Supporting Information

Association equilibria of organo-phosphoric acids with imines from a combined dielectric and nuclear magnetic resonance spectroscopy approach

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Chemical shifts of the proton H3
As described in the main text, we use the chemical shift of the residual solvent protons for referencing the NMR spectra. These shifts of the solvents may however also be affected by the addition of DPP. In Figure S1 we show the chemical shift of H3 of Qu or PhQu as a function of $c_{\text{DPP}}$, which is – within experimental error – constant at $c_{\text{DPP}} \geq 0.1 \text{ mol L}^{-1}$. This insensitivity of $\delta_{\text{H3}}$ to a large excess of DPP suggests that also the protons of the solvent are rather insensitive to the added DPP.

![Figure S1: Chemical shift of H3 of 0.1 mol L$^{-1}$ (a) Qu and (b) PhQu as a function of $c_{\text{DPP}}$. Open symbols show data at $c_{\text{DPP}} < 0.1 \text{ mol L}^{-1}$ and filled symbols depict data at $c_{\text{DPP}} \geq 0.1 \text{ mol L}^{-1}$. The solid lines show the average values at $c_{\text{DPP}} \geq 0.1 \text{ mol L}^{-1}$. Error bars were estimated to $\pm 0.05 \text{ ppm}$ to account for systematic errors due to medium effects.](image)

Modelling only the NMR chemical shifts
As described in the main text, we test modelling of the association equilibria based on $K_1$ and $K_2$ (eqs. 2-4 of the main manuscript), or based on $K'_1$ and $K'_2$ (see main text). This is achieved by optimizing the sum of the squared deviations, $\chi_{\text{NMR}}$:

$$
\chi_{\text{NMR}} = \frac{\sum \left( \frac{(\delta(\text{H8})_{\text{exp}} - \delta(\text{H8})_{\text{fit}}) / \Delta_{\text{NMR}}}{N_{\text{NMR}}} \right)^2}{N_{\text{NMR}}} + \frac{\sum \left( \frac{(\delta(\text{H4})_{\text{exp}} - \delta(\text{H4})_{\text{fit}}) / \Delta_{\text{NMR}}}{N_{\text{NMR}}} \right)^2}{N_{\text{NMR}}}
$$

(S1)

where $N_{\text{NMR}}$ is the number of data points, $\Delta_{\text{NMR}}$, are the errors in the experimentally determined chemical shifts, $\delta_{\text{exp}}$, $\delta_{\text{fit}}$ corresponds to the fit according to eq 2 of the main manuscript. $\chi_{\text{NMR}}$ is optimized using, $\delta_{\text{Qu}}$, $\delta_{\text{IP}}$, $\delta_{\text{M}}$, $K_1$, and $K_2$ (or $K'_1$, and $K'_2$) as adjustable parameters. Yet, comparing the model taking DPP2 dimerization into account ($K_1$ and $K_2$) to the model neglecting dimerization ($K'_1$ and $K'_2$) provides no evidence for clearly lower $\chi_{\text{NMR}}$ values for one of the two models (Figure S2).

The insensitivity of the fit quality to the association model can be explained by correlation of the adjustable parameters. As described in the main manuscript, variation of the association
constant $K_1$ can be – predominantly – compensated by a variation of the chemical shift of the ion pair, $\delta_{IP}$, when fitting eq 2 (see main manuscript) to the experimentally determined chemical shifts of Qu’s protons. This is illustrated in Figure S3, where we show the variation of $\delta_{IP}$ when fitting eq 4 to the data for Qu in CDCl$_3$ for different values of $K_1$.

Figure S2: Comparison of the fit quality ($\chi_{NMR}$) when fitting eq 2 to the NMR chemical shifts. Blue columns correspond to fits taking DPP dimerization into account (eqs 3-4), while red columns show fits based on free DPP monomers in solution.

Figure S3. Chemical shift of the ion-pairs, $\delta_{IP}$, as obtained from fitting eq 2 (main manuscript) to the data shown in Figure 1 of the main manuscript as a function of constrained values of $K_1$. Selected fits are shown as solid lines in Figure 1 of the main manuscript.
Analysis of the dielectric spectra

In order to quantify the concentration of ion-pairs and multimers in solution, we analyse the dielectric spectra of the imine – DPP mixtures. Therefore, we fit a relaxation model to the experimental spectra. In line with our previous study, we find that a combination of three Debye type equations\(^1\) can describe the experimental spectra (see also Figure 2 of the main manuscript). In this model the relaxation of the multimers (M), ion-pairs (IPs), and the solvent (solv) is each modelled with a separate Debye relaxation. Each relaxation is characterized by its relaxation strength \(S_j\) and relaxation time \(\tau_j\). Using this model, we assume uncorrelated dipolar relaxation of the different molecules and/or molecular aggregates. All polarizations at frequencies \(\nu\) higher than the experimentally covered frequency range are modelled by the limiting permittivity at infinite frequencies, \(\varepsilon_\infty\). Ohmic losses due to translational polarization are taken into account by the last term of eq S1, with the d.c. conductivity \(\kappa\) assumed to be real and independent of frequency. \(\varepsilon_0\) is the vacuum permittivity:

\[
\hat{\varepsilon}(\nu) = \frac{S_M}{1 + 2\pi i \nu \tau_M} + \frac{S_{IP}}{1 + 2\pi i \nu \tau_{IP}} + \frac{S_{solv}}{1 + 2\pi i \nu \tau_{solv}} + \varepsilon_\infty + \frac{\kappa}{2\pi i \nu \varepsilon_0} \tag{S2}
\]

