

Supporting information

Experimental determination of solvation free energy of protons in non-protic ionic liquids using Raman spectroscopy

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1. Synthesis of the ionic liquids

First, the 1-alkyl-3-methylimidazolium bromide (either [EMIm]Br, [BMIm]Br or [OMIm]Br) was prepared by quaternization of 40 mL of freshly distilled MIm in 150 mL of AN by introducing, dropwise and at reflux under argon atmosphere, the corresponding alkyl bromide (1.05 equivalent of either bromoethane, 1-bromobutane or 1-bromooctane). The mixture was maintained at room temperature for 24h, then heated to 60°C for another 24h to ensure the completion of the reaction. The [EMIm]Br and the [BMIm]Br were obtained as solids by adding AE (antisolvent) at 60°C until the precipitation started, then the mixture was let to cool down to room temperature. The solids were filtered and washed with freshly-distilled cold AE under inert atmosphere then ¹ by recrystallisation in a mixture of AE and AN. The purified solids were then dried under vacuum (10^{-2} mbar) at 50°C overnight. The precursors were obtained as white solids. [OMIm]Br was obtained as a viscous oil and was purified² by first evaporating the solvent, then washing the oil with fresh portions of AE (antisolvent, 6 x 100 mL). The [OMIm]Br was finally dried overnight under vacuum at 70°C to remove the traces of AE.

Second, the three ionic liquids were obtained by exchanging³ the bromide with the bistriflimide anion. 1.1 equivalent of LiNTf₂ was added to ~15 g of the bromide imidazolium (either [EMIm]Br, [BMIm]Br or [OMIm]Br) and dissolved in 100 mL of DCM under inert atmosphere. The reaction mixture was stirred at room temperature for 48h. The suspension was then filtered to eliminate the LiBr (washed with three fractions of fresh DCM). The collected fractions of DCM containing the ionic liquid were washed with tridistilled water until no bromide was detected in the aqueous phase by precipitation with AgNO₃. The DCM was then evaporated under vacuum to isolate the ionic liquids (either [EMIm][NTf₂], [BMIm][NTf₂] or [OMIm][NTf₂]) that were further dried under vacuum at 60°C for 5 days.

2. Preparation of acidic solutions of HNTf₂ in the synthesized [BMIm][NTf₂]

A series of acidic solutions of HNTf₂ in the synthesized [BMIm]NTf₂ were prepared by adding increasing amounts of HNTf₂ to a certain amount of the ionic liquid (Table S1).

Table S1. Preparation of acidic solutions of HNTf₂ in the synthesized [BMIm][NTf₂]. These solutions were used for the determination of the solvation number of protons in this ionic liquid. m_{IL} is the mass of [BMIm][NTf₂], m_{HNTf_2} and x_{HNTf_2} are respectively the mass and the molar fraction of HNTf₂.

Samples	m_{IL} (mg)	m_{HNTf_2} (mg)	x_{HNTf_2}
S01	728.2	1149	0.703
S02	726.7	721.2	0.603
S03	724.5	470.3	0.495
S04	724.3	389.3	0.448
S05	723.1	348.8	0.418
S06	722.3	285.9	0.373
S07	720.4	242.9	0.333
S08	717.2	195.2	0.287
S09	717.0	167.3	0.259
S10	716.1	142.8	0.226
S11	715.3	122.1	0.202
S12	714.0	99.5	0.171
S13	707.3	48.8	0.091

3. Preparation of acidic solutions of concentrated 2,6-dichloro-4-nitroaniline (51.17 mM) in commercial [BMIm][NTf₂]

A concentrated stock solution of pH-reporter (R) was obtained by dissolving 59.6 mg of 2,6-dichloro-4-nitroaniline in 8.0453 g of commercial [BMIm][NTf₂] to obtain a solution with a concentration in pH-reporter $[R]_{\text{Conc}} = 51.17$ mM. A series of acidic solutions, with increasing concentrations of strong acid were prepared from the concentrated stock solution to guarantee that the concentration of pH-reporter remains constant, by adding increasing amounts of HNTf₂ to a certain amount of stock solution (Table S2).

