NMR Characterization of Three New Ionic Liquids

Triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium formate (12, [Me(OEt)3-Et3N][HCOO]):
$^1$H NMR (300 MHz, CDCl$_3$, [ppm]): $\delta = 1.37$ (t, 9H, N(CH$_2$CH$_3$)$_3$, $J = 7.2$ Hz), 3.36 (s, 3H, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$), 3.61 (m, 4H, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$), 3.68 (m, 2H, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$), 8.85 (s, 1H, HCOO). $^{13}$C-NMR (DMSO-d$_6$, [ppm]) $\delta = 7.78, 53.3, 56.2, 58.6, 64.1, 70.0, 70.3, 71.8, 165.6$.

1-ethyl-3-(2-(2-methoxyethoxy)ethoxy)ethyl)-2-methylimidazolium acetate (18, [Me(OEt)3-Me-Et-Im][OAc]). $^1$H-NMR (400 MHz, DMSO-d$_6$, [ppm]) $\delta = 1.30$ (3H, t, CH$_3$CH$_2$N, $J = 3.8$ Hz), 1.49 (3H, s, CH$_3$CN), 2.62 (3H, s, CH$_3$COO), 3.20 (3H, s, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$), 3.34-3.49 (8H, m, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$), 3.70 (2H, t, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$, $J = 5.2$ Hz), 4.19 (2H, q, CH$_3$CH$_2$N, $J = 7.2$ Hz), 4.36 (2H, t, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$, $J = 4.8$ Hz), 7.86 (1H, d, NCHCHN, $J = 2.1$), 7.92 (1H, d, NCHCHN, $J = 2.1$). $^{13}$C-NMR (DMSO-d$_6$, [ppm]) $\delta = 9.70, 15.4, 26.7, 43.2, 47.9, 58.6, 69.2, 70.0, 70.1, 70.2, 70.3, 71.8, 121.4, 122.4, 144.7, 173.1$.

1-ethyl-3-(2-(2-methoxyethoxy)ethoxy)ethyl)imidazolium dicyanamide (19, [Me(OEt)$_3$-Et-Im][dca]). $^1$H-NMR (400 MHz, DMSO-d$_6$, [ppm]) $\delta = 1.41$ (3H, t, CH$_3$CH$_2$N, $J = 4.1$ Hz), 3.20 (3H, s, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$), 3.39 (2H, m, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$), 3.43-3.54 (6H, m, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$), 3.75 (2H, t, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$, $J = 4.8$ Hz), 4.20 (2H, q, CH$_3$CH$_2$N, $J = 7.2$ Hz), 4.31 (2H, t, NCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$OCH$_3$, $J = 6.0$ Hz), 7.71 (1H, m, NCHCHN), 7.76 (1H, m, NCHCHN), 9.10 (1H, s, NCHN). $^{13}$C-NMR (DMSO-d$_6$, [ppm]) $\delta = 15.6, 44.7, 49.3, 58.6, 68.6, 70.1, 70.3, 71.8, 122.4, 123.3, 136.5$.

NMR Characterization of Glucose Laurate

$^1$H NMR (300 MHz, CDCl$_3$, [ppm]) $\delta = 0.87$ (3 H, t, -CH$_3$), 1.25 (16 H, m, aliphatic CH$_2$), 1.62 (2 H, m, -O$_2$CCH$_2$CH$_2$), 2.32 (2 H, t, -O$_2$CCH$_2$), 3.5-5.0 (7H, m, glucose H2-H6), 5.50 (1H, d, glucose H1). The glucose hydrogen signals have been assigned by a literature.$^1$

$^{13}$C NMR (75.6 MHz, CDCl$_3$, [ppm]) $\delta$(C-1) = 90.8, $\delta$(C-2) = 70.7, $\delta$(C-3) = 72.0, $\delta$(C-4) = 69.4, $\delta$(C-5) = 63.7, $\delta$(C-6) = 59.1, $\delta$(C-1') = 178, $\delta$(C-2') = 33.8, $\delta$(C-3') = 32.0, $\delta$(C-4' – C-9') = 29.5, $\delta$(C-10') = 24.8, $\delta$(C-11') = 22.8, $\delta$(C-12') = 14.2 (chloroform 77.1 ppm). Glucose-$^{13}$C$_6$ laurate was used for $^{13}$C NMR spectrum.

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Table S.1 Assignments of infrared amide I band components of proteins

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References

Infrared Spectra of Free CALB in ILs

(a) [OMIM][OAc] (8)

(b) [EMIM][EtSO₄] (9)
Figure S.1 Second derivative ($d^2A/d\nu^2$) spectra of free CALB in water (dashed line) and in ILs (solid lines, with different incubation times at 50 °C).

(c) $[\text{Me}(\text{OE}t)_3\text{-Et}_3\text{N}][\text{HCOO}]$ (12)
(d) $[\text{BMIM}][\text{dca}]$ (6)
Fluorescence Spectra of Free CALB in ILs

Figure S.2 Fluorescence emission spectra of free CALB in water and ILs at 50 °C (a Varian Eclipse BioMelt™ fluorescence spectrophotometer was used to excite the lipase at 295 nm, and the emission maximum of tryptophan (Trp) residues was observed at 325 nm in water. The enzyme concentration was 0.1 mg/mL.).
Figure S.3 $^{13}$C NMR spectra of D-glucose-$^{13}$C$_6$ in D$_2$O and IL 3

(a) D-glucose in D$_2$O

(b) D-glucose in [Me(OEt)$_3$-Et-Im][OAc] (3) for 30 min at r.t.

(c) D-glucose in [Me(OEt)$_3$-Et-Im][OAc] (3) for 52 days at r.t.
Figure S.4 $^{13}$C NMR spectra of D-glucose-$^{13}$C$_6$ in D$_2$O and IL 4