

INTRODUCTION

Ionic liquids are organic salts in the liquid state at room-temperature, enabling their use as non-aqueous solvents. They possess attractive properties, such as low vapour pressure and low flammability.¹

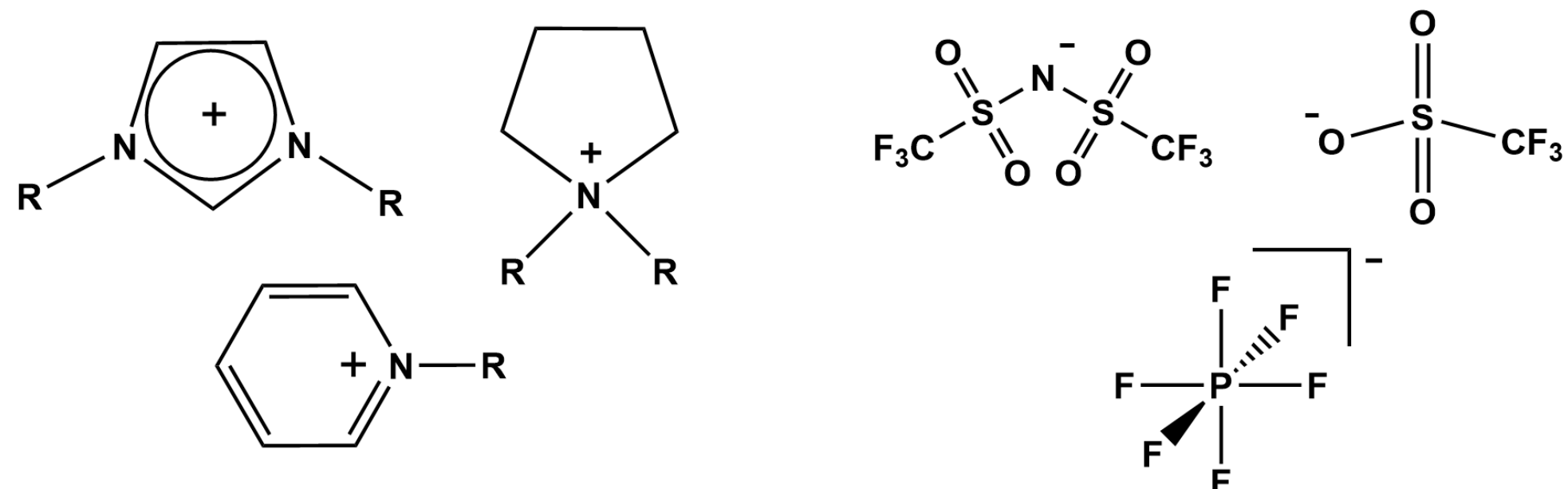


Fig 1. Examples of common cations and anions used in ionic liquids

Many of their physico-chemical properties can be tuned according to their constitutive ions, including their solvation properties and Bronsted acidity. The latter are crucial in applications such as organic synthesis and catalysis, in fuel cells technologies, or lignocellulose depolymerisation.^{2,3}

Yet, the experimental measurement of the acidity in these media is not straightforward and difficult to predict.

One common method to assess the acidity in ILs involves the measurement of the Hammett acidity functions, H_0 , based on the protonation equilibrium of a family of colour indicators (CIs), usually nitroanilines⁴:

$$H_0 \equiv pK_{BH^+} + \log\left(\frac{[B]}{[BH^+]}\right) = -\log(a_{H^+}) + \log\left(\frac{f_B}{f_{BH^+}}\right)$$

Hammett's hypothesis: $\frac{f_B}{f_{BH^+}}$ is the same for all bases of the same family (e.g. nitroanilines)

The protonation equilibrium of the CI is followed by UV-Visible spectroscopy (UV-Vis), but this method suffers from a few limitations:

- ✗ Limited to colour indicators as pH-probes, and transparent systems
- ✗ Use of nitroanilines: possible π interactions between the CI and IL

➔ **Implementation in Raman spectroscopy, which has multiple advantages:**

- ✓ Not limited to colour indicators as pH-probes and transparent systems
- ✓ In situ measurements during chemical processes
- ✓ Information on the solvation properties

RESULTS

Effect of the anionic moiety

Studied systems:

