Supplementary Material (ESI) for PCCP

Nanocomposites of ionic liquids confined in mesoporous silica gels: synthesis, characterization and performance

Preparation of ILs

ILs (Scheme 1 in the article) were synthesized carefully and purified rigorously in our laboratory according to literature. [1, 2] S-butyltetrahydrothiophene chloride BThCl was prepared with high yield from the reaction of tetrahydrothiophene and appropriate amount of chlorobutane in acetone. Silver dicyanamide $AgN(CN)_2$, (4.0 g, 11 mmol) was added to a solution of BThCl (5.2 g, 11 mmol) in water (60 ml), and the resulting suspension was stirred for 24 h. Then the filtrate was evaporated under vacuum. The obtained crude compound was dissolved in dichloromethane CH_2Cl_2 and the solution was dried over anhydrous magnesium sulphate. Finally, the colorless $BThN(CN)_2$ was obtained by subjecting the liquid to a higher vacuum to eliminate volatile components.

Experimental process and instruments

N_2 adsorption measurements were obtained using a Micromeritics ASAP 2020 instrument to measure the surface area and porosity of silica gel using nitrogen at 77 K as the standard adsorptive gas. The surface area was obtained by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

Thermal measurements were carried out on a Mettler-Toledo differential scanning calorimeter, model DSC 822^e, and the data were evaluated using the Mettler-Toledo STARe software version 7.01. Samples (weight, 20-60 mg) were placed in a 40 μL sealed aluminum pan with a pinhole at the top of the pan. An empty aluminum pan was used as the reference. The samples inside the DSC furnace were exposed to a flowing dry N_2 atmosphere. All samples were dried in situ on the DSC by holding the sample at 120 °C for 2 h. The rate of heating/cooling was 10 °C/min. Specific heat capacity was obtained after calibrating by the software with sapphire as the reference. In order to obtain accurate values of specific heat capacity, three specimens of every material were measured and the results were averaged. Comparisons of pure water with literature values showed that the accuracy of the specific heat capacity measurement was within 1%. *C*p of ILs confined into mesoporous silica gel and ILs coatings onto silica gel with variations of temperatures were calculated by subtraction of *C*p of sg-IL from IL-sg and IL/sg, respectively, as following:

$$C_p = \frac{C_p(IL-sg) - C_p(sg-IL) \times (1 - w.t.\%)}{w.t.\%}$$

*C*p was specific heat capacity of ILs after being confined, *C*p (IL-sg) was specific heat capacity of the nanocomposites of IL-sg, *C*p (sg-IL) was the specific heat capacity of silica gel after IL was washed out, and w.t.% was the weight loading of IL in the nanocomposites.

For gas adsorption measurement, all the samples were pretreated through the following procedure. The sample was stuffed into the U-shaped glass tube with inner diameter 8 mm and length 200 mm, and was kept from 30 ºC to 180 ºC with a rate of 8 ºC /min under 10 mL/min dry argon. After being retained at 180 ºC for 5 h, the sample was exposed to a dry and pure CO_2 gas flow with a rate of 15 mL/min at 30 ºC for 2 h for the saturation of CO_2 absorption.

TPD measurement was carried out from 30 ºC to 150 ºC with a rate of 8 ºC /min using dry argon as carrier gas with a flow rate of 50 mL/min. TPD profiles were recorded by GC 112 gas chromatography with thermal conductivity detector. In the meanwhile, the desorbed CO_2 was completely absorbed by the standard barium hydroxide aqueous solution. The amount of the desorbed CO_2 was determined according to the standard method of volumetric titration using oxalic acid aqueous solution as titrant.

