Supporting Information

Complexity in Acid–Base Titrations: Multimer Formation Between Phosphoric Acids and Imines

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Supporting Information

$^1$H-NMR titration

In Figure S1 we show the variation of the chemical shifts of all aromatic protons (H3-H7, see inset of Figure 2a of the main manuscript) of quinaldine with concentration of DPP. The protons H3-H7 show a similar dependence on the acid concentration as H4 (Figure 2a): the values of $\delta$ increase with increasing $c_{\text{DPP}}$ up to $c_{\text{DPP}} = 0.1$ mol/L and plateau for an excess of DPP. The variation of the chemical shift of H8 (Figures 2a and S1) is markedly different and the dependence on concentration of acid is similar to that of the methyl group (Figure S2).

Figure S1: Chemical shift of the aromatic protons of quinaldine H3-H8 for solutions contained 0.1 mol/L quinaldine in dichloromethane as a function of DPP concentration. Symbols show experimental data and the solid lines show fits of eq 5 (see main manuscript) with the association constants (eqs 3 & 4) obtained from the DRS experiments.
As discussed in the main manuscript we fit eq 5 to the measured chemical shifts of all protons of quinaldine. Here we use the association model as elaborated in eqs 3 & 4 and the association constants obtained from the DRS experiments ($K_1 = 104 \, \text{L/mol}$, $K_2 = 16 \, \text{L/mol}$) to model the concentrations $\text{[Qu]}$, $\text{[IP]}$, and $\text{[mult]}$ at all concentrations of DPP. Thus, the only parameters to describe the data in Figures 2, S1 & S2 are the chemical shifts $\delta_{\text{Qu}}$, $\delta_{\text{IP}}$, and $\delta_{\text{mult}}$. The shifts for the three species obtained from fitting eq 5 to the data are listed in Table S1 and are compared to the measured chemical shift of a solution of only quinaldine.

Table S1: Experimentally determined chemical shifts for a 0.1 mol/L solution of quinaldine ($\delta(\text{Qu})$) in deuterated dichloromethane, together with the chemical shifts of quinaldine, $\delta_{\text{Qu}}$, of the QuH$^+$-DPP$^-$ ion-pair, $\delta_{\text{IP}}$, and the multimers, $\delta_{\text{mult}}$, obtained by fitting eq 5 to the concentration dependent experimental chemical shifts.

| Qu proton position | Experimental $\delta(\text{Qu})$ / ppm | $\delta_{\text{Qu}}$ / ppm | $\delta_{\text{IP}}$ / ppm | $\delta_{\text{mult}}$ / ppm |
|-------------------|----------------------------------------|----------------------------|-----------------------------|----------------------------|
| H3                | 7.30                                   | 7.30                       | 7.60                        | 7.41                       |
| H4                | 8.06                                   | 8.05                       | 8.70                        | 8.47                       |
| H5                | 7.79                                   | 7.79                       | 8.07                        | 7.89                       |
| H6                | 7.48                                   | 7.48                       | 7.83                        | 7.63                       |
| H7                | 7.67                                   | 7.67                       | 7.97                        | 7.72                       |
| H8                | 7.96                                   | 7.96                       | 8.60                        | 7.92                       |
| H9 (methyl)       | 2.71                                   | 2.71                       | 2.98                        | 2.66                       |
Dielectric spectra of DPP in dichloromethane

In the main manuscript (Figure 3b) we show the static permittivity for solutions of DPP in dichloromethane as a function of $c_{\text{DPP}}$. These values were determined from spectra measured at frequencies ranging from 800 MHz to 54 GHz (Figure S3) and are dominated by a relaxation mode centered at ~50 GHz, the rotational diffusion of the dipolar solvent dichloromethane. The measured spectra for these solutions show little variation with increasing concentration of DPP. To extract the static permittivity of these solutions we fit – analogously to the relaxation model in the main manuscript, eq 2 – a relaxation model based on a single Debye relaxation to the spectra:

$$
\tilde{\varepsilon}(\nu) = \frac{S_{\text{DCM}}}{1 + 2\pi i \nu \tau_{\text{DCM}}} + \varepsilon_\infty + \frac{\kappa}{2\pi i \nu \varepsilon_0}
$$

where $S_{\text{DCM}}$ and $\tau_{\text{DCM}}$ correspond to the relaxation amplitude and the relaxation time of the solvent dichloromethane, respectively. $\varepsilon_\infty$ is the infinite frequency permittivity and $\kappa$ the sample conductivity. The static permittivity, i.e. the limiting value of $\varepsilon'$ at low frequency is defined as: $\varepsilon_s = \varepsilon_\infty + S_{\text{DCM}}$. Such fits are shown as solid lines in Figure S3 and the parameters obtained from fitting eq S1 to the spectra are listed in Table S2.

Figure S3 Complex permittivity spectra of solutions containing only DPP in dichloromethane. Symbols show experimental data and lines correspond to fits of eq S1 to the spectra.

