Formation of large nanodomains in liquid solutions near the phase boundary

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Experimental Section

Materials: ILs, EmimBF₄ (purity>99%), HmimBF₄ (purity>99%) and BmimPF₆ (purity>99%) were purchased from the Centre of Green Chemistry and Catalysis, LICP, CAS. ILs were dried at 60°C for 48 hours before used, and the water content was less than 0.07wt% as determined by Karl-Fischer method.^{S1} Cyclohexanol (A. R. grade), ethanol (A. R. grade), acetone (A. R. grade), $Zn(NO_3)_2$ ·6H₂O (A. R. grade), (NH₄)₂S₂O₈ (A. R. grade), acrylamide (A. R. grade) and pyrene (A. R. grade) were provided by Sinopharm Chemical Reagent Co., Ltd. Tetrabutyl titanate (purity>98%), 2-methylimidazole (purity>98%) and N,N'-methylenebisacrylamide (purity>98%) were purchased from Alfa Aesar China Co., Ltd.

Phase behavior investigation: We describe the mainly procedures to study the phase behavior of EmimBF₄/ethanol system because those to study the phase behaviour of HmimBF₄/water system, BmimPF₆/ethanol, and cyclohexanol/water systems were similar. In a typical experiment, 10 g of EmimBF₄ were added into a glass tube, and the total mass of the tube was determined by an electronic balance (Ohaus) with a resolution of 0.1 mg. Then, the tube was immersed in a water bath of 25 $^{\circ}C \pm 0.1^{\circ}C$ controlled by a YKKY A2 temperature controller (Beijing Changliu S2 Scientific Instruments Co., Ltd.). After the temperature was constant, ethanol was added into the tube until the solution became cloudy. The tube was taken out to determine the mass, and the cloud-point concentration was calculated. The phase behaviour of other three systems was investigated using similar procedures.

SAXS study: SAXS experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility.^{S2} The data were collected using a CCD detector (MAR) with maximum resolution of 2048×2048 pixels. The wavelength of the X-ray was 1.54 Å, and the distance of the sample to detector was 1.50 m. In a typical experiment, the sample was added into the sample cell controlled at 25 °C, and the X-ray scattering data were recorded. The 2-D SAXS images were obtained from the detector and then transformed into the profiles of intensity (I) *vs* wave vector (q) by the software SAXS Data Pre-process V2.0.0. The pair-distance distribution function, *p*(*r*), was obtained from SAXS data by using an Irena tool suite within the Igor pro and Gnom application softwares.^{S3}

DLS measurements: The measurements of the systems were carried out at 25.0 \pm 0.1 °C with an LLS spectrometer (ALV/SP-125) which employed a multi- τ digital time correlator (ALV-5000). A solid-state He-Ne laser (output power of 22 mW at λ = 632.8 nm) was used as a light source, and the measurements were conducted at a scattering angle of 90°. All solutions were freshly made and stabilized for 24 hours. All samples were filtered through a 0.22 μ m hydrophilic PVDF membrane filter. Each sample was measured for at least three times, and reproducibility of the aggregate sizes was found to be within \pm 5%.^{S4}

Fluorescence studies: Steady-state fluorescence experiments were carried out using a HITACHI F-4600 fluorescence spectrophotometer connected to a personal computer. The fluorescence cell and experimental procedures were similar to those used previously.^{S5} Pyrene was used as the probe. An excitation wavelength of 335 nm was chosen, and the emission wavelength varied from 350 to 500 nm. The excitation and emission slit widths were kept at 2.5 nm, and the scan rate was 60 nm·min⁻¹. In a typical experiment, the sample containing pyrene was added into the sample cell and the fluorescence spectrum was recorded. The concentration of pyrene in the binary solutions was 10 mM.

Conductivity measurements: The conductivities of all the binary solutions were measured using a conductivity meter (FE30) and a LE703 conductivity electrode, produced by Mettler-Toledo Instruments Co., Ltd. (Shanghai, China).^{S6} The electrode was calibrated by standard NaCl solution with a conductivity of 12.88 ms·cm⁻¹. In a typical experiment, the solution was added into a glass tube and the head of the electrode was immersed in the solution. The tube was sealed and immersed in a water bath of 25°C ± 0.1°C controlled by a YKKY A2 temperature controller (Beijing Changliu Scientific Instruments Co., Ltd.).

Synthesis of ZIFs: The method to synthesize ZIFs was similar to that reported via the coordination of $Zn(NO_3)_2$ and 2-methylimidazole.^{S7} In a typical experiment, 20 g EmimBF₄ and desired amount of ethanol were mixed at 25 °C, and then 0.02 g $Zn(NO_3)_2$ · GH_2O and 2-methylimidazole were added into the solution with stirring for 24 h. The obtained mixture containing ZIFs was centrifuged with a centrifugal speed of 5000 rpm. The obtained material was washed with acetone for 5 times (5×50 mL), and then was dried in a vacuum oven at 40 °C for 24 h.

Synthesis of TiO₂: The method to synthesize TiO₂ was similar to that reported via the hydrolysis of tetrabutyl titanate.^{S8} In a typical experiment, 20 g HmimBF₄ was mixed with desired amount of water at 25 °C, and then 0.05 g tetrabutyl titanate was added into the solution with stirring for 24 h. The obtained mixture containing TiO₂ was centrifuged with a centrifugal speed of 5000 rpm. The obtained material was washed with acetone for 5 times (5×50 mL), and then was dried in a vacuum oven at 40 °C for 24 h.