For column efficiency testing, Sp 6890 gas chromatography with a thermal conductivity detector was used with dry argon as carrier gas. The carrier gas flow rate was determined by a Field-Cal 570 flow calibrator placed at the outlet of the detector. The flow rate was set for a series of runs for stabilization for at least 15 min before any determinations. The flow rates were corrected for water vapor pressure and ranged from 25-40 mL/min. Sample injections for liquid was 0.6 to 1 μL. The error bar was 2~3% on determining the carrier gas flow rate (0.1 mL/min), the solute retention time (0.008 min) and the amount of the solvent on the column (0.2 mg).

Fourier transform infrared (FT-IR) and temperature-controlled Raman spectroscopy were performed on a Thermo Nicolet 5700 FT-IR spectrophotometer and Thermo Nicolet Laser Raman spectrometer with AsGaIn detector and Nd : YAG laser (1064 nm). The experiment was carried out in a dry and closed environment.

The fluorescence spectra were recorded at 25 ºC on a Hitachi model F-7500 FL spectrophotometer (Hitachi, Japan) with a xenon lamp as the excitation source. The excitation and emission slit widths were 2.5 and 2.5 nm, respectively. The photomultiplier voltage was 700 V.

Net retention volume V_N and specific retention volume V_g^0 can be calculated as shown in Eq. (1) and Eq. (2):[34]

$$V_N = j \cdot F \cdot (t_R - t_0) \cdot \frac{P_0 - P_W}{P_0} \cdot \frac{273}{T_r} \qquad (1)$$

$$V_g^0 = \frac{j}{m} \cdot F \cdot (t_R - t_0) \cdot \frac{P_0 - P_W}{P_0} \cdot \frac{273}{T_R} \qquad (2)$$

$$j_2^3 = \frac{3}{2} \cdot \frac{(\frac{P_i}{P_0})^2 - 1}{(\frac{P_i}{P_0})^3 - 1} \qquad (3)$$

In the Equations, T_r is the room temperature. m is the mass of stationary phase in the colum or the IL mass in the column. F is the carrier gas flow rate. t_R is the retention time for the adsorbing probe. t_0 is the mobile phase hold-up time (dead-time). J is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed. P_0 is the outlet column pressure. P_w is the vapour pressure of water at the flowmeter temperature. P_i is the inlet column pressure.

In the thiophene adsorption experimental, IL loading in IL-sg was 30 wt%, C_0, the initial concentration of thiophene in octane, C_1, the final concentration of thiophene in octane at equilibrium, q, the amount of adsorbed thiophene per gram adsorbent, and adsorptions were carried out at room temperature for 5 h to obtain the equilibrium, as following:

$$q = \frac{(C_0 - C_1) \times w_0}{w_1}$$

q was the adsorption capacity of thiophene in the adsorbents, C_0 was the initial concentration of thiophene in octane), C_1 was the final concentration of thiophene in octane after equilibrium, w_0 was the mass of the adsorbate, and w_1 was the mass of the adsorbent.