Table S2. Preparation of acidic solutions from the concentrated stock solution of 2,6-dichloro-4-nitroaniline in commercial [BMIm][NTf₂]. These solutions were used for the determination of the Hammett acidity function by Raman spectroscopy. m_{CR} is the mass of the concentrated stock solution of 2,6-dichloro-4-nitroaniline (C and R stand for concentrated and reporter, respectively), m_{HNTf_2} and $[\text{HNTf}_2]$ are respectively the mass and the concentration of HNTf₂ (a strong acid in that medium).

Samples	m_{CR} (mg)	m_{HNTf_2} (mg)	$[\text{HNTf}_2]$ (mM)
C01	565.2	23.6	212.4
C02	566.6	13.1	117.6
C03	605.0	9.9	83.2
C04	588.5	4.7	40.6
C05	515.8	3.8	37.4
C06	479.6	2.1	22.5
C07	637.1	1.7	13.8

4. Preparation of acidic solutions of diluted 2,6-dichloro-4-nitroaniline (531.3 μM) in commercial [BMIm][NTf₂]

A diluted stock solution of pH-reporter was obtained by diluting 605.7 mg of the concentrated stock solution with 5.4045 g of fresh commercial [BMIm][NTf₂] to obtain a solution with a concentration in pH-reporter $[\text{R}]_{\text{Dil}} = 531.3 \mu\text{M}$. Again, a series of acidic solutions, with increasing concentrations of strong acid were prepared from that diluted stock solution of pH-reporter and an acidic stock solution containing 56.5 mM of HNTf₂ (Table S3).

Table S3. Preparation of acidic solutions from the diluted stock solution of 2,6-dichloro-4-nitroaniline in commercial [BMIm][NTf₂]. These solutions were used for the determination of the Hammett acidity function by Raman spectroscopy. m_{DR} is the mass of the diluted stock solution of 2,6-dichloro-4-nitroaniline (D and R stand for diluted and reporter, respectively), m_{HNTf_2} and $[\text{HNTf}_2]$ are respectively the mass and the concentration of HNTf₂ (a strong acid in that medium), m_{D1} is the mass of solution D1.

Samples	m_{DR} (mg)	m_{HNTf_2} (mg)	m_{D1} (mg)	$[\text{HNTf}_2]$ (mM)
D1	2475	27.4	0.0	56.5
D2	333.2	0.0	358.1	29.2
D3	369.5	0.0	252.0	22.8
D4	542.8	0.0	187.2	16.5
D5	461.7	0.0	186.6	16.2
D6	587.3	0.0	76.8	6.5

5. Hammett acidity function of acidic solutions of 2,6-dichloro-4-nitroaniline (74.22 mM) in synthesized [BMIm][NTf₂]

A stock solution of pH-reporter was obtained by dissolving 56.0 mg of 2,6-dichloro-4-nitroaniline in 5.2117 g of synthesized [BMIm][NTf₂] to obtain a solution with a concentration in pH-reporter of 74.22 mM. A series of acidic solutions, with increasing concentrations of strong acid, were prepared from that 74.22 mM stock solution of pH-reporter and an acidic stock solution containing 157.3 mM or 41.6 mM of HNTf₂ (Table S4).

Table S4. Preparation of acidic solutions from the 74.22 mM stock solution of 2,6-dichloro-4-nitroaniline in synthesized [BMIm][NTf₂]. These solutions were used for the determination of the Hammett acidity function by Raman spectroscopy. m_{BR} is the mass of the 74.22 mM solution of 2,6-dichloro-4-nitroaniline (B and R stand for [BMIm][NTf₂] and reporter, respectively), m_{HNTf_2} and $[HNTf_2]$ are respectively the mass and the concentration of HNTf₂, m_{B1} is the mass of solution B1, and m_{B5} is the mass of solution B5.

Samples	m_{HNTf_2} (mg)	m_{BR} (mg)	m_{B1} (mg)	m_{B5} (mg)	$[HNTf_2]$ (mM)
B1	49.2	1590.4	0.0	0.0	157.3
B2	0.0	134.9	291.5	0.0	107.6
B3	0.0	215.9	213.4	0.0	78.5
B4	0.0	282.9	152.8	0.0	55.2
B5	0.0	951.6	342.5	0.0	41.6
B6	0.0	105.8	0.0	320.1	31.3
B7	0.0	210.9	0.0	220.0	21.3
B8	0.0	263.7	0.0	160.9	15.8
B9	0.0	486.7	0.0	166.6	10.6

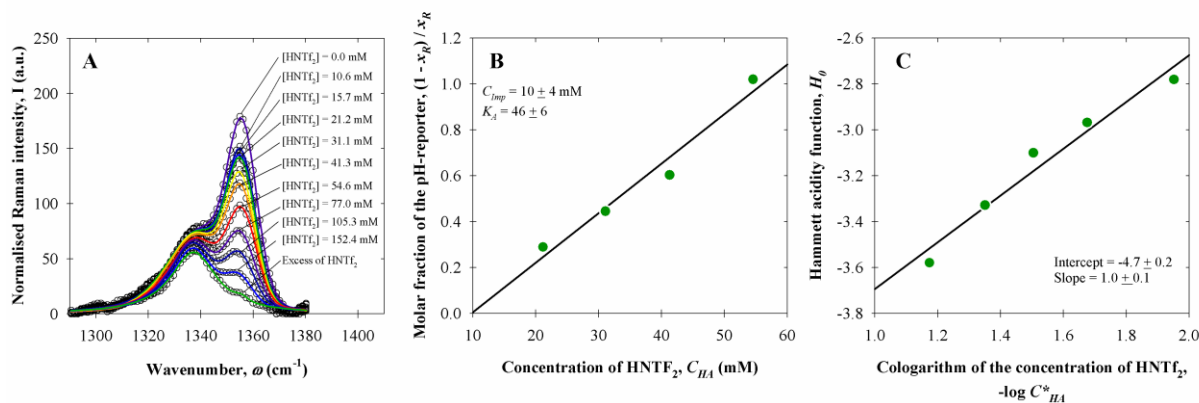


Figure S1. (A) Raman spectra obtained for the solutions containing 74.22 mM of the pH-reporter 2,6-dichloro-4-nitroaniline in the synthesized [BMIm][NTf₂], with increasing amounts of HNTf₂. Experimental data are shown as grey circles, Voigt-fitted data are shown as plain lines. (B) Evolution of the ratio of the molar fraction of the acidic ($1 - x_R$) and basic (x_R) forms of the 2,6-dichloro-4-nitroaniline calculated from the Raman spectra as a function of the added concentration of HNTf₂ (C_{HA}). (C) H_0 values calculated from Raman data as a function of the cologarithm of the concentration of HNTf₂, corrected for the basic impurities (C^*_{HA}).

6. Hammett acidity function of acidic solutions of 2,6-dichloro-4-nitroaniline (79.17 mM) in synthesized [EMIm][NTf₂]

A stock solution of pH-reporter (R) was obtained by dissolving 59.3 mg of 2,6-dichloro-4-nitroaniline in 5.4992 g of synthesized [BMIm][NTf₂] to obtain a solution with a concentration in pH-reporter of 79.17 mM. As previously, a series of acidic solutions, with increasing concentrations of strong acid, were prepared from that 79.17 mM stock solution of pH-reporter and an acidic stock solution containing 165.3 mM or 44.8 mM of HNTf₂ (Table S5).

Table S5. Preparation of acidic solutions from the 79.17 mM stock solution of 2,6-dichloro-4-nitroaniline in synthesized [EMIm][NTf₂]. These solutions were used for the determination of the Hammett acidity function by Raman spectroscopy. m_{BR} is the mass of the 79.17 mM solution of 2,6-dichloro-4-nitroaniline (E and R stand for [EMIm][NTf₂] and reporter, respectively), m_{HNTf_2} and $[HNTf_2]$ are respectively the mass and the concentration of, m_{E1} is the mass of solution E1, and m_{E5} is the mass of solution E5.