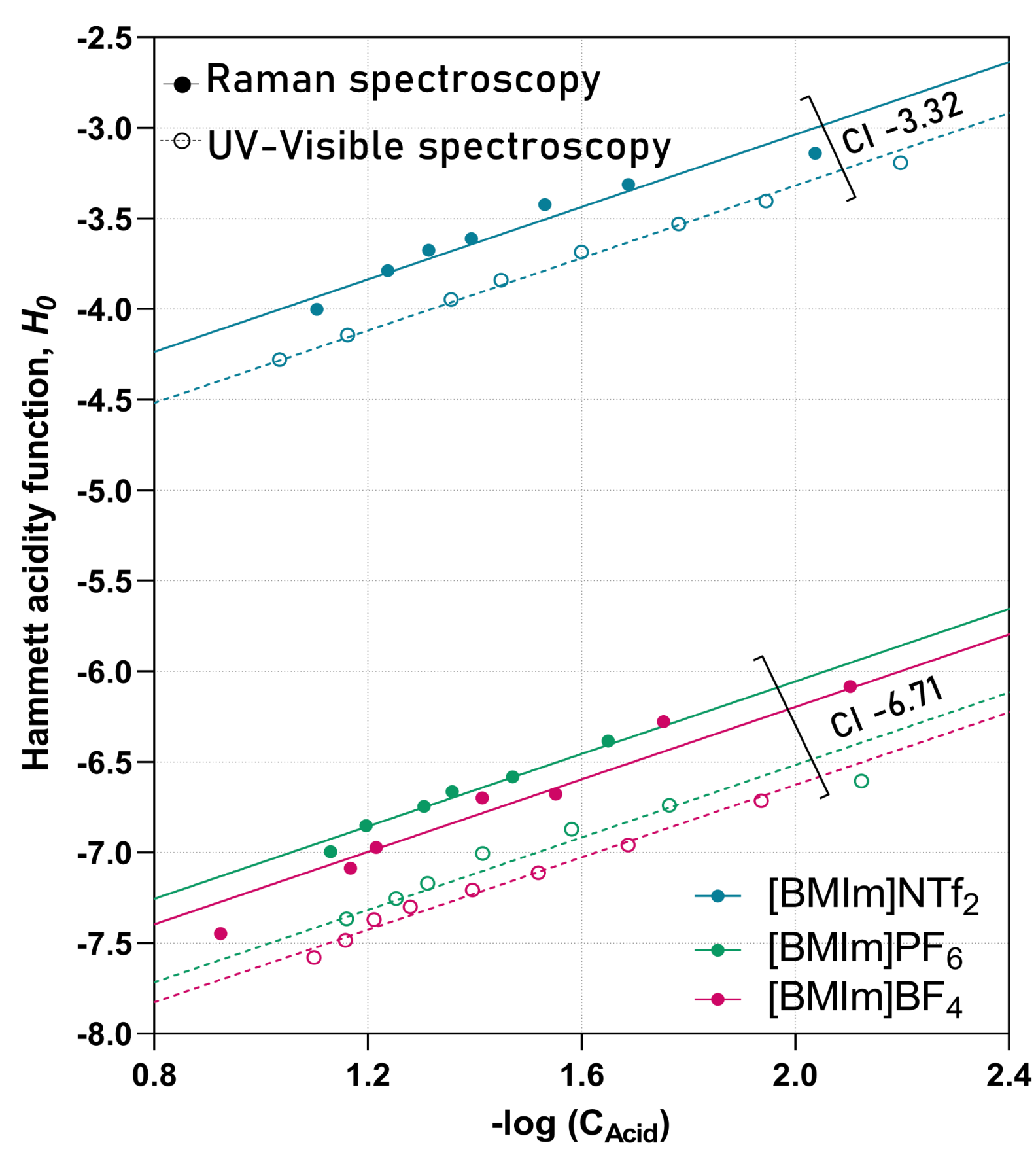
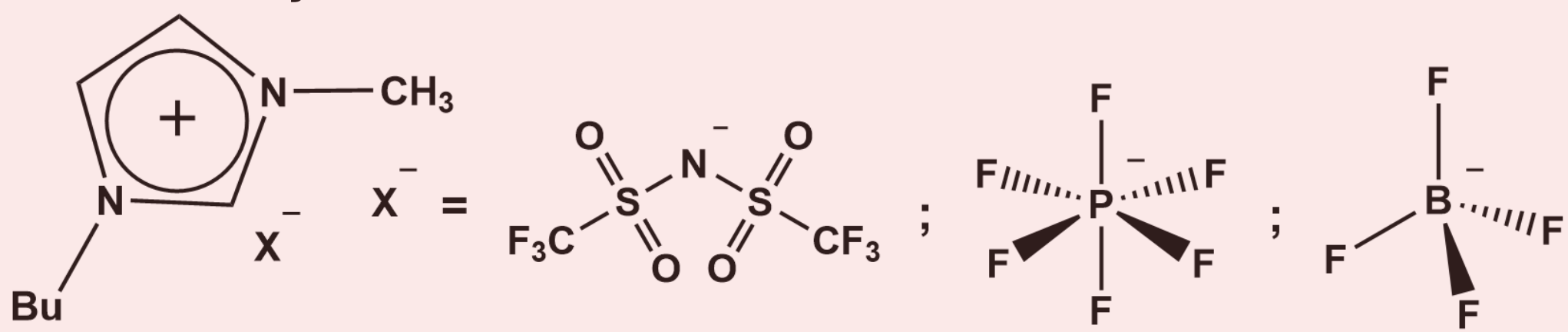