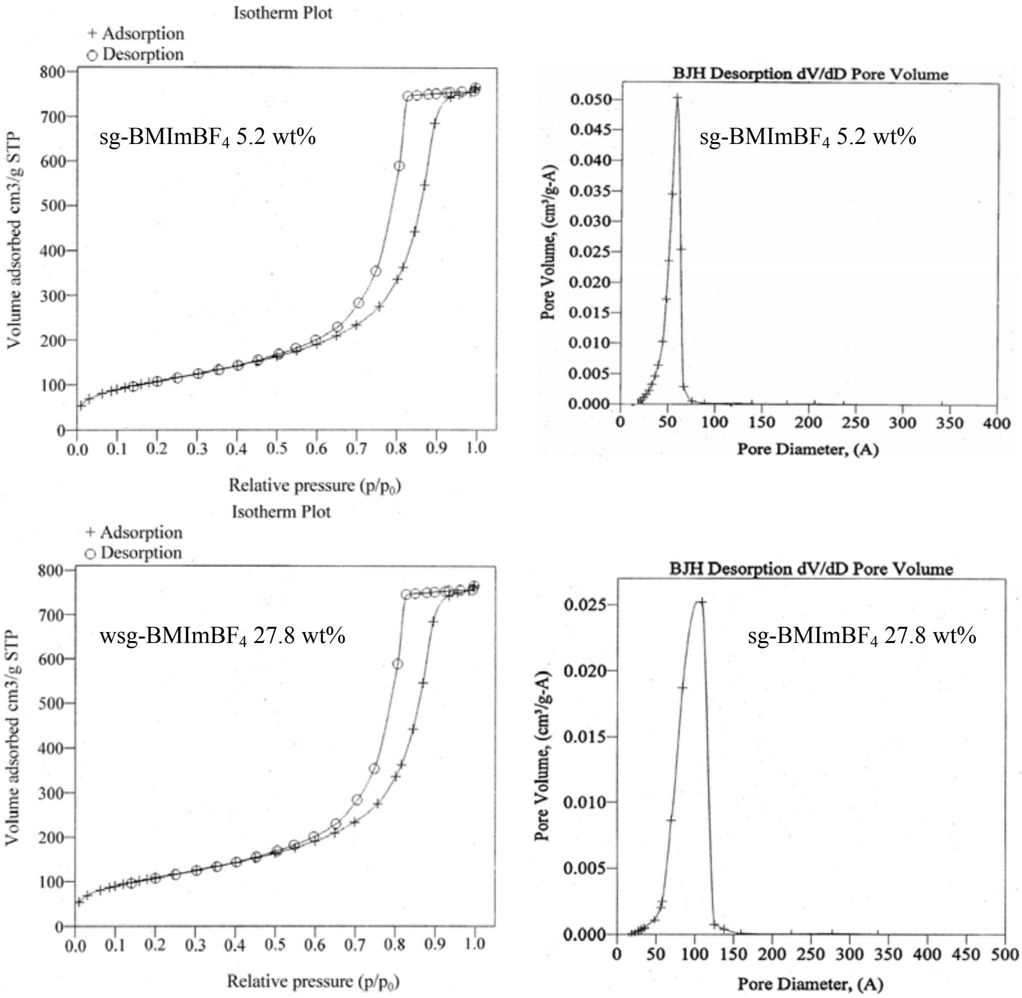

Fig. S1 N_2 adsorption-desorption isomer and pore size distribution plots of sg-BMImBF$_4$

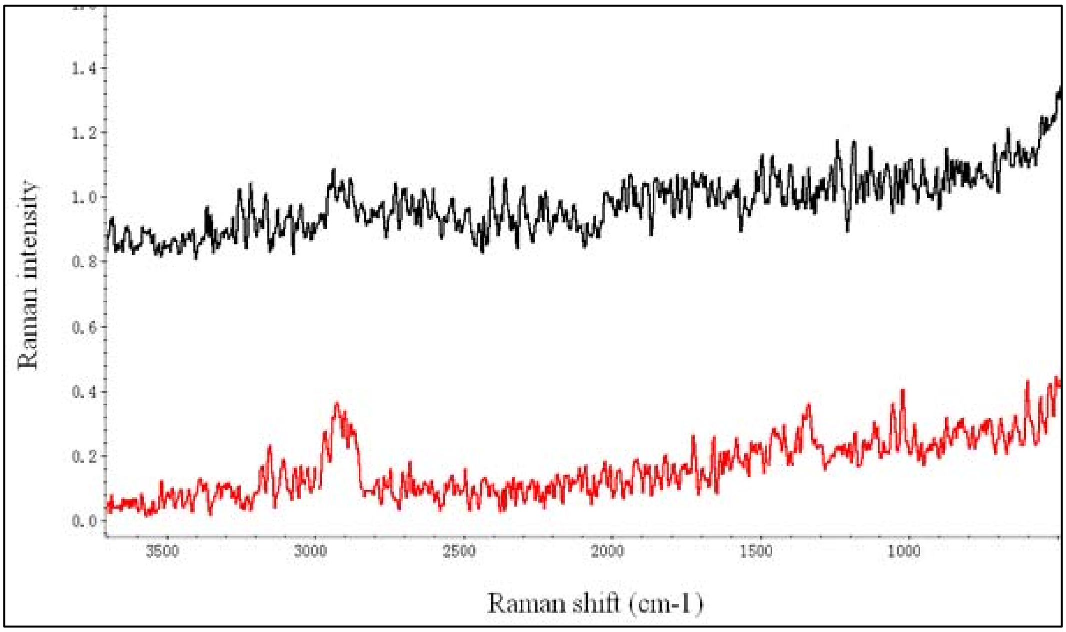

Fig. S2 Raman spectra of sg-BMImBF$_4$ (IL loading of 27.8 wt%) and sg-C$_{16}$MImBF$_4$ (IL loading of 27.6 wt%)

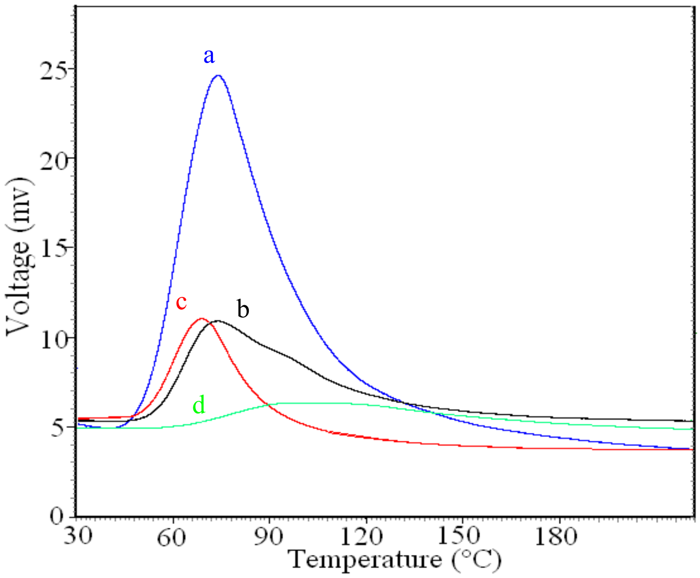

Fig. S3 CO$_2$ desorption profiles for — IL-sg, a, — IL/sg, b, — IL/g, IL/g, c, — sg-IL, d (IL, OMImBF$_4$, loading 27.6%)

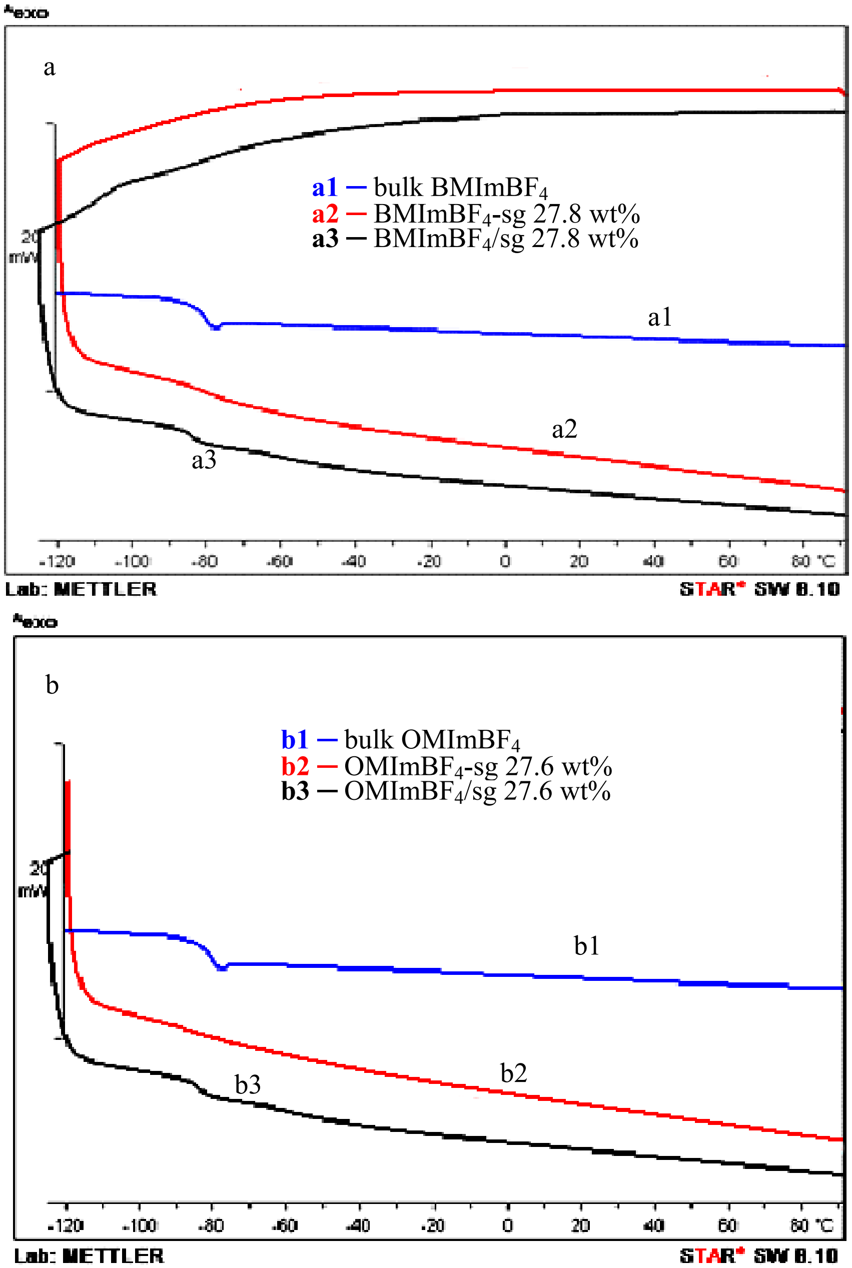

Fig. S4 DSC charts of $BMImBF_4$, $BMImBF_4$-sg and $BMImBF_4$/sg (a); $OMImBF_4$, $OMImBF_4$-sg and $OMImBF_4$/sg (b)

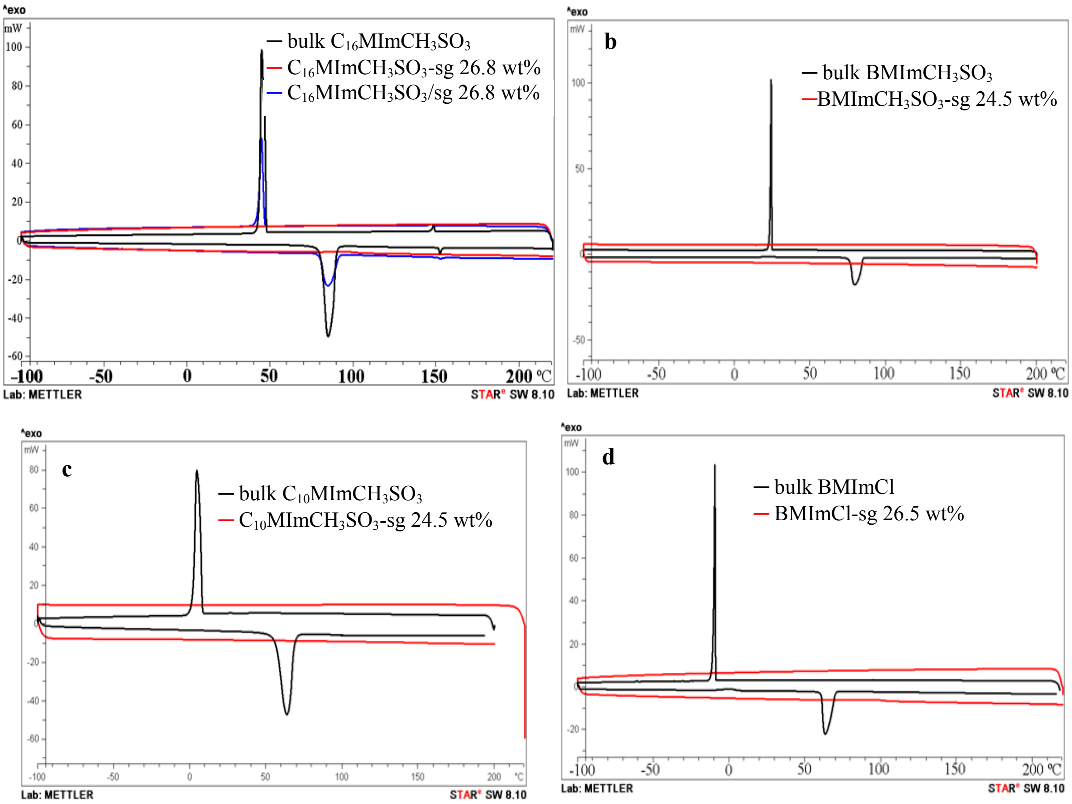

Fig. S5 DSC charts of IL, IL-sg and IL/sg

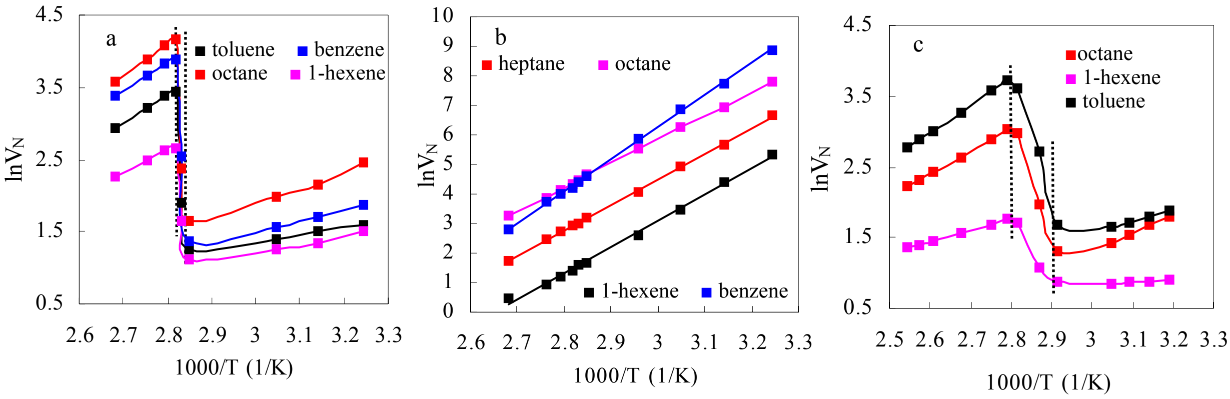

Fig. S6 *ln* (V_N) vs 1/*T* for different probe solutes over (a) $C_{16}MImCH_3SO_3$ coatings on 101 AW support, (b) $C_{16}MImCH_3SO_3$ -sg and (c) $C_{16}MImCH_3SO_3$ /sg