Samples	m_{HNTf_2} (mg)	m_{ER} (mg)	m_{E1} (mg)	m_{E5} (mg)	$[HNTf_2]$ (mM)
E1	49.2	1608.7	0.0	0.0	165.3
E2	0.0	154.9	307.1	0.0	109.9
E3	0.0	224.5	223.4	0.0	82.5
E4	0.0	310.4	155.1	0.0	55.1
E5	0.0	1026.9	381.4	0.0	44.8
E6	0.0	116.3	0.0	335.5	33.2
E7	0.0	232.6	0.0	227.3	22.1
E8	0.0	291.3	0.0	166.6	16.3
E9	0.0	527.0	0.0	170.7	10.9

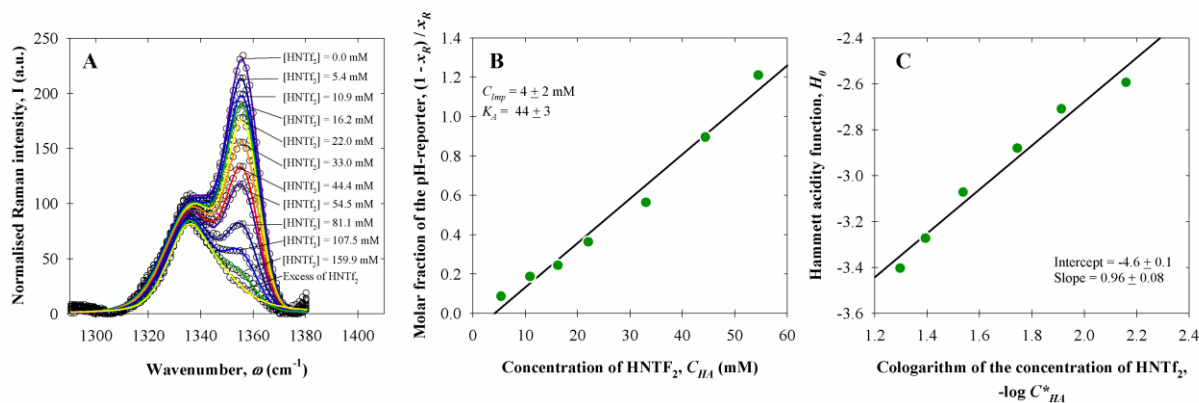


Figure S2. (A) Raman spectra obtained for the solutions containing 79.17 mM of the pH-reporter 2,6-dichloro-4-nitroaniline in the synthesized [EMIm][NTf₂], with increasing amounts of HNTf₂. Experimental data are shown as grey circles, Voigt-fitted data are shown as plain lines. (B) Evolution of the ratio of the molar fraction of the acidic ($1 - x_R$) and basic (x_R) forms of the 2,6-dichloro-4-nitroaniline calculated from the Raman spectra as a function of the added concentration of HNTf₂ (C_{HA}). (C) H_0 values calculated from Raman data as a function of the cologarithm of the concentration of HNTf₂, corrected for the basic impurities (C_{HA}^*).

7. Hammett acidity function of acidic solutions of 2,6-dichloro-4-nitroaniline (65.87 mM) in synthesized [OMIm][NTf₂]

A stock solution of pH-reporter (R) was obtained by dissolving 51.7 mg of 2,6-dichloro-4-nitroaniline in 5.0048 g of synthesized [BMIm][NTf₂] to obtain a solution with a concentration in pH-reporter of 65.87 mM. As previously, a series of acidic solutions, with increasing concentrations of strong acid, were prepared from that 65.87 mM stock solution of pH-reporter and an acidic stock solution containing 171.4 mM or 45.9 mM of HNTf₂ (Table S6).

Table S6. Preparation of acidic solutions from the 65.9 mM stock solution of 2,6-dichloro-4-nitroaniline in synthesized [OMIm][NTf₂]. These solutions were used for the determination of the Hammett acidity function by Raman spectroscopy. m_{BR} is the mass of the 65.9 mM solution of 2,6-dichloro-4-nitroaniline (O and R stand for [OMIm][NTf₂] and reporter, respectively), m_{HNTf_2} and $[HNTf_2]$ are respectively the mass and the concentration of, m_{O1} is the mass of solution O1, and m_{O5} is the mass of solution O5.

