Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2015

Supporting Information:

Reversible Switching of Amphiphilic Self-assemblies Between Micelles and Microemulsions by a Thermal Stimulus

Bin Dong,[a,‡] Xueqing Xing,[b,‡] Rui Wang,[a,c] Bing Wang,[d] Xiaoyan Zhou,[d] Chang Wang,[a] Li Yu,[c,*] Zhonghua Wu,[b] and Yanan Gao[a,*]

[a]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. Fax: +86 411 84379992; Tel: +86 411 84379992; E-mail: ygao@dicp.ac.cn*

[b]*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

[c]*Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China. E-mail: ylmlt@sdu.edu.cn*

[d]*Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety and Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China*

‡*These authors contributed equally to this work*

Materials

Triton X-100 was purshased from Alfa Aesar and used as received. The ionic liquid tetrabutylphosphonium trifluoroacetate ($[P_{4444}][CF_3COO]$) was prepared according to the literature.[1] Water was doubly deionized and distilled. The samples of the $[P_{4444}][CF_3COO]/H_2O$/Triton X-100 ternary system were stirred for at least 10 min to obtain macrohomogeneous solutions before any characterization.

Characterization

The size and size distributions of the investigated self-assembly systems were determined by dynamic light scattering (DLS) using Zetasizer Nano S90 (ZEN1690) with a He–Ne laser operating at 633 nm. All measurements were made at a scattering angle of 90^{o}. Surface tension measurements were carried out by a surface tensiometer (model JYW-200B, Chengde Dahua Instrument Co., Ltd., accuracy (0.01 mN/m). The surface tension was determined with a single-measurement method. All measurements were repeated at least twice. A low-frequency conductivity analyzer (model MP522, Shanghai Sanxin Instrument Co., Ltd., accuracy ±1%) was used to measure the electrical conductivity of the aqueous solutions. Freeze-fracture transmission electron microscopy (FF-TEM) observations on the replicated samples were carried out with a JEOL TEM 200CX electron microscope. The replicas were first prepared as follows: a small amount of sample was placed in a gold cup. The temperature of the sample was controlled to a desired temperature before the preparation of sample replicas. The gold cup was then swiftly plunged into a liquid Freon that has been cooled with liquid nitrogen in advance. The frozen samples were fractured and replicated in a freeze-fracture apparatus BAF 400 (Bal-Tec, Balzer, Liechtenstein) at 133 K. Pt/C was deposited at an angle of 45^o. The in-situ small-angle X-ray scattering (SAXS) experiment was performed at beamline 1W2A of BSRF (Beijing, China). The incident X-ray wavelength (λ) was chosen to be 0.154 nm by a triangle bending Si(111) monochromator. A two-dimensional Pilatus detector was used to record the two-dimensional scattering intensity distribution. All these 2D data were integrated into the 1D $I(q)$ profiles as function of the magnitude of the scattering vector q ($q = 4\pi\sin\theta/\lambda$, where 2θ is the total scattering angle). The sample-to-detector distance was fixed to 1.6 m to cover a q-range of 0.25~4.00 nm^{-1}.

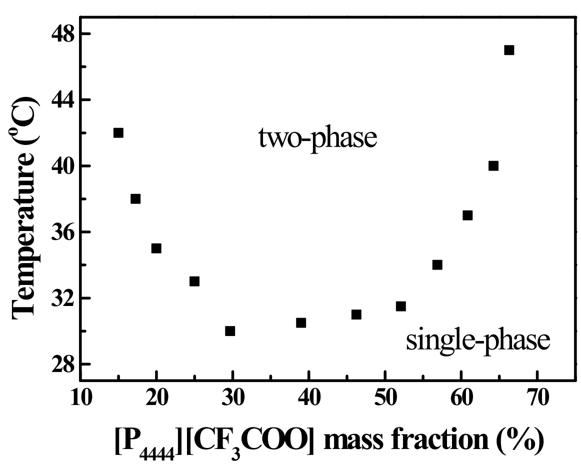

Fig. S1 Phase separation temperature (LCST) of $[P_{4444}][CF_3COO]$ after mixing with different amounts of water. The two phases became homogeneous again when temperature was decreased down to a certain extent. This means that such phase change was reversibly induced only by a small temperature change.

