Supplementary Material (ESI) for Green Chemistry

Switching the basicity of ionic liquids by CO_2

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Supporting Information

Experimental

Materials The indicators, 4-Nitrobenzylcyanide (Acros Organics) and 2,5-dinitrophenol (Merk) were used as received. N-methylimidazole and potassium tetrafluoroborate were purchased from Acros Organics. 1,1,3,3-tetramethylguanidine, perchloric acid, choline chloride, urea and all organic solvents were A.R. grade and supplied by Beijing Chemical Reagents Company. 2-Bromoethylamine hydrobromide was a product of Shanghai Nanxiang Reagent Co., Ltd. N-methylimidazole and 1,1,3,3-tetramethylguanidine were redistilled before use. Solvents were dried over 3Å molecular sieves.

Preparation of ILs All used ionic liquids were synthesized following procedures reported in the literature.[S1-S4] [TMG][ClO_4] was prepared by neutralizing 1,1,3,3-tetramethylguanidine and perchloric acid in ethanol.[S1] CH/urea was prepared simply by heating mixture of choline chloride and urea with a molar ratio of 1 : 2 at 80 °C until a homogeneous liquid was formed.[S2] [AEMIM][BF_4] was prepared by reacting 1-methylimidazol with 2-bromoethylamine hydrobromide, and then metathesizing with potassium tetrafluoroborate.[S3] [BMIM][BF_4] was prepared by reacting 1-methylimidazol with chlorobutane.[S4] All ionic liquids were dried under vacuum for at least 24 h at 70 °C prior to use. The water content in the ILs was below 100 ppm, as analyzed by Karl Fischer titration.

UV-Vis measurement The apparatus and experimental procedures were similar to those reported previously.[S5] It consisted mainly of a gas cylinder, a pressure gauge, an UV-Vis spectrometer and a temperature-controlled UV cell. UV-Vis spectrophotometer was produced by Beijing General Instrument Company (Model TU-1910, resolution: 0.1 nm). The high-pressure UV cell was composed mainly of a stainless steel body, two quartz windows, a stirrer, and a temperature controlling system. The optical path length and the inner volume of the cell were 1.32 cm and 1.74 cm^3, respectively. In a typical experiment, known amount of solution of the probe in ethanol was transferred to a high-pressure UV cell. The cell was flushed with nitrogen to remove the ethanol. Then an appropriate amount of IL or IL/water mixture was transferred into the cell in a glove box. The temperature of the cell was kept at 25 ± 1°C. The sample in the cell was stirred to promote equilibration. The measurement was done after complete equilibration, which was confirmed by the fact that the UV–vis absorption spectrum was not changed with time. All the spectra have been corrected by subtraction the absorption of the corresponding samples without indicators. In the presence of CO_2, the procedures were similar as described above. The main difference was that CO_2 was charged to the cell. The equilibration time for the IL/CO_2 mixtures was affected by the stirring speed and the viscosity of ILs. Generally, CH/urea could be equilibrated in half an hour while it takes about an hour for [AEMIM][BF_4].

$H_–$ measurement of ILs during the cycles of treatment with CO_2 and N_2 Upon bubbling CO_2 through the ILs in a test tube of 10 mL, appropriate amounts of ILs were taken at intervals and the corresponding $H_–$ values were determined. After the $H_–$ value remained constant, N_2 was introduced to recover the ILs. The gas flow rate was about 40 ml/min at ambient pressure. The operation was repeated three times for each ILs. 25 min and 45 min were enough for CH/urea to reach equilibration under bubbling CO_2 and N_2, separately. For [AEMIM][BF_4], the equilibration time was about 90 min and 180 min under CO_2 and N_2 treatment, separately.

References

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