Supplementary Material (ESI) for Chemical Communications

Supporting Information

Gelation, Functionalization, and Dispersion of Nanodiamonds with Ionic Liquid

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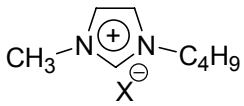
1. Materials: Detonation nanodiamod particles (ND-1) with average diameter of 5 nm, 99% purity, and specific area of 300 m^2/g (purchased from JSC Diamond Center, Russia) were used. All chemicals used as received without further purification. The structure of ionic liquids use in this work described in Figure S1, and they were prepared according to the reported procedure.[1] Ionic liquids contained less than 10 ppm of chlorine in chlorine analysis and less than 15 ppm of water in Karl Fischer analysis (Metrolm Model: 756KF Coulometer).



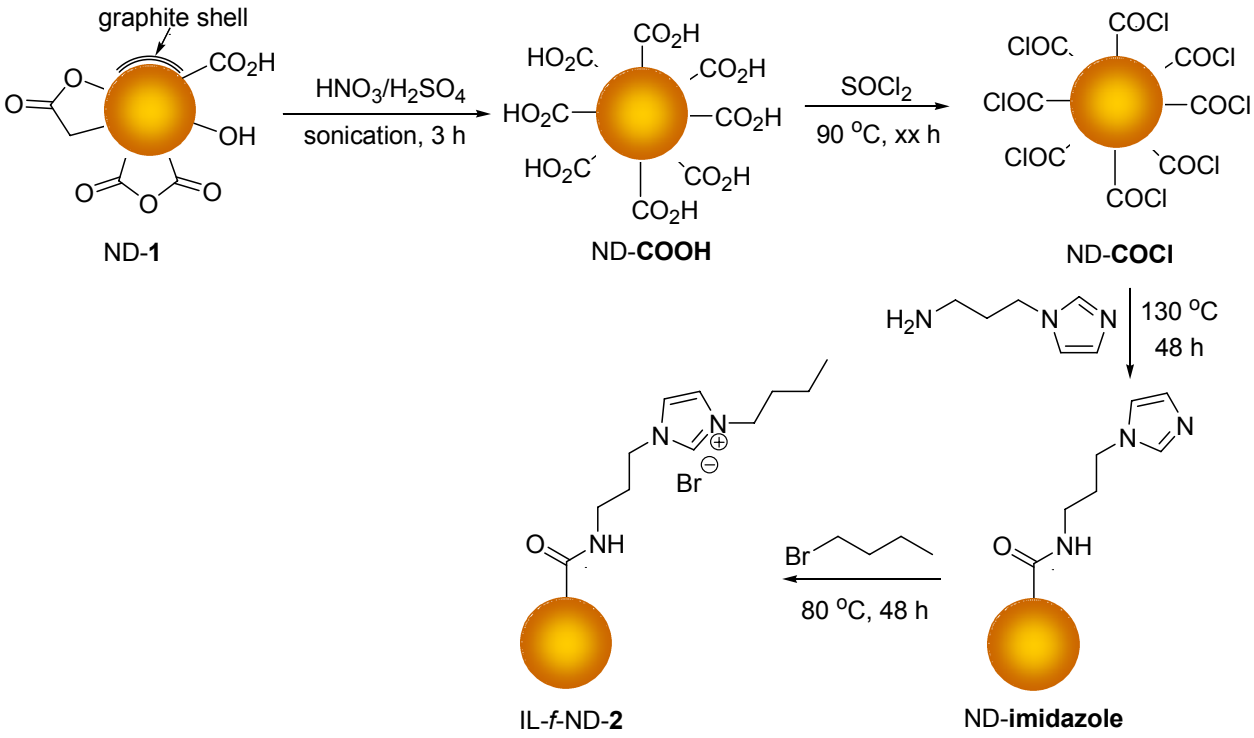
[bmim][X] (X = PF_6, NTf_2, SbF_6, BF_4)

2. Measurements: Fourier transform infrared (FT-IR) spectra were obtained from KBr pallet with a Varian Scimitar Series FT-IR spectrometer. The nuclear magnetic resonance (NMR) spectrum of IL-*f*-ND-2 in D_2O was obtained from Bruker 9503DPx 250 MHz spectrometer. The high resolution scanning transmission electron microscopy (HR-TEM) images were obtained by placing one drop of sample on copper grids coated with carbon using JEM-2100F (JEOL, 200kV). XPS were measured by using Parallel ARXPS System (energy source: monochromated Al-Kα). The AFM images were

[1] J. D. Holbrey, K. R. Seddon, *J. Chem. Soc., Dalton Trans.* **1999**, 2133.

obtained with an imaging cantilever (NCHR, PSIA Co.) on the non-contacting mode at the force constant of 42N/m at 320 kHz, and all nanodiamond samples were prepared by spin coating on silicon wafer with 500 rpm for 30 sec.

3. Preparation of imidazolium bromide-functionalized IL-*f*-ND-2:



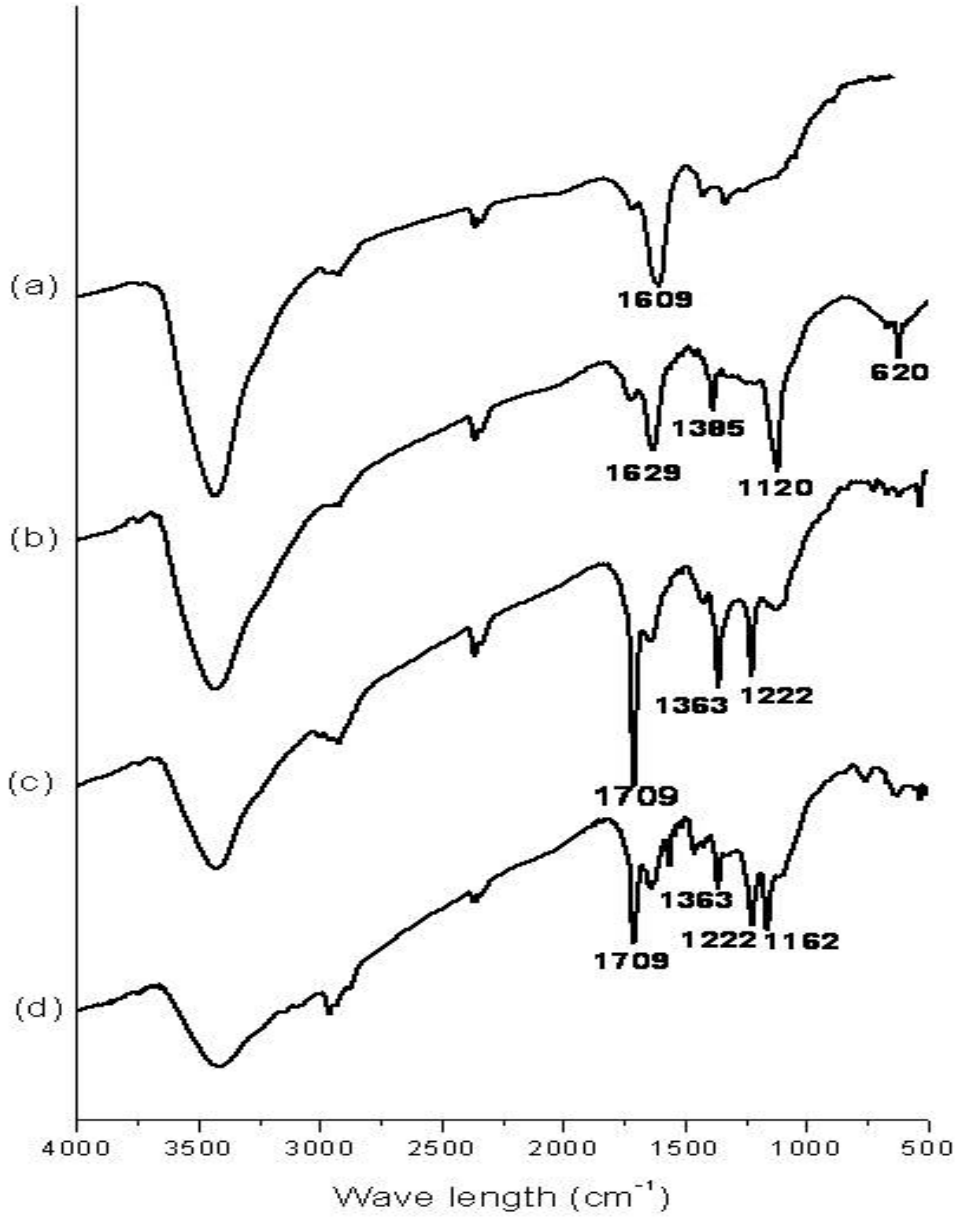
Preparation of ND-COOH: A suspension of detonation nanodiamond particles (ND-1) (100 mg) in a mixture of H_2SO_4 and HNO_3 (60 mL, 3/1, 45 ml/15 ml) was sonicated at 40 ^oC for 3 h. The reaction mixture was poured into distilled water (1 L), and stirred for 10 h at room temperature. After filtration by using polycarbonate membrane filter (Pore size 0.2 μm), the filter-cake was washed with distilled water several times, and dried at 80 ^oC for 12 h to provide carboxylic acid-functionalized nanodiamond particles (ND-COOH) (94 mg).

Preparation of ND-COCl: A solution of ND-COOH (85 mg) in $SOCl_2$ (30 mL) was refluxed under nitrogen atmosphere for 48 h. Excess $SOCl_2$ was distilled off under reduced pressure to give the acid chloride-functionalized ND-COCl, which used directly for next reaction.

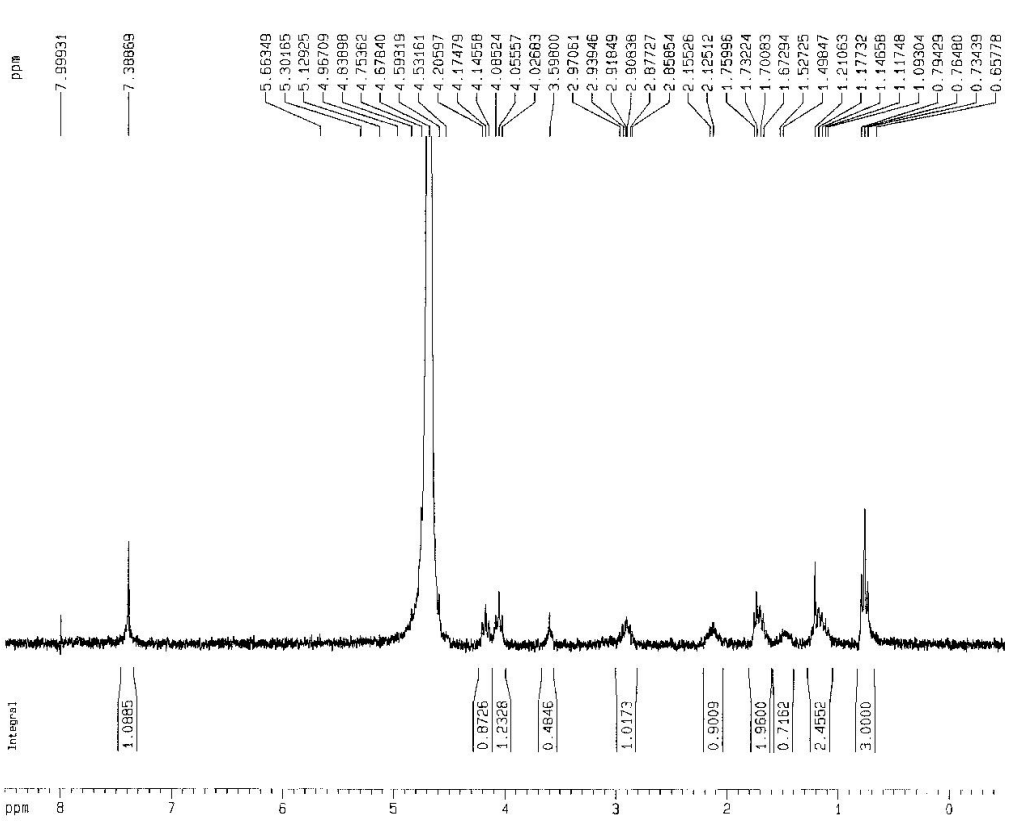
Preparation of ND-imidazole: A mixture of ND-COCl prepared above and 3-aminopropylimidazole (25 mL) was stirred at 130 ^oC for 48 h under nitrogen atmosphere. The mixture was diluted with anhydrous THF, and filtered through polycarbonate membrane (0.2 μm, Milipore). To remove non-covalently attached aminopropylimidazole, the filter-cake was stirred with 1N HCl solution, and then neutralized with saturated Na_2CO_3 solution and successively washed with H_2O, THF and acetone, and finally dried at 80 ^oC for 12 h to afford imidazole-functionalized ND-imidazole (77 mg).

Preparation of nButylimidazolium bromide-functionalized IL-*f*-ND-2: A mixture of ND-imidazole (70 mg) and 1-bromobutane (30 mL) was stirred at 80 oC for 36 h under nitrogen atmosphere, and filtered, after cooling to room temperature, through polycarbonate membrane (pore size: 0.2 μm, Milipore). The filter-cake was washed with THF several times to remove excess of 1-bromobutane, and dried at 80 ^oC for 12 h to afford IL-*f*-ND-2 (66 mg).

4. FT-IR spectra of (a) detonation NDs, (b) ND-COOH, (c) ND-imidazole, (d) IL-*f*-ND-2:



5. ^{1}H NMR spectrum of IL-*f*-ND-2: Due to the hydrophilic nature of the imidazolium bromide, the IL-*f*-ND-2 is partially soluble in D_2O allowing ^{1}H NMR analysis. The characteristic imidazolium proton at 8.0 and 7.4 ppms as well as methylene and methyl protons signals clearly indicated formation of imidazolium bromide.

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PROCNO                  1

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PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     32
DS                      0
SWH               4990.020 Hz
FIDRES            0.076142 Hz
AQ                6.5667572 sec
RG                   912.3
DW                 100.200 use
DE                   6.00 use
TE                    0.0 K
D1                1.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 =======
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PL1                 -3.00 dB
SFO1           250.1320010 MHz

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SSB                     0
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GB                      0
PC                   1.00

1D NMR plot parameters
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F1                 2126.11 Hz
F2P                -0.500 ppm
F2                 -125.06 Hz
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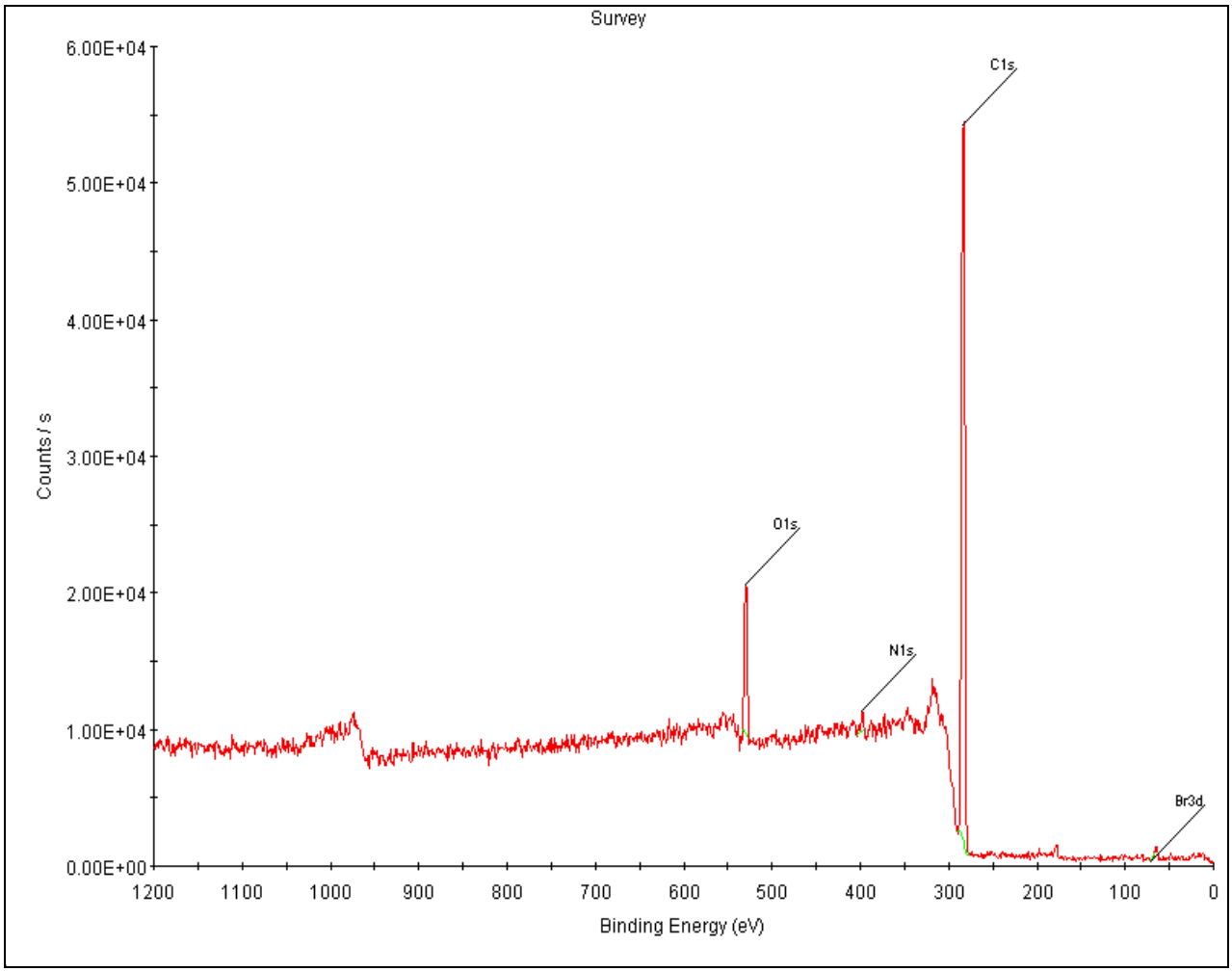
6. XPS of IL-*f*-ND-2:



7. Photographs of the ND-1 gels formed with different ionic liquids after centrifugation at high speed (13000 rmp) for 3 h.

To investigate the gelation of ND-**1** particles with ionic liquids, the 1.25-5 wt% of ND-**1** particles with an ionic liquid were ground for 15 min in an agate mortar and a pestle. During this time the suspension turned viscous, affording a gel. Centrifugation at 13000 rpm for 3 h, the gel and ionic liquid phases were clearly separated from each other. However, under this condition, it does not take a lot of fine ND particles to gel, and showed pony-tail gel as shown in following photos.

[bmim][NTf_2]	**[bmim][SbF_6]**
	
[bmim][PF_6]	**[bmim][BF_4]**
	

A suspension of ND-**1** (5 mg) in [bmim][NTf_2] (100 mg, 200 mg, 300 mg, 400 mg, and 500 mg, from left to right) was mixed in an agate mortar with a pestle for 15 min, and centrifuged at 13000 rpm for 3 h. For other ionic liquids, 100mg, 200 mg, and 300 mg of ionic liquid was used (from left to right).

8. Photographs of the ND-1 gels formed with [bmim][PF6] after centrifugation at low speed (1200 rmp) for 1 min.

After pointed this point by referee, the ND-**1** particles (2, 5, 7, and 10 wt%) in [bmim][PF_6] were ground for 5 min, and the resulting gel was centrifuged at 1200 rpm for 1 min, in which only the 10 wt% concentration of ND-**1** can trap all ionic liquid.

A suspension of 2 wt%, 5wt%, 7wt%, and 10wt% of ND-**1** (from left) in [bmim][PF_6] was mixed in an agate mortar with a pestle for 5 min, and centrifuged at 1200 rpm for 1 min.