Fig 2. Hammett acidity functions H_0 obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the logarithm of HNTf₂ concentration in [BMIm]NTf₂ (●, CI = 2,4-dichloro-6-nitroaniline, pK_a -3.32), [BMIm]PF₆ (●) and [BMIm]BF₄ (● and ●, CI = 2-bromo-4,6-dinitroaniline, pK_a -6.71)

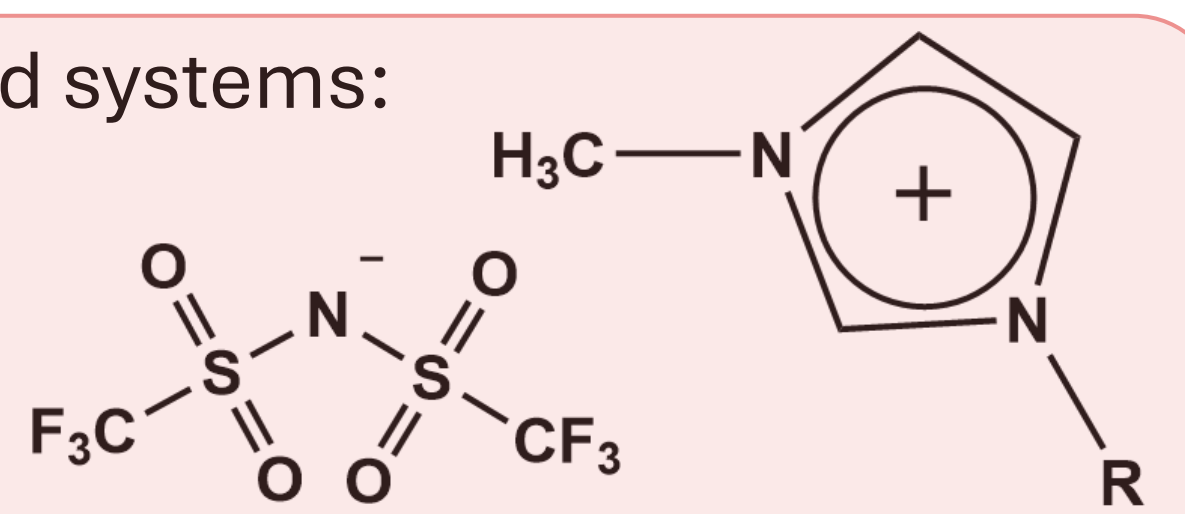
⇒ Same order of acidity in Raman and UV-Vis

BUT the H_0 acidity functions are shifted towards higher values (less acidic) in Raman

⇒ Higher concentration of CI used in Raman spectroscopy (~ 55 mM vs. ~ 1-2 mM in UV-Vis), acting as a basic impurity

Effect of the cationic moiety

Studied systems:



Order of acidity: Octyl < Hexyl < Butyl < Ethyl

⇒ Observed both in Raman and UV-Vis

⇒ H_0 acidity functions shifted again in Raman spectroscopy (vs. UV-Vis)

Smaller shifts of H_0 between the ILs when the cation is varied, compared to the anion

⇒ Acidity in ILs not prominently governed by the cation, yet a small effect is measured