Table S2: Parameters obtained by fitting eq S1 to the dielectric spectra for solutions of DPP in dichloromethane.

| $c_{\text{DPP}}$ / mol/L | $S_{\text{DCM}}$ | $\varepsilon_\infty$ | $\tau_{\text{DCM}}$ / ps | $\kappa$ / S/m |
|--------------------------|------------------|---------------------|---------------------|----------------|
| 0.025                    | 4.44             | 4.05                | 3.4                 | 0.00           |
| 0.05                     | 4.63             | 3.96                | 3.3                 | 0.00           |
| 0.075                    | 5.53             | 3.86                | 3.1                 | 0.00           |
| 0.1                      | 5.68             | 3.86                | 3.1                 | 0.00           |
| 0.2                      | 5.69             | 3.83                | 3.0                 | 0.00           |
| 0.3                      | 4.41             | 3.8                 | 3.0                 | 0.00           |
Dielectric relaxation parameter for DPP + Qu mixtures

As discussed in the main manuscript, we fit eq 2 to the spectra for solutions of 0.1 mol/L Qu with varying DPP concentration in dichloromethane. The fits are shown together with the experimental spectra in Figure 3a. The parameters obtained from fitting eq 2 to the spectra are listed in Table S3 and shown in Figure S4.

As discussed in the main manuscript, we constrain $\tau_{\text{mult}}$ to 458 ps at $c_{\text{DPP}} \leq 0.1$ mol/L. As can be seen from the comparison of the parameters of the constraint fit to those obtained from a free fit in Figure S4, this constraint hardly affects the relaxations strengths, which are used to extract the concentration of ion-pairs an multimers.

Table S3: Relaxation amplitudes, $S_j$, relaxation times, $\tau_j$, limiting permittivity, $\varepsilon_{\infty}$, and conductivity, $\kappa$ for solutions containing 0.1 mol/L Qu and varying concentration of DPP in dichloromethane. These fit parameters were obtained by fitting eq 2 to the experimental spectra

| $c_{\text{DPP}}$ / mol/L | $S_{\text{mult}}$ | $S_{\text{IP}}$ | $S_{\text{DCM}}$ | $\varepsilon_{\infty}$ | $\tau_{\text{mult}}$ / ps | $\tau_{\text{IP}}$ / ps | $\tau_{\text{DCM}}$ / ps | $\kappa$ / S/m |
|-----------------|------------------|-----------------|-----------------|--------------------|------------------|----------------|-----------------|----------------|
| 0.025           | 0.02             | 1.27            | 5.41            | 2.76               | 458.2            | 58.4           | 2.1             | 0.00           |
| 0.05            | 0.18             | 1.62            | 5.37            | 2.78               | 458.2            | 65.3           | 2.1             | 0.00           |
| 0.075           | 0.50             | 1.96            | 5.33            | 2.82               | 458.2            | 71.2           | 2.1             | 0.00           |
| 0.1             | 0.97             | 2.24            | 5.29            | 2.89               | 458.2            | 77.2           | 2.2             | 0.01           |
| 0.15            | 1.38             | 2.19            | 5.22            | 2.89               | 501.5            | 76.0           | 2.2             | 0.02           |
| 0.2             | 2.13             | 1.87            | 5.14            | 2.89               | 420.6            | 65.6           | 2.1             | 0.02           |
| 0.3             | 2.65             | 1.73            | 5.01            | 2.91               | 452.5            | 58.9           | 2.1             | 0.02           |

Figure S4: Comparison of the relaxation amplitude and relaxation time obtained using a free fit (filled symbols) based on eq 2 of the main manuscript to the spectra together with the results using the constraint fit (open symbols, see text).

Electrical dipole moments of the ion-pair and the multimer

To relate the dielectric relaxation amplitudes of the ion-pair, $S_{\text{IP}}$, and the multimer, $S_{\text{mult}}$, to their molar concentrations in solution, $[\text{IP}]$ and $[\text{mult}]$, we use the Cavell equation. In general, the Cavell equation relates the relaxation amplitude $S_j$ to the molar concentration, $c_j$, of a species $j$ and its electrical the dipole moment $\mu_j$.
\[
\frac{2\varepsilon_s + 1}{\varepsilon_s} \cdot S_j = \frac{N_A c_j}{k_B T \varepsilon_0} \cdot \mu_j^2
\]  
(S2)

with the Boltzmann constant \( k_B = 1.38065 \times 10^{-23} \) A Vs/K, the vacuum permittivity \( \varepsilon_0 = 8.85419 \times 10^{-12} \) As/Vm, and the Avogadro number \( N_A = 6.02214 \times 10^{23} \) mol\(^{-1}\). \( T = 294.15 \) K is the thermodynamic temperature. For convenience we summarize all constants specific to each sample into \( W \) resulting in:

\[
W \cdot S_j = c_j \cdot \mu_j^2
\]  
(S3)

As for our experiments, both the concentrations and the dipole moments of the ion-pairs and of the multimers are unknown, we use the following approach to determine the dipole moment of both species. We assume for an excess of DPP (\( c_{\text{DPP}} > 0.1 \) mol/L) that the concentration, \( c_{\text{lim}} \), that limits the total number of formed intermolecular aggregates is given by the concentration of quinaldine (all quinaldine molecule form either ion-pairs or multimers):

\[
c_{\text{lim}} = c_{\text{Qu}} \text{ for } c_{\text{DPP}} > 0.1 \text{ mol/L}
\]  
(S4)

At low concentrations the limiting concentration is the DPP concentration (all DPP molecules from either ion-pairs or multimers)

\[
c_{\text{lim}} = c_{\text{DPP}} \text{ for } c_{\text{DPP}} \leq 0.1 \text{ mol/L}
\]  
(S5)

Using mass conservation, the limiting concentration \( c_{\text{lim}} \) can be related to the concentration of ion-pairs, \([\text{IP}]\), and multimers, \([\text{mult}]\):

\[
c_{\text{lim}} = [\text{IP}] + z \times [\text{mult}]
\]  
(S6)

where \( z = 1 \) for \( c_{\text{DPP}} > 0.1 \) mol/L (\( c_{\text{lim}} = c_{\text{Qu}} \)). At low concentrations of acid, we assume that only ion-pairs and trimers are formed, hence mass conservation for DPP yields \( z = 2 \) for \( c_{\text{DPP}} \leq 0.1 \) mol/L.

Based on eq S3, the concentration of the multimer can be related to the dielectric relaxation strength:

\[
W \cdot S_{\text{mult}} = \mu_{\text{mult}}^2 \cdot [\text{mult}]
\]  
(S7)

and analogously for the ion-pair:

\[
W \cdot S_{\text{IP}} = \mu_{\text{IP}}^2 \cdot [\text{IP}]
\]  
(S8)

Inserting eqs S7 & S8 into eq S6 gives:

\[
c_{\text{lim}} = z \cdot \frac{W \cdot S_{\text{mult}}}{\mu_{\text{mult}}^2} + \frac{W \cdot S_{\text{IP}}}{\mu_{\text{IP}}^2}
\]  
(S9)

which can be rearranged to

\[
\frac{c_{\text{lim}}}{W \cdot S_{\text{IP}}} = \frac{1}{\mu_{\text{mult}}^2} \cdot z \cdot \frac{S_{\text{mult}}}{S_{\text{IP}}} + \frac{1}{\mu_{\text{IP}}^2}
\]  
(S10)
Eq S10 can be used to determine the values for $\mu_{\text{mult}} = 21.4$ D and $\mu_{\text{IP}} = 21.5$ D using a linear regression (Figure S4) from the intercept $1/\mu_{\text{IP}}^2$ and the slope $1/\mu_{\text{mult}}^2$. We note that these values are in excellent agreement with the dipole moment that we determined in our previous study,² using only a single broad relaxation mode to describe the solute relaxation (i.e. which subsumed contributions from ion-pairs and multimers). Using these values for the dipole moments eqs S7 & S8 can be used to determine the molar concentrations of ion-pairs and multimers for all samples, which are shown in Figure 3d of the main manuscript.

![Figure S5: Linear regression according to eq S10 to obtain the dipole moments of the ion-pair and the multimer.](image)

**Ab initio calculations**

The values for the electrical dipole moments are supported by *ab initio* calculations. Geometries of a QuH⁺·DPP⁻ ion-pair and a QuH⁺·DPP⁻·DPP trimer were optimized using the ORCA program package⁵ at the HF/SVP⁷ level of theory. The solvent was approximated by a continuum using the conductor-like screening model (COSMO, $\varepsilon = 8.83$).⁸ The optimized geometries yielded similar electrical dipole moments for the trimer $\mu_{\text{trimer}}=15.2$ D and for the ion-pair $\mu_{\text{IP}} = 16.2$ D, in agreement with the approach using the experimental values (see above). We note that the *ab initio* values are somewhat lower than the values obtained using eq S10. The lower values from the *ab initio* calculations can be explained from the fact that these were obtained from the energetically most stable structure. Thus, unlike the experimental values, the *ab initio* values do not account for conformational flexibility and deviations from the ideal geometry due to thermal fluctuations. The optimized geometry of the ion-pair and trimer are illustrated in Figure S5.
Figure S6: Optimized geometry of the QuH\(^+\)-DPP\(^-\) ion-pair (left) and the QuH\(^+\)-DPP-DPP trimer. For the trimer, the optimized geometry shows a bridging hydrogen-bond connecting the two DPP molecules with a hydrogen-bonding distance of 1.57 Å. The hydrogen-bond between the QuH\(^+\) and the negatively charged DPP\(^-\) is 1.68 Å, which is comparable to the hydrogen-bonding distance in the ion-pair (1.63 Å).

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