Samples	m_{HNTf_2} (mg)	m_{OR} (mg)	m_{O1} (mg)	m_{O5} (mg)	$[HNTf_2]$ (mM)
O1	51.1	1399.3	0.0	0.0	171.4
O2	0.0	129.0	260.6	0.0	114.7
O3	0.0	198.1	190.0	0.0	83.9
O4	0.0	265.3	127.5	0.0	55.6
O5	0.0	875.1	319.7	0.0	45.9
O6	0.0	89.8	0.0	276.6	34.6
O7	0.0	178.6	0.0	179.9	23.0
O8	0.0	231.3	0.0	132.9	16.7
O9	0.0	446.3	0.0	157.4	12.0

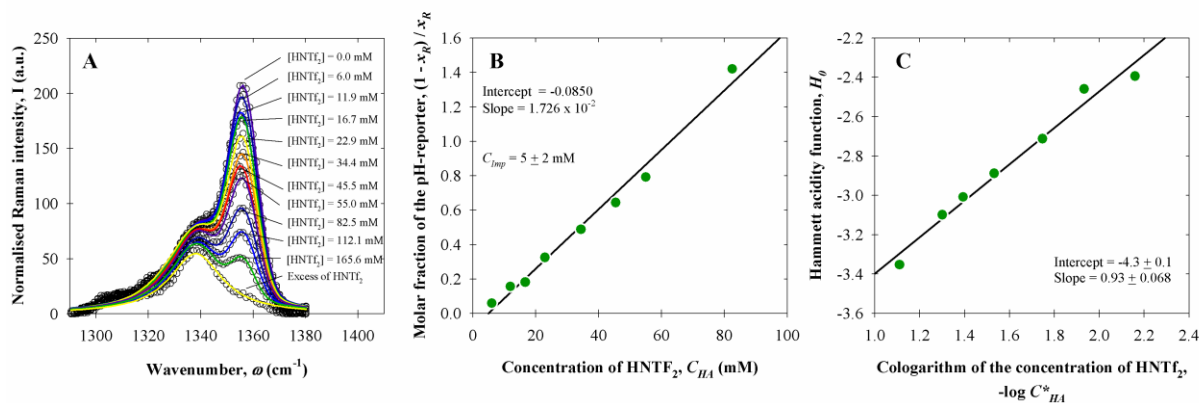


Figure S3. (A) Raman spectra obtained for the solutions containing 65.87 mM of the pH-reporter 2,6-dichloro-4-nitroaniline in the synthesized [OMIm][NTf₂], with increasing amounts of HNTf₂. Experimental data are shown as grey circles, Voigt-fitted data are shown as plain lines. (B) Evolution of the ratio of the molar fraction of the acidic ($1 - x_R$) and basic (x_R) forms of the 2,6-dichloro-4-nitroaniline calculated from the Raman spectra as a function of the added concentration of HNTf₂ (C_{HA}). (C) H_0 values calculated from Raman data as a function of the cologarithm of the concentration of HNTf₂, corrected for the basic impurities (C_{HA}^*).

8. Processing of the Raman spectra

The Raman spectra were treated as follows. The raw spectra (200-3600 cm^{-1} , Figure S4A) were first extracted from 700 to 1600 cm^{-1} (Figure S4B). Due to the fluorescence background, the spectra were thereafter baseline corrected with a Savitzky-Golay fourth-order polynomial on the entire Raman shift range (Figure S4C). For comparison purposes between the Raman spectra from different solutions, the spectra were finally normalized according to the intensity of the 1134 cm^{-1} band (Figure S4D), attributed to the breathing mode of the imidazolium ring of the solvent (supposed to be constant in all spectra).

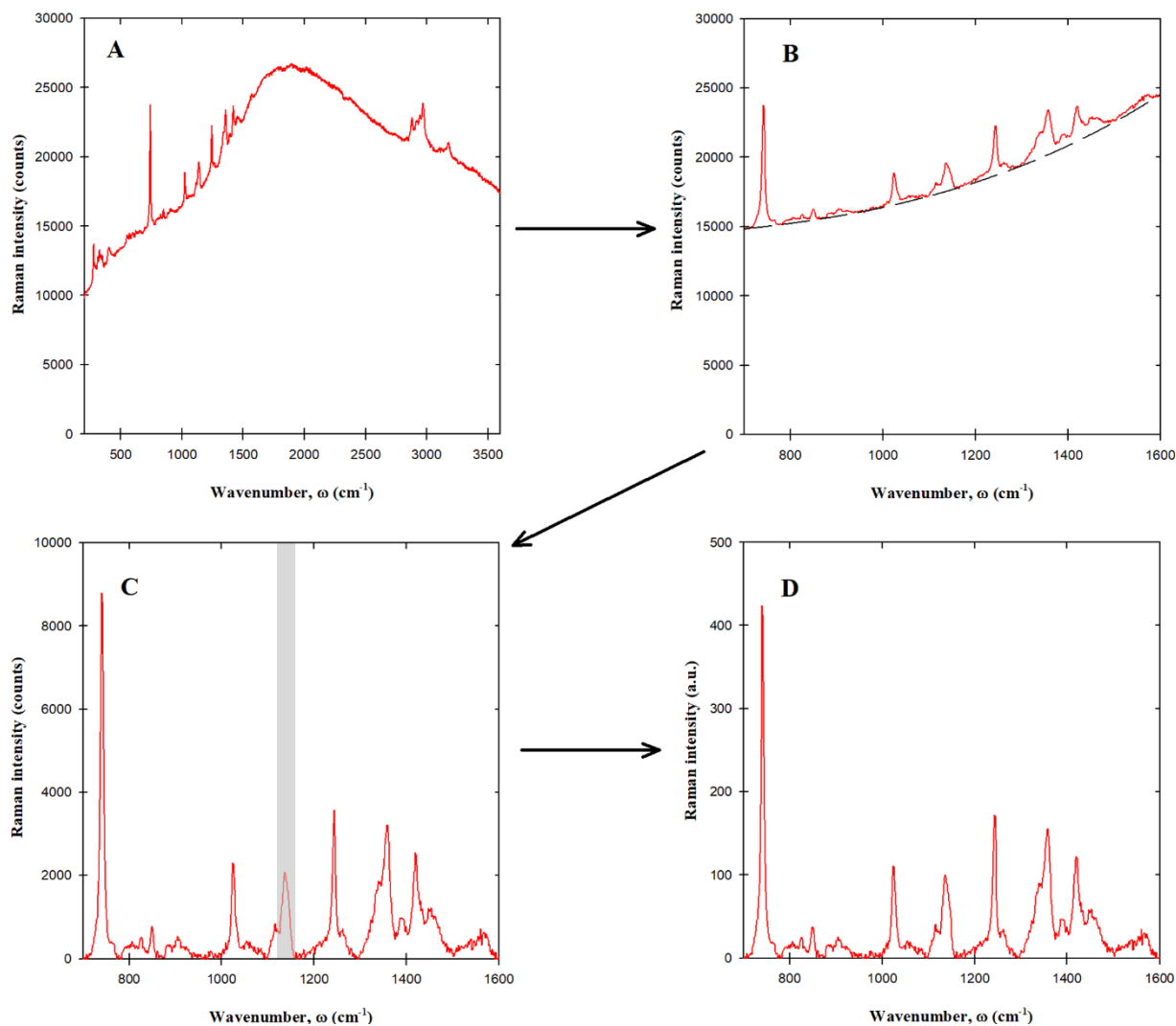


Figure S4. Data processing of the Raman spectra. (A) Raw spectrum obtained from the 22.5 mM solution in HNTf_2 containing 51.17 mM of the pH-reporter 2,6-dichloro-4-nitroaniline in the commercial $[\text{BMIm}][\text{NTf}_2]$. (B) Spectrum extracted from 700-1600 cm^{-1} . The fourth-order polynomial for the baseline correction is shown by the black dashed line. (C) Baseline corrected spectrum. The grey rectangle highlights the 1134 cm^{-1} band used to normalize the spectrum. (D) Normalized spectrum.

9. References

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