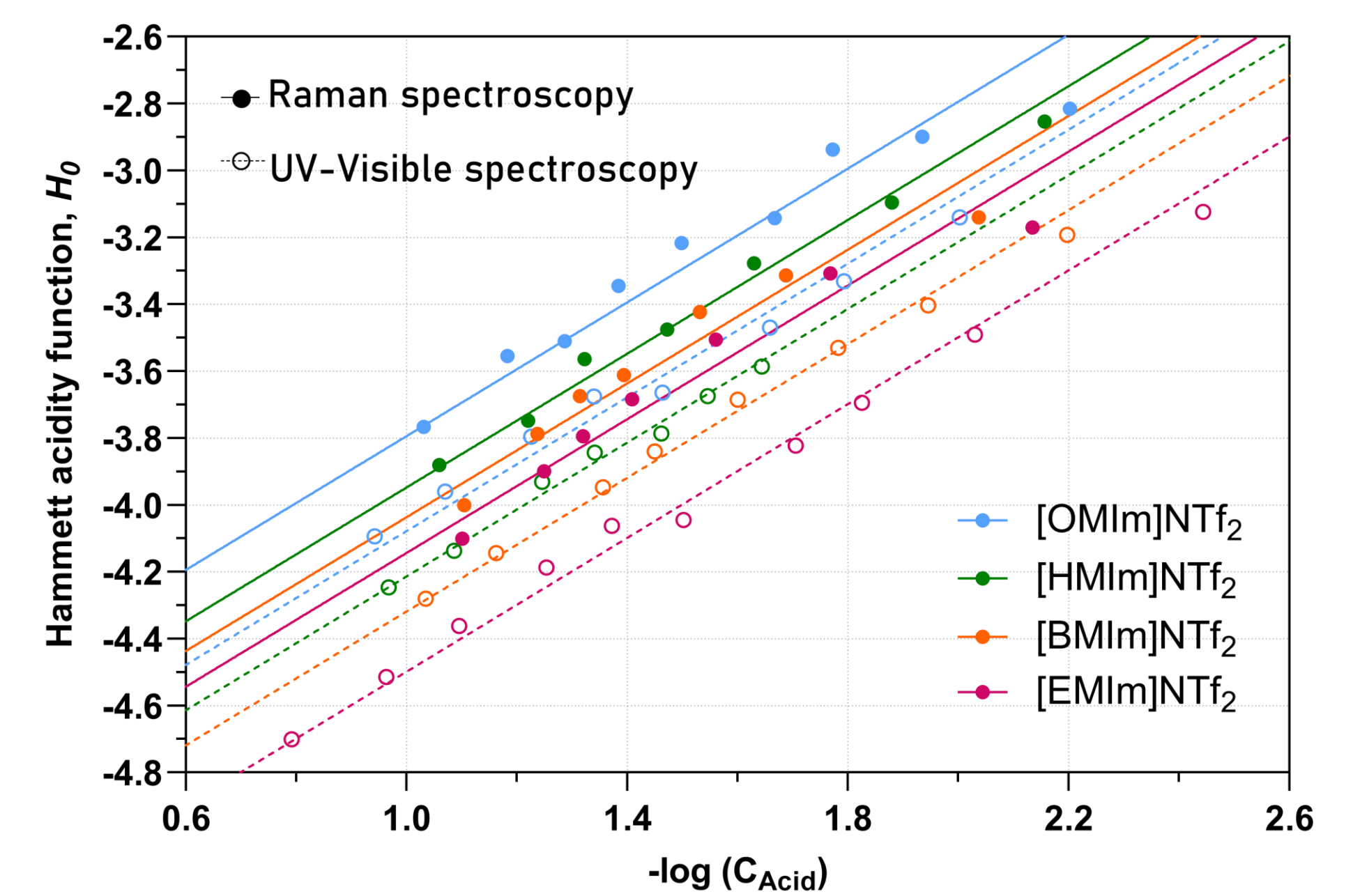
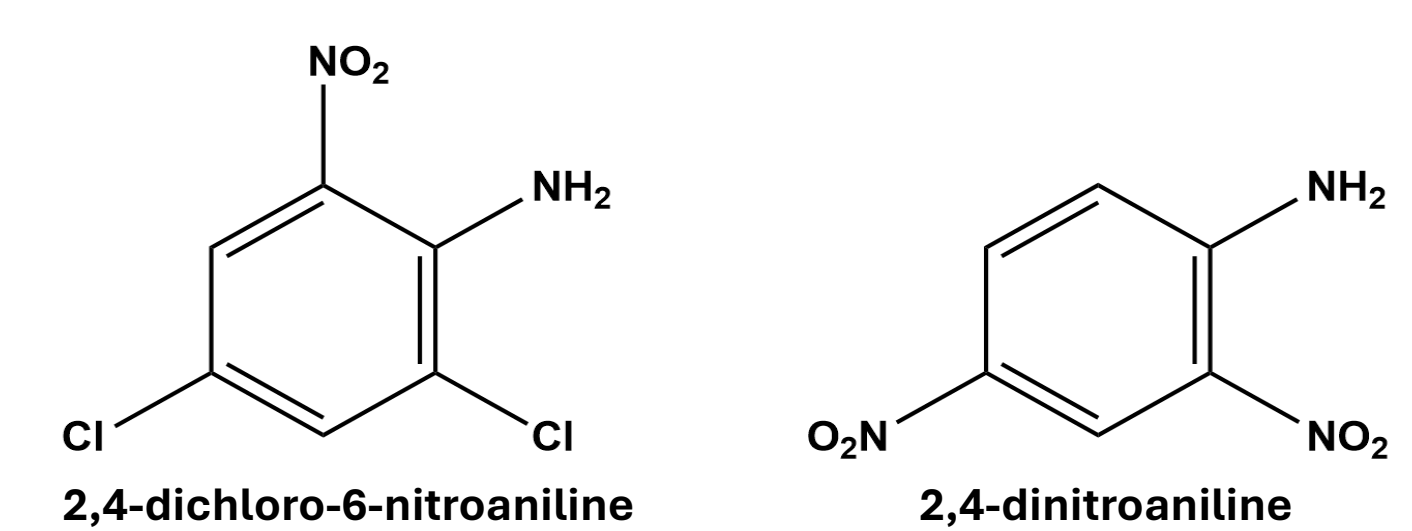