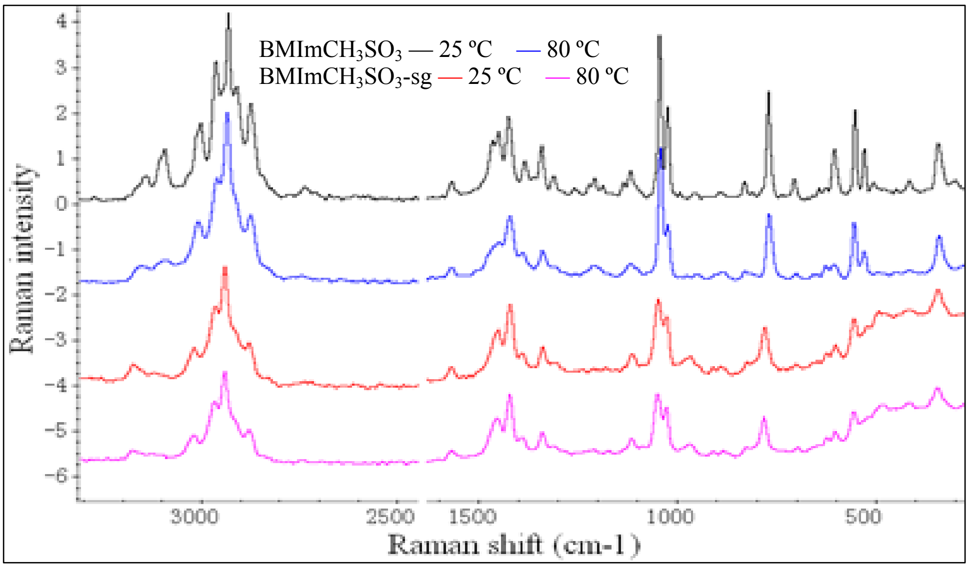

Fig. S7 FT-Raman spectra of BMImCH$_3$SO$_3$-sg compared with bulk ILs with varied temperatures

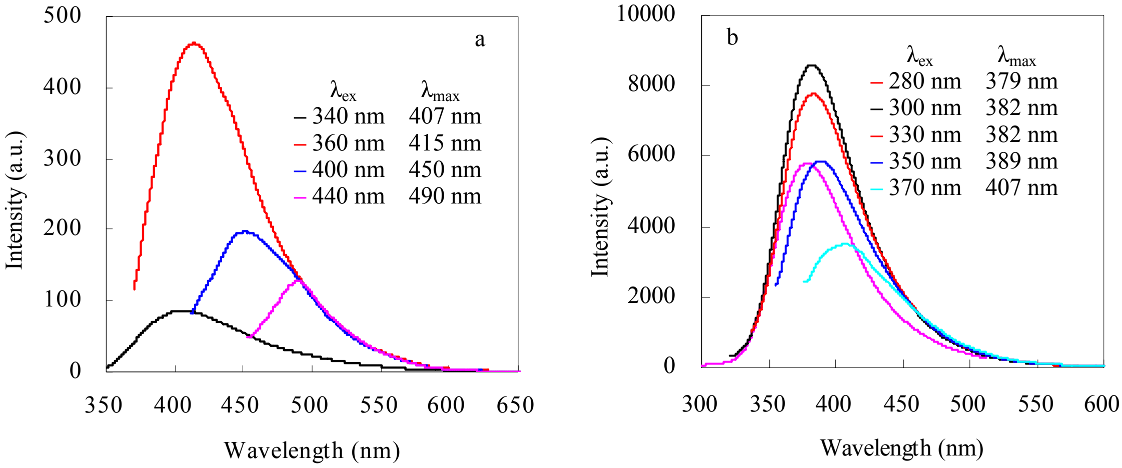

Fig. S8 Fluorescence emissions of (a) bulk BMImN(CN)$_2$ and (b) BMImN(CN)$_2$-sg (IL loading: 25 wt%)

References

(1) *Ionic Liquids in Synthesis.* Wasserscheid, P., Welton, T., Eds. *Wiley-VCH: Weinheim*, Germany, **2003**.

(2) Yang J.; Zhang, Q.; Zhu, L.; Zhang, Sh.; Li J.; Zhang, X.; Deng, Y., *Chem. Mater.* **2007**, *19*, 2544.