Synthesis of PAMs: The procedures for the synthesis of TiO₂ was similar to that reported via the polymerization reaction of acrylamide.^{S9} In a typical experiment, 20 g BmimPF₆ was mixed with desired amount of ethanol at 80 °C, and then 0.05 g acrylamide, 0.005 g N,N'-methylenebisacrylamide and 0.005 g $(NH_4)_2S_2O_8$ were added into the solution with stirring for 5 min. The mixture was then cooled quickly to 25 °C within 5 min, and was stirred for another 24 h. The obtained mixture containing PAM was centrifuged with a centrifugal speed of 5000 rpm. The obtained material was washed with acetone for 5 times (5×50 mL), and then was dried in a vacuum oven at 40 °C for 24 h.

Material Characterization: XRD analysis of the samples was performed on the X-ray

diffractometer (Model D/MAX2500, Rigaka) with Cu-K α radiation, and the scan speed was 5°/min. The morphologies of the products were characterized by JEOL-2100F transmission electron microscopy (TEM). For the sample preparation, 1 mg sample powder was dispersed in 5 mL acetone, then 10 μ L solution was added on the ultrafine carbon film. The pore properties were obtained from N₂ adsorption-desorption isotherms determined using a Micromeritics ASAP 2020M system.



Supplementary Figures

Fig. S1 SAXS curves (left column) and pair-distance distribution function curves (right column) of different systems at 25 °C: (A-B) HmimBF₄/water systems with water mass fractions of 0.038 (a), 0.074 (b), 0.138 (c), 0.170 (d) and 0.183 (e); (C-D) BmimPF₆/ethanol systems with mass fractions of 0.039 (a), 0.074 (b), 0.108 (c), 0.160 (d) and 0.165 (e); (E-F) cyclohexanol/water systems with water mass fractions of 0.020 (a), 0.059 (b), 0.092 (c), 0.118 (d) and 0.130 (e).



Fig. S2 Dependence of size of the nanodomains in different systems on composition determined by SAXS at 25 °C: (A) HmimBF₄/water system; (B) BmimPF₆/ethanol system; (C) cyclohexanol/water system.



Fig. S3 Dependence of size of nanodomains in different systems on composition determined at 25 °C by DLS (left column) and size distributions of the nanodomains (right column): (A-B) HmimBF₄/water systems with water mass fractions of 0.107 (a), 0.138 (b), 0.170 (c) and 0.183 (d); (C-D) BmimPF₆/ethanol systems with ethanol mass fractions of 0.039 (a), 0.074 (b), 0.108 (c), 0.160 (d) and 0.165 (e); (E-F) cyclohexanol/water systems with water mass fractions of 0.020 (a), 0.059 (b), 0.092 (c), 0.118 (d) and 0.130 (e).



Fig. S4 Size distribution curves on the x-axis in logarithmic scale of different systems: (A) EmimBF₄/ethanol systems with ethanol mass fraction of 0.121 (a), 0.153 (b), 0.183 (c) and 0.189 (d); (B) HmimBF₄/water systems with water mass fractions of 0.107 (a), 0.138 (b), 0.170 (c) and 0.183 (d); (C) BmimPF₆/ethanol systems with ethanol mass fractions of 0.039 (a), 0.074 (b), 0.108 (c), 0.160 (d) and 0.165 (e); (D) cyclohexanol/water systems with water mass fractions of 0.092 (c), 0.118 (d) and 0.130 (e).



Fig. S5 The dependence of I_1/I_3 ratio on composition in HmimBF₄/water (A), BmimPF₆/ethanol (B) and cyclohexanol/water (C) systems using pyrene as probe determined at 25 °C.



Fig. S6 The variation of conductivity with composition for $HmimBF_4$ /water (A) and $BmimPF_6$ /ethanol (B) systems at 25 °C.



Fig. S7 TEM images of TiO_2 synthesized HmimBF₄/water system at water mass fractions of 0.038 (A), 0.170 (B), 0.180 (C) and PAM synthesized in BmimPF₆/ethanol system at ethanol mass fractions of 0.039 (D), 0.160 (E), 0.163 (F) at 25 °C.



Fig. S8 XRD patterns of TiO_2 synthesized in HmimBF₄/water system at water mass fractions of 0.038 (a), 0.170 (b), 0.180 (c) at 25 °C and standard pattern (d).



Fig. S9 (A) Total mesopore volume of TiO_2 synthesized in $HmimBF_4$ /water systems with different water mass fractions; (B) average mesopore size of TiO_2 synthesized in $HmimBF_4$ /water systems with different water mass fractions; (C) total mesopore volume of PAMs synthesized in $BmimPF_6$ /ethanol systems with different ethanol mass fractions; (D) average mesopore size of PAMs synthesized in $BmimPF_6$ /ethanol systems with different ethanol systems with different ethanol mass fractions.

Supplementary Tables

Table S1 Phase separation concentrations (M_{BS}) of different systems with the addition of material precursors at 25 °C and materials yield in these systems.

Entry	Systems	Added precursors	M _{BS}	Yield
1	EmimBF ₄ /ethanol	0.1 wt% Zn(NO ₃) ₂ .6H ₂ O,	0.187	55.1%
		0.1 wt% 2-methylimidazole		
2	HmimBF ₄ /water	0.25 wt% tetrabutyl titanate	0.181	98.4%
		0.25 wt% acrylamide,		
3	BmimPF ₆ /ethanol	0.025 wt% (NH ₄) ₂ S ₂ O ₈ , 0.025 wt%	0.164	86.6%
		N,N'-methylenebisacrylamide		

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