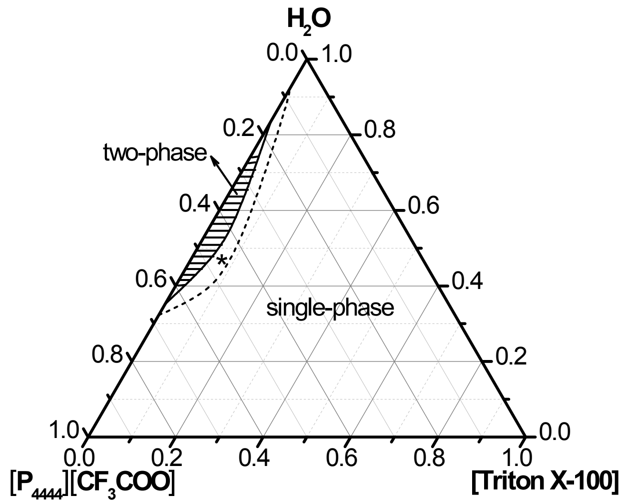

Fig. S2 Ternary phase diagram of [P_{4444}][CF_3COO]/H_2O/Triton X-100 system at 40 °C (solid line with shadow) and 50 °C (dashed line). The two-phase region is larger at higher temperatures, in accordance with the results of the binary phase diagram of [P_{4444}][CF_3COO]/H_2O system.

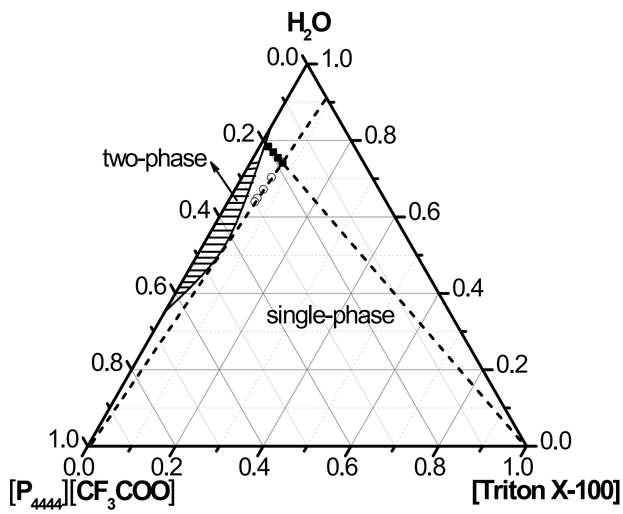

Fig. S3 Ternary phase diagram of [P_{4444}][CF_3COO]/H_2O/Triton X-100 system at 40 °C. The solid squares are on the line of [P_{4444}][CF_3COO]/H_2O (1:4, w/w), while the hollow circles are on the line of H_2O/Triton X-100 (10:1, w/w).

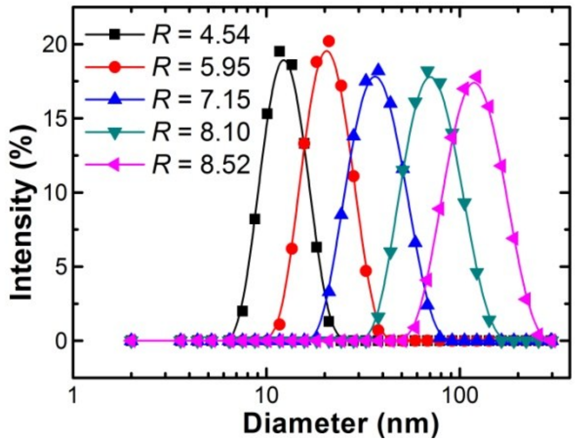

Fig. S4 Sizes and size distributions of the $[P_{4444}][CF_3COO]/H_2O$/Triton X-100 assembly (H_2O/Triton X-100, 10:1, w/w) at different *R* values (*R* = $[P_{4444}][CF_3COO]$/Triton X-100 molar ratio) at 40 °C. The droplet sizes of self-assemblies increased from 12.7, 21.3, 38.5, 74.8, to 124.6 nm with increasing *R* from 4.54, 5.95, 7.15, 8.10, to 8.52. Such a swelling phenomenon is characteristic of microemulsion, also suggesting the formation of $[P_{4444}][CF_3COO]$-in-H_2O microemulsions at 40 °C.