Based on the Cavell equation

\[
\frac{2\varepsilon_s + 1}{\varepsilon_s} \cdot S_j = \frac{N_A}{k_B T \varepsilon_0} \cdot \mu_j^2 \tag{S3}
\]

the obtained relaxation amplitudes, \(S_j\) are directly related to concentration of the species, \([j]\), in solution\(^1\text{"}^3\) and their (squared) electrical dipole moment, \(\mu_j\). In eq S3, \(\varepsilon_s = S_M + S_{IP} + S_{solv} + \varepsilon_\infty\) is the static dielectric constant, \(N_A\) Avogadro’s constant, \(k_B\) the Boltzmann constant, and \(T\) the thermodynamic temperature.

To relate the observed relaxation strengths to the concentration of the relaxing species, their electrical dipole moment is required. Here, we assume the dipole moment of the ion-pair and of the multimer to be the same \(\mu_{IP,M} = \mu_{IP} = \mu_M\). This assumption is supported by \textit{ab initio} calculations and experiments for DPP-Qu aggregates in DCM, which both indicate very similar dipole moments for both species.\(^1\) Further \textit{ab initio} calculations (DFT\(^4\text{"}^6\) / B3LYP 6-31+G(d)\(^7\text{"}^9\) as implemented in Gaussian 09\(^10\)) for Qu-DPP ion-pairs and Qu-(DPP)\(_2\) trimers in continuum solvents (PCM) suggest very similar dipole moments in the other studied solvents: CHCl\(_3\) \((\mu_{IP} = 14.4\ \text{D}, \ \mu_M = 13.1\ \text{D})\), THF \((\mu_{IP} = 15.0\ \text{D}, \ \mu_M = 15.0\ \text{D})\).

Given that all imine bases form either ion-pairs or multimers \((c_{Qu} \approx [IP] + [M])\), which can be justified for an excess of DPP, \(\mu_{IP,M}\) is obtained from the analytical concentration of base and from the combined relaxation strength \(S_{IP,M} = S_{IP} + S_M\) using eq S3. Here, we use the spectra with a five-fold excess of DPP to determine the dipole (see Table S1). These values allow obtaining the equilibrium concentrations [IP] and [M] from the experimental \(S_{IP}\) and \(S_M\) values (eq S3), respectively, at all three studied concentrations of each measurement series.
Table S1. Calculated combined dipole moments for ion-pairs and multimers.

| Solvent | $\mu_{IP,M}(\text{Qu})$ [D] | $\mu_{IP,M}(\text{PhQu})$ [D] |
|---------|-----------------------------|-----------------------------|
| DCM     | 23.6                        | 25.2                        |
| CHCl$_3$| 19.2                        | 23.3                        |
| THF     | 20.8                        | 23.9                        |

Combined DRS and NMR fit

As described in the main manuscript, we perform a combined fit of the experimental chemical shifts for H8 ($\delta$H8$_{\text{exp}}$) and H4 ($\delta$H4$_{\text{exp}}$) and the experimental concentrations of ion-pairs [IP]$_{\text{DRS}}$ and multimers [M]$_{\text{DRS}}$ based on the association equilibria as outlined in the main manuscript. To model the chemical shift of both protons we use eq 2 (main manuscript). In the combined fit, we optimize the weighted sum of the square deviations from both experiments:

$$\chi_{\text{DRS}+\text{NMR}} = \frac{\sum (\delta(\text{H}8)_{\text{exp}} - \delta(\text{H}8)_{\text{fit}})/\Delta_{\text{NMR}})^2}{N_{\text{NMR}}}$$

$$+ \frac{\sum (\delta(\text{H}4)_{\text{exp}} - \delta(\text{H}4)_{\text{fit}})/\Delta_{\text{NMR}})^2}{N_{\text{NMR}}}$$

$$+ \frac{\sum (([\text{M}]_{\text{DRS}} - [\text{M}])/\Delta_{\text{M,DRS}})^2}{N_{\text{DRS}}} + \frac{\sum (([\text{IP}]_{\text{DRS}} - [\text{IP}])/\Delta_{\text{IP,DRS}})^2}{N_{\text{DRS}}}$$

where $N_{\text{DRS}}$ is the number of data points of DRS experiments. $\Delta_{\text{M,DRS}}$ and $\Delta_{\text{IP,DRS}}$ are the errors in [M]$_{\text{DRS}}$ and [IP]$_{\text{DRS}}$, respectively. $\chi_{\text{DRS}+\text{NMR}}$ is optimized using $\delta_{\text{Qu}}$, $\delta_{\text{IP}}$, $\delta_{\text{M}}$, $K_1$, and $K_2$ (or $K'_{1}$, and $K'_{2}$) as adjustable parameters. As can be seen from Figure S4, using the data from both experiments provides much steeper minima in $\chi_{\text{DRS}+\text{NMR}}$, as compared to the fit based on only NMR data ($\chi_{\text{NMR}}$).
Figure S4: Comparison of the relative fit quality for DPP + Qu in chