Electronic Supplementary Information:

Compression of ionic liquid when confined in porous silica nanoparticles

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Materials

Mesoporous silica (99%) used in our investigation was purchased from Xiamen Macren and Sigma. The average pore diameters of the two samples were 3.7 and 7.1 nm, respectively.

Characterizations

Phase transition temperatures of bulk and adsorbed ILs were measured by DSC (DSC-822e, Mettler-Toledo Corp.). Samples of about 10 mg were placed in aluminum pans with pierced lids. The sample was scanned from 30 to 200 °C at a programmed rate of 10 °C/min. STEM images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. The x-ray absorption data of the Br K-edge of the samples were recorded at room temperature in transmission mode using ion chambers, or in fluorescent mode with a silicon drift fluorescence detector at beam line BL14W1 of Shanghai Synchrotron Radiation Facility. The station was operated using an Si(111) double crystal monochromator. During the measurement, the synchrotron was operated at an energy of 3.5 GeV and a current between 150 and 210 mA. The photon energy was calibrated with the first inflection point of Se K-edge in platinum metal foil.

Experimental details

In a manner similar to our previous procedure for a typical filling experiment,[1] 200.5 mg SiO_2 was put into a two-necked flask (one of the necks was sealed by a rubber stopper and the other was connected with a high-vacuum line). The flask was boiled using a gas burner for 4 h under vacuum to draw out the gas inside the SiO_2. Then 100 mg [Emim]Br dissolved in ethanol was transferred into the flask through a syringe and the mixture was ultrasonically vibrated for 6 h at 100 °C to fill the SiO_2 with IL. The resulting mixture was cooled for 3 h to room temperature. The filled samples were separated from the mixture by centrifugation and purified by three cycles of washing with acetonitrile or ethanol and filtration, in order to completely remove the [Emim]Br adsorbed on the SiO_2 surface.

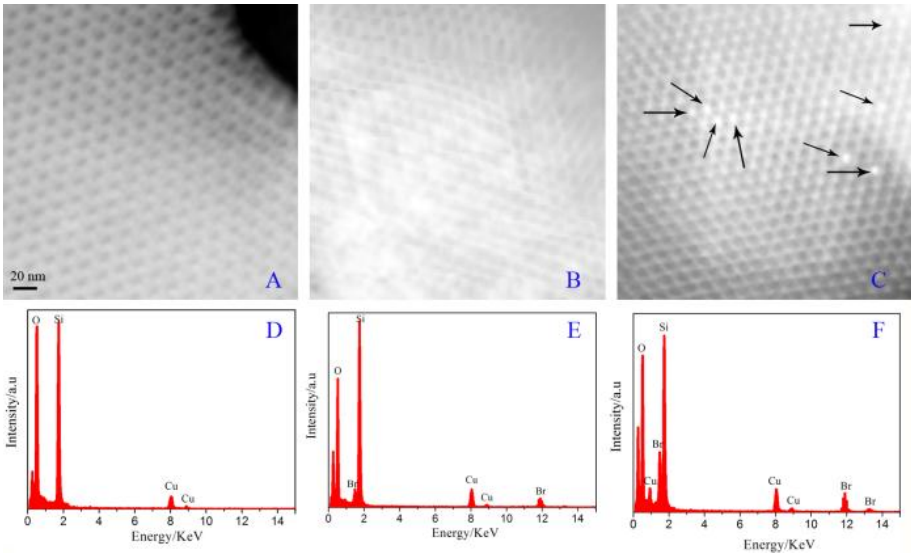

Figure S1. A larger format of Fig. 1

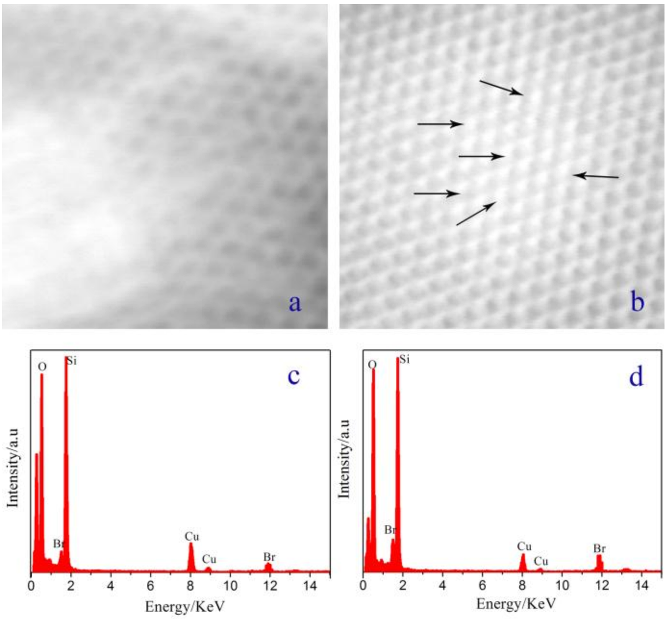

Figure S2. HAADF-STEM images and the corresponding EDX spectra of [Emim]Br/SiO_2−7.1 nm (a, c) and [Emim]Br@SiO_2−7.1 nm (b, d).

Computational methods

Natural bond orbital atomic charge analysis[2, 3] for free and confined [Emim]Br molecules was carried out to obtain a more quantitative picture of the confinement effect on the electron transfer between cation and anion of [Emim]Br. The molecular structure of isolated [Emim]Br was first fully optimized using the Becke's three-parameter hybrid functional B3LYP[4] that includes the correlation functionals of Lee, Yang, and Parr (LYP)[5] along with the 6-311+G** basis set. The frequency calculations were employed to verify the resulting geometry as minima. The distance between the Br^- anion and the $[Emim]^+$ cation was then adjusted to the XAFS experimental values under confinement. Finally, the NBO atomic charges on the free and confined [Emim]Br molecules were analysed at the B3LYP/6-311+G** level[6, 7, 8]. All density functional theory calculations on [Emim]Br presented here were carried out with the Gaussian 03 program.[9]

Computational results

Table S1 shows the respective NBO atomic charge values on Br^- anions of free and confined [Emim]Br molecules. As shown in Table S1, the Br^- anion of free [Emim]Br has an atomic charge of −0.910 e. However, the net charges on the Br^- anions are −0.862 e and −0.838 e when the distances between Br^- and $[Emim]^+$ are 2.24 and 2.15 Å, respectively. The net charges of the electron transfer from Br^- to $[Emim]^+$ are 0.048 e and 0.072 e for [Emim]Br confined in mesoporous SiO_2 with pore diameters of 7.1 and 3.7 nm. This indicates that compression of [Emim]Br in porous SiO_2 promotes the electron transfer from anion to cation.

Table S1. The cation-anion distance and Mulliken charges for Br^- in [Emim]Br.

	[Emim]Br		
	free	@SiO_2−7.1nm	@SiO_2−3.7nm
distance	2.56 Å	2.24 Å	2.15 Å
atomic charges on Br^-	-0.910 e	-0.862 e	-0.838 e

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