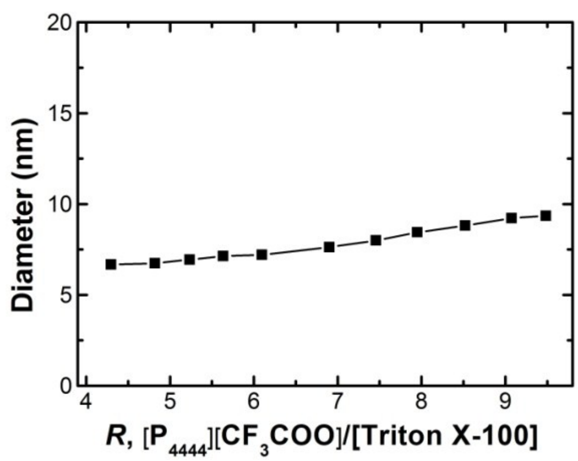

Fig. S5 Sizes of the $[P_{4444}][CF_3COO]/H_2O$/Triton X-100 assembly ($[P_{4444}][CF_3COO]/H_2O$, 1:4, w/w) at different *R* values (*R* = $[P_{4444}][CF_3COO]$/Triton X-100 molar ratio) at 20 °C.

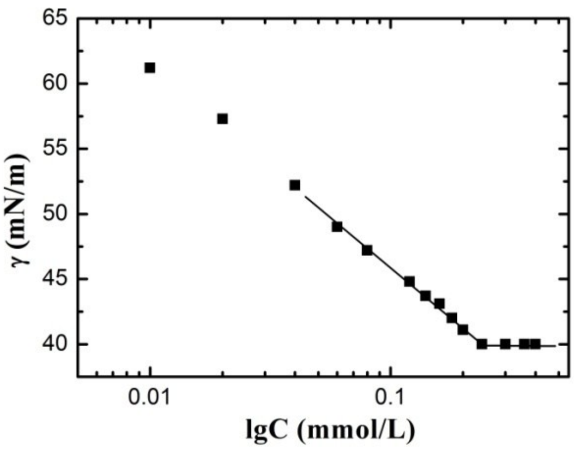

Fig. S6 Surface tension of $[P_{4444}][CF_3COO]$ aqueous solution ($[P_{4444}][CF_3COO]/H_2O$, 1:4, w/w) as a function of Triton X-100 concentration at 20 °C.

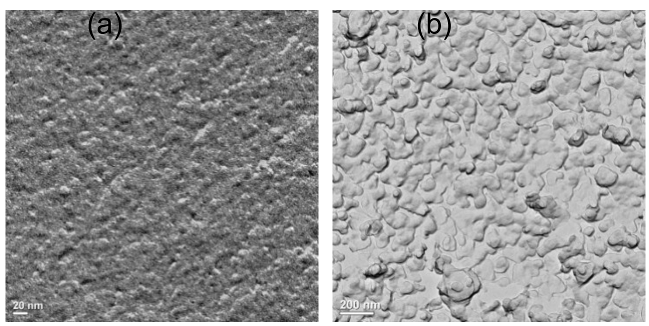

Fig. S7 FF-TEM images of $[P_{4444}][CF_3COO]/H_2O$/Triton X-100 (1:4:0.3, w/w) aggregates at (a) 20 °C and (b) 40 °C.

Table S1 R_g and D_{max} of the particle at 25, 35, 45, and 50 °C calculated from SAXS.

	25 °C	35 °C	45 °C	50 °C
R_g (nm)	1.9	3.5	4.9	5.1
D_{max} (nm)	5.5	12.1	16.8	18.1

Reference

1 (*a*) Y. Kohno, H. Arai, S. Saita and H. Ohno, *Aust. J. Chem.*, 2011, **64**, 1560; (b) R. Wang, W. G. Leng, Y. A. Gao and L. Yu, *RSC Adv.*, 2014, **4**, 14055.