Electronic Supplementary Information

Excited-State Prototropism of 7-Hydroxy-4-methylcoumarin in [$C_n$mim][BF_4] Series of Ionic Liquid-Water Mixtures: Insights on Reverse Micelle-like Water Nanocluster Formation

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Note S1: Materials, Synthesis and ^{1}H NMR of the [$C_n$mim][BF_4] series of ionic liquids

Materials:

The chemicals, 1-methylimidazole, bromoethane, 1-bromobutane, 1-bromohexane, 1-bromooctane and 1-bromodecane were purchased from Sigma Aldrich and were distilled prior to use. Sodium tetrafluoroborate salt was used as obtained from Sigma Aldrich.

Synthesis of the ionic liquids:

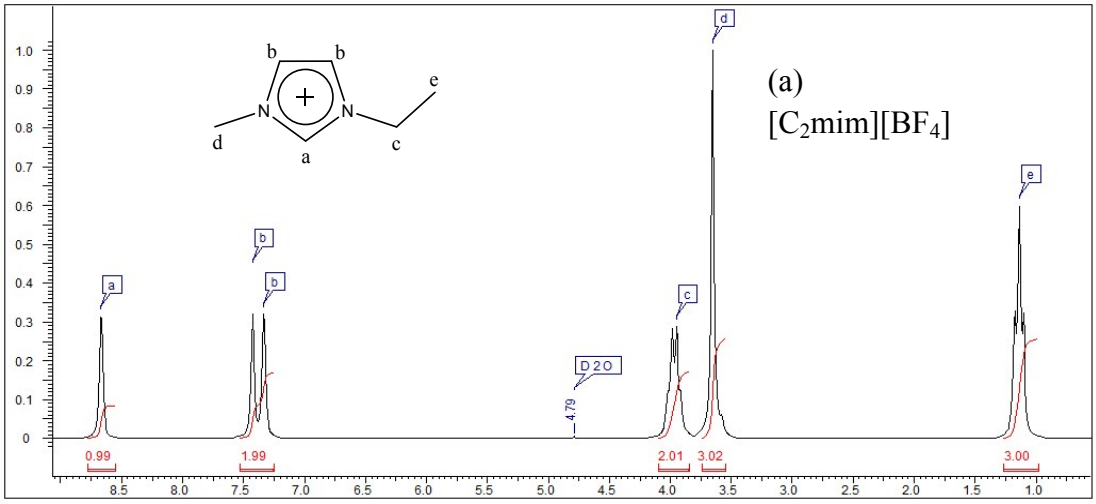
The synthesis of the 1-alkyl-3-methylimidazolium tetrafluoroborate ([$C_n$mim][BF_4]) ionic liquids, with n = 2, 4, 6, 8 and 10, was carried out as per the previously reported literature procedures.[1-5] First, the 1-bromoalkanes were added (in 1.2 molar ratio) to 1-methylimidazole and the reaction mixture was refluxed at 60°C to 70°C for 12 to 16 h. This reaction is called quarternisation reaction and results in the formation of 1-alkyl-3-methylimidazolium bromide ([$C_n$mim]Br) ionic liquids. Excess of the 1-bromoalkanes was removed by repeated washing of the reaction mixture with ethyl acetate. The leftover impurities were removed with the help of

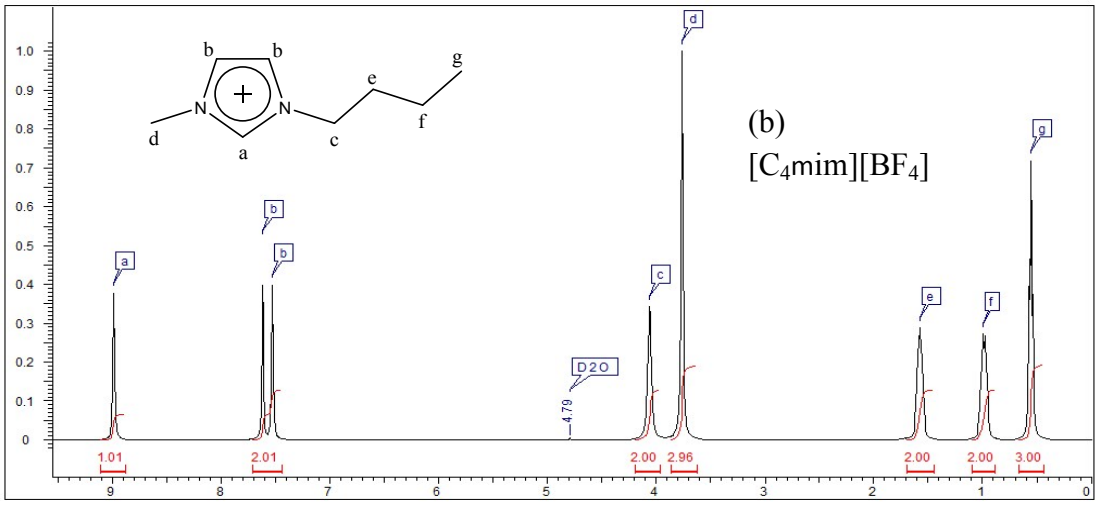
rota-vapor followed by ultrahigh vacuum treatment at 70°C for 6-8 h. The [$C_n$mim]Br ionic liquids thus obtained were used as intermediates to synthesize the [$C_n$mim][BF_4] ionic liquids via anion exchange or metathesis reaction. For this, the Na[BF_4] salt was added in 1.2 molar ratio to the [$C_n$mim]Br ionic liquids dissolved in DCM, which acts as solvent for the reaction. The reaction mixture was allowed to stir for about 24 h at room temperature. After the completion of reaction, excess Na[BF_4] and NaBr salts were filtered out using Büchner funnel via celite using DCM as the solvent. Subsequently, DCM and other remaining impurities were removed by rota-vapor followed by ultrahigh vacuum treatment at 60-65°C for 8-10 h.

