass fraction; *c* 35% mass fraction in aqueous solution.

The synthetic route of ionic liquid 4-butylazobenzene-4’-hexyloxy-trimethylammonium trifluoroacetate (BHATfO) is shown in Scheme 1.
The synthesis process is as follows: 15ml concentrated HCl was added into the round-bottom flask containing 50mmol 4-butylaniline placed in an ice bath. Then 50mmol sodium nitrite and 10ml cold water was added to the solution and stirred for 1 hour with temperature being controlled near 0 ℃. Thereafter, 50mmol phenol and 120mmol sodium carbonate was dissolved in 15ml water and added to the above solution followed by stirring for 1 hour. The resulting precipitate (product 1) was filtered and washed by water and hexane for three times and dried under vacuum at 60 ℃ for 12 hours. 20mmol product 1 and 50mmol sodium hydroxide was dissolved in 100ml ethanol (solution I). 60mmol 1,6-dibromoethane was dissolved in 20ml ethanol and the solution was added slowly into the above solution I, followed by refluxed at 80 ℃ for 8 hours. The precipitate NaBr was removed and the filtrate was set for one day. The precipitate was then filtered and washed by water and ethanol, and dried under vacuum to obtain product 2. 5mmol product 2 was dissolved in 100ml
THF and trimethylamine gas was bubbled through the solution for 30 min, and the solution was left for 2 days in room temperature. The precipitate was filtered and washed by THF for three times, and dried under vacuum. Thereafter, the raw product was recrystallized twice from ethanol to get product 3. 1mmol product 3 and 2mmol sodium trifluoroacetate was dissolved in 40ml CH₂Cl₂ and stirred in room temperature for 1 day. The mixture was centrifuged and the transparent liquid was collected. Thus, the CH₂Cl₂ was rotary evaporated and the obtained solid was dried under vacuum at 60°C to get orange colored product 4. The total yield was about 10%.

The product was characterized by ¹H NMR (CDCl₃, 400MHz): \( \delta_{\text{ppm}} 0.93 \) (t, 3H), 1.3-1.5 (m, 6H), 1.6-1.83 (m, 6H), 2.86 (t, 2H), 3.2 (s, 9H), 3.35 (t, 2H), 3.96 (t, 2H), 6.9-8.0 (m, 8H).

Scheme S2 ¹H NMR spectrum profile of BHATfO in CDCl₃

The product was characterized by ¹³C NMR (D₂O, 500MHz): \( \delta_{\text{ppm}} 14.40, 22.93, \)
23.04, 25.65, 29.32, 33.61, 35.94, 53.35, 66.98, 68.77, 115.20, 123.24, 125.26, 129.23, 145.63, 147.07, 151.20, 161.84, 117.06(q), 163.00(q)

**Scheme S3** $^{13}$CNMR spectrum profile of BHATfO in D$_2$O

The product was characterized by IR

**Scheme S4** IR spectrum profile of BHATfO

The melting point were determined by Micro-DSC III (Setaram, France) to be about
77°C.

**Figure S1** Melting curve of BHATfO measured by micro-DSC III

**UV-Vis spectroscopy:** The UV-vis spectra of BHATfO aqueous solutions before and after UV irradiation were obtained using a UV-2450 spectrometer (Shimadzu) with 1.0 cm quartz cell at 298.15K. The spectra were recorded in a wavelength range from 250 nm to 500 nm with a step of 0.1 nm and water as the blank.

The changes of UV absorbance at 365nm of 2.5mM BHATfO aqueous solution after UV irradiation (24W, 365nm) and further vis-light irradiation (natural light) are presented in Figure S2, which shows that about 1 hour is enough for the completion of trans-cis isomerization.

**Figure S2** The changes of UV absorbance at 365nm after UV irradiation and vis-light
irradiation

**Surface tension measurements:** The surface tensions of aqueous surfactant solutions were measured using the hanging platinum plate method by a tensionmeter supplied by Shanghai Hengping Instrument Company (Shanghai, China) with an accuracy of ± 0.1 mN·m\(^{-1}\). The temperature was controlled by a water circulating bath with a precision of ± 0.1K. The tensionmeter was calibrated with pure water, and the plate was washed and burned over flame before each measurement to ensure its cleanness. Typically, it took 0.5-1 h to reach equilibrium before the measurement.

**Conductivity measurement:** Conductivity measurements were performed with a digital conduct meter supplied by Leici Co. (Shanghai, China) with a titration method. The conduct meter was initially calibrated by standard KCl solution with concentration of 0.01 mol·L\(^{-1}\). A certain amount of water was transferred into a cell, which was placed in a water bath with temperature being controlled within ±0.1 K. The concentrated aqueous solution of BHATfO was prepared and titrated into the cell by a microsyringe. The cell was shaken after each titration and kept undisturbed to reach thermal equilibrium before measurement. The experiments were conducted at 298.15±0.1 K.

The obtained conductivity values are fitted by the following equation to get CAC:

\[
\kappa = \kappa_0 + S_1 C + p(S_2 - S_1) \ln \frac{1 + \exp\left(\frac{(C - CAC)/\rho}{S_1}\right)}{1 + \exp\left(-\frac{C - CAC}{S_2}\right)}
\]  

(S1)

where \(C\) is the surfactant concentration; \(\kappa_0\) is the conductivity when \(C=0\); \(S_1\) and \(S_2\) are slopes bellow and after CAC, respectively; \(\rho\) is the parameter related to the width of the transition between two linear dependences.
Figure S3 Plots of conductivities against BHATfO concentration. (●) and (○) refer to that before and after UV irradiation, respectively. The lines are fitting results from Equation (S1).

**Dynamic light scattering:** Hydrodynamic diameters of the surfactant aqueous solutions were measured by dynamic light scattering using Malvern Zetasizer Nano ZS instrument (Southborough, MA) with a backscattering detector (173°) and a laser of 633 nm wavelength. Measurements were taken in a batch mode at 298.15 K using a quartz cuvette with a path length of 1 cm.

**Transmission Electron Microscopy (TEM):** A drop of solution was placed on a carbon coated cooper grid (300 mesh). The samples for negative stained TEM measurements were prepared by using 1% uranyl acetate solution as staining agent. The excess liquid was sucked away by filter paper. The images of samples after drying in room temperature were obtained by using JEM-1400 electron microscope at working voltage of 120kV. For cryo-TEM, the copper grid was plunged into liquid ethane cooled by liquid nitrogen and imaged by FEI Tecnai G2 F20 Twin electron microscope at an acceleration voltage of 200kV.