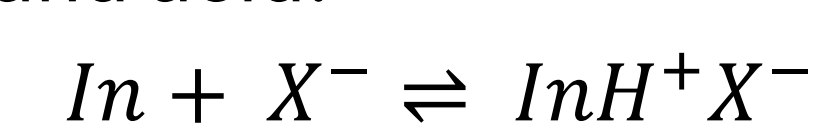
Fig 3. Hammett acidity functions H_0 obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the logarithm of HNTf₂ concentration in 2,6-dichloro-4-nitroaniline solutions in [EMIm]NTf₂ (●), [BMIm]NTf₂ (●), [HMIm]NTf₂ (●) and [OMIm]NTf₂ (●).

Ion pairs in ionic liquids

Use of two CIs: different H_0 acidity functions obtained



Non-dissociating behavior of ILs, leading to ion pairs between the CI and acid:



Definition of an **apparent acidity function** (H_0)_{app}⁵:

$$(H_0)_{app} = pK_{IC, H_2O} + \log\left(\frac{[In]_{IL}}{[InH^+X^-]_{IL}}\right) = pK_{IC, H_2O} + pK_f^{InH^+X^-} - \log(C_{HX})$$

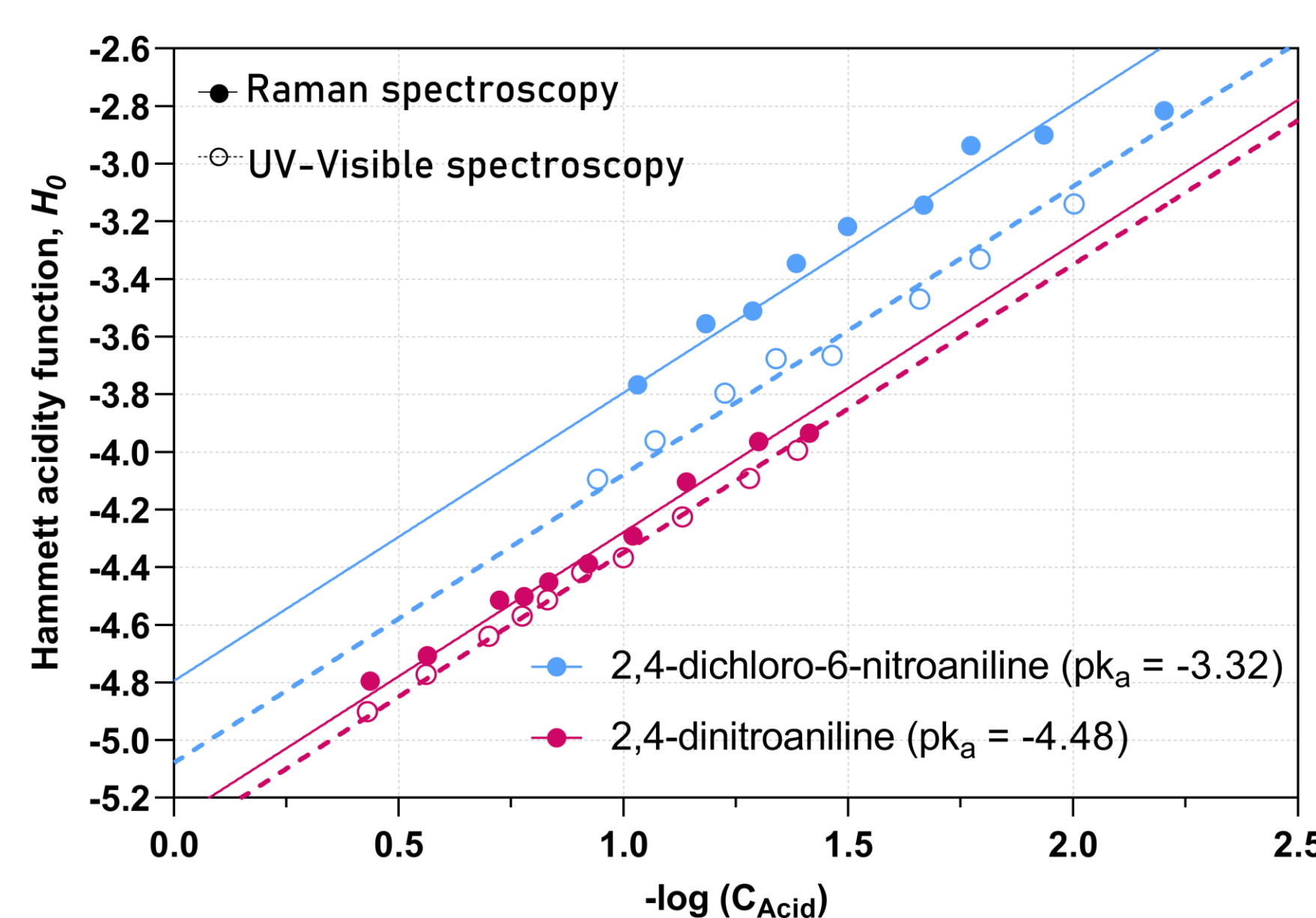


Fig 4. Hammett acidity functions H_0 in [OMIm]NTf₂ obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the logarithm of HNTf₂ concentration for CI = 2,4-dichloro-6-nitroaniline (●) and 2,4-dinitroaniline (○).