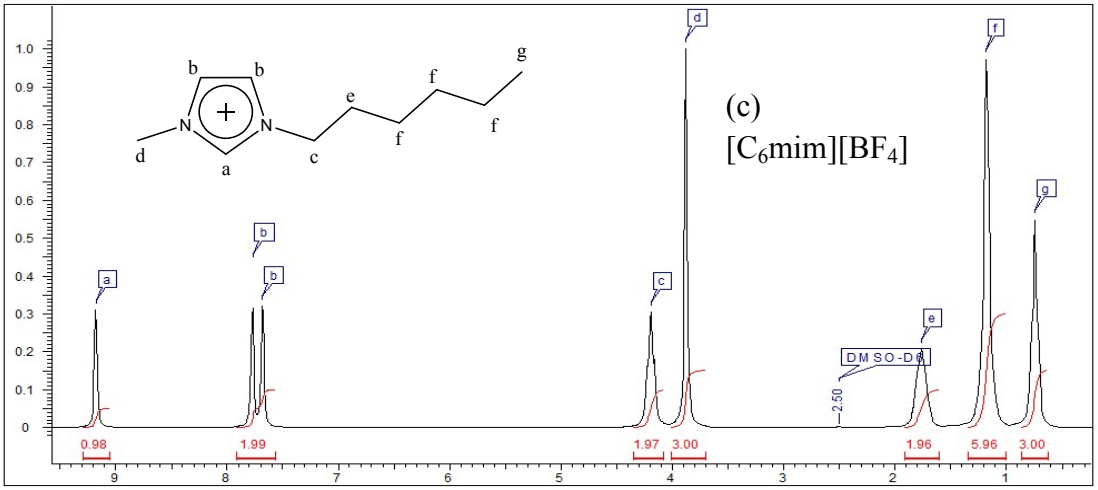
Characterization of the ionic liquids:

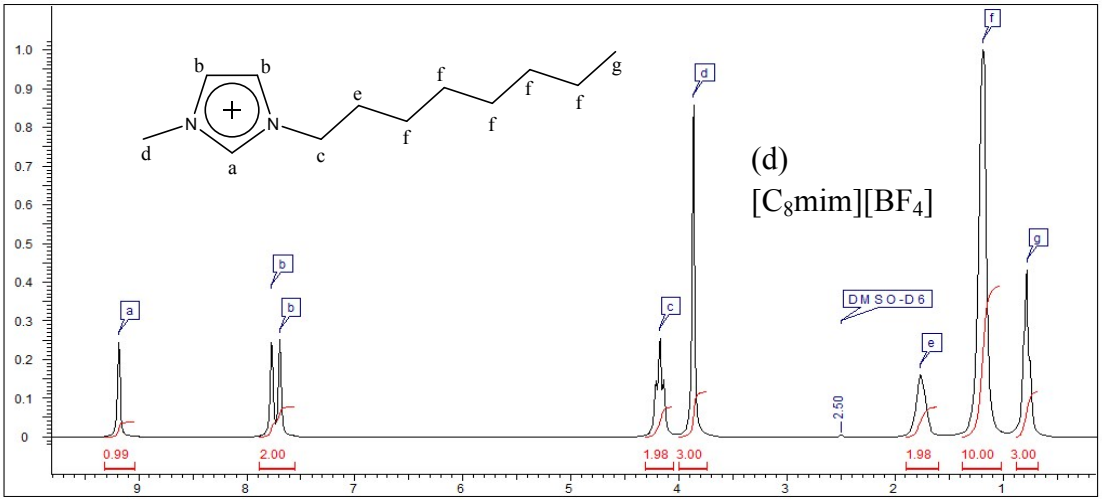
The characterization of the ionic liquids was performed with the help of ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of the ionic liquids were recorded with the help of 200 MHz spectrometer from Bruker India Pvt. Ltd. The NMR spectra for the synthesized [$C_n$mim][BF_4] ionic liquids are shown in **Figure S1**.