9. A example of fabrication of the ND-1 gel

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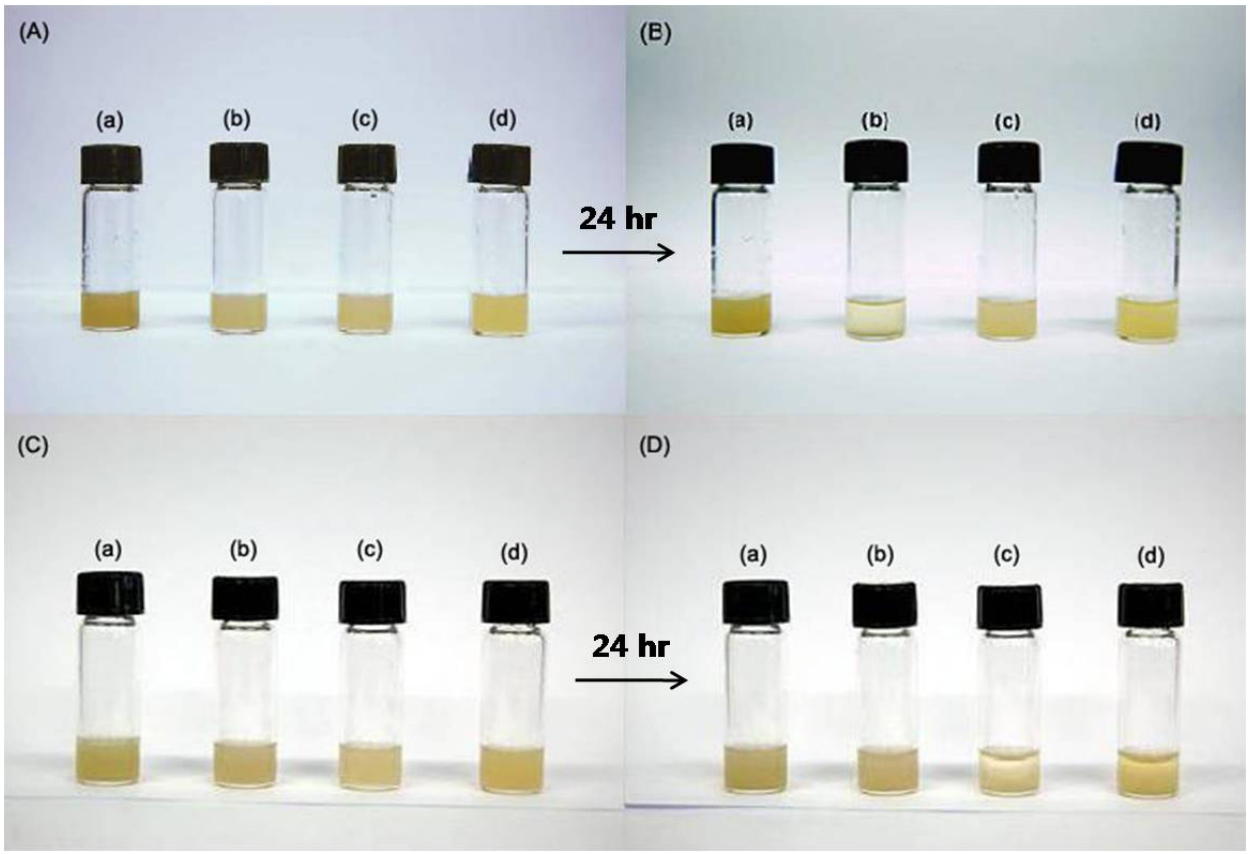
10. Photos for the solution of ND-1 and IL-f-ND-2 in different ionic liquids

Photographs of (A) ND-1 (1 mg) dispersed in the ionic liquids (1 mL) and (B) after 24 h standing: (a) [bmim][PF_6], (b) [bmim][NTf_2], (c) [bmim][SbF_6], and (d) [bmim][BF_4] and (C) IL-*f*-ND-2 (1 mg) dispersed in the ionic liquids (1 mL) and (D) after 24 h: (a) [bmim][PF_6], (b) [bmim][SbF_6], (c) [bmim][NTf_2], and (d) [bmim][BF_4].



10. Details for dynamic light scattering (DLS) methods

DLS data were obtained by Scatteroscope I (Qudix, Inc.). We directly used the particle size distribution generated by the software (scatteroscope 1.3 version) from the DLS manufacturer. The viscosities of ionic liquids were obtained from the literature.

Viscosity data for ionic liquids at 298K (reference: Green Chem, 2001, 3, 156)

[bmim][BF4]: 219 cP , [bmim][PF6]: 450 cP, [bmim][NTf2]: 69 cP

[bmim][SbF6]: 108 cP (reference Electroanal Chem. 2004, 568, 167)