CONCLUSION

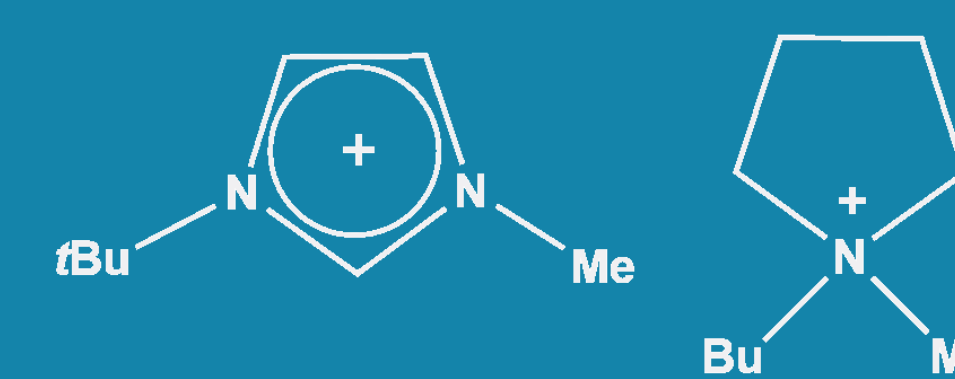
✓ First implementation of the Hammett acidity functions in Raman spectroscopy, leading to similar results as in UV-Visible spectroscopy:

- Small influence of the IL cation on the achieved acidity, compared to the anion
- Ion pairs seem to form between the CI and the acid

✗ Lower acidities measured in Raman, due to higher concentrations in basic probe

PERSPECTIVES

- Study of the CI concentration
- Study of other cations to probe specific interactions between the IC and IL



- Probing the non-dissociating behaviour of ILs: determine formation constant of ion pairs in the ILs

Acknowledgements

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(5) Bruckenstein, S., *J. Am. Chem. Soc.* **1960**, *82* (2), 307–310