The halide contents of the ionic liquids were estimated with the help of standard Volhard titration method using a chloride selective electrode and were found to be less than 30 ppm for all the ionic liquids.[6] Water contents of the ionic liquids were recorded with the help of Karl Fisher Coulometer and were found to be in the range of 200-300 ppm for all the ionic liquids.




(b)
[C4mim][BF4]
D2O
4.79
1.01
2.01
2.00
2.96
2.00
2.00
3.00


(c)
[C6mim][BF4]
DMSO-D6
2.50
0.98
1.99
1.97
3.00
1.96
5.96
3.00


(d)
[C8mim][BF4]
DMSO-D6
2.50
0.99
2.00
1.98
3.00
1.98
10.00
3.00

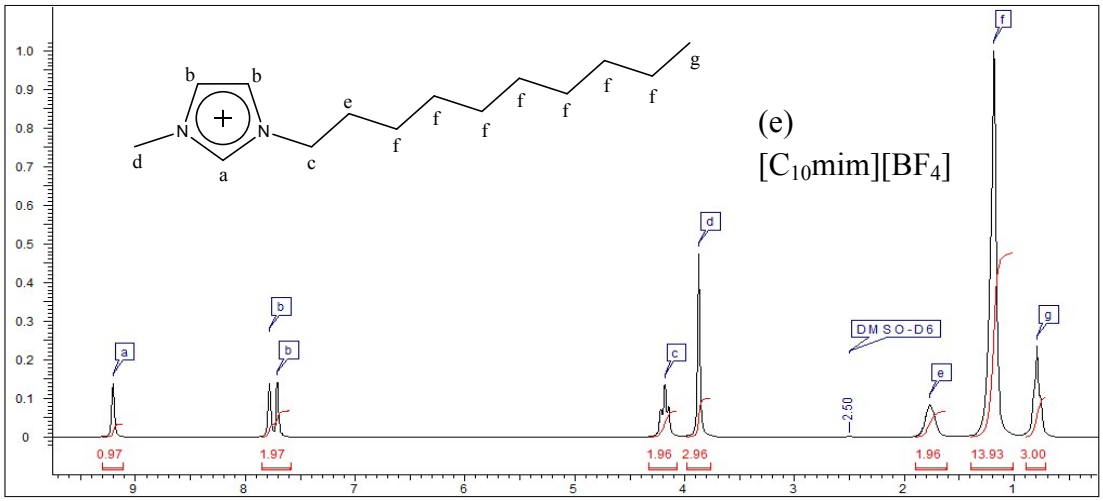


Fig. S1. The ^{1}H NMR spectra of the $[C_nmim][BF_4]$ series of the IL solvents: (a) $[C_2mim][BF_4]$, (b) $[C_4mim][BF_4]$, (c) $[C_6mim][BF_4]$, (d) $[C_8mim][BF_4]$ and (e) $[C_{10}mim][BF_4]$.

Table S1. Molecular weights and densities of the studied ionic liquids.

IL	Molecular weight	Density (g/cm^3)
$[C_2mim][BF_4]$	197.97	1.294
$[C_4mim][BF_4]$	226.02	1.210
$[C_6mim][BF_4]$	254.08	1.149
$[C_8mim][BF_4]$	282.13	1.120
$[C_{10}mim][BF_4]$	310.18	1.070

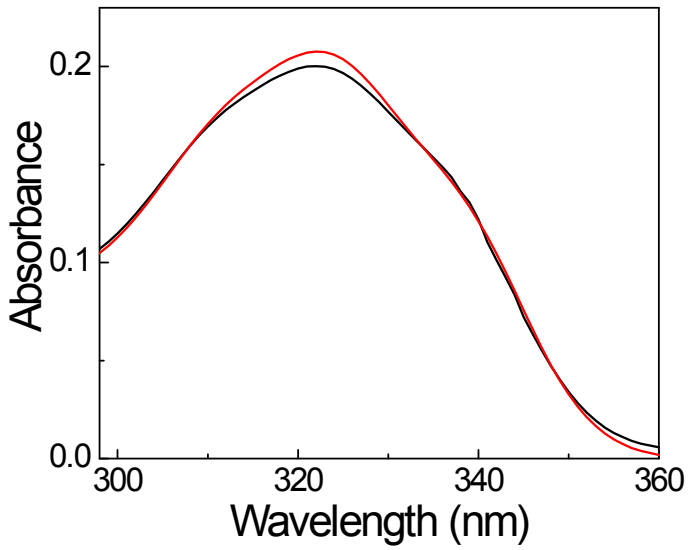


Fig. S2. Representative absorption spectra of 7H4MC in $[C_8mim][BF_4]$ at w_0=1 (black) and 1.2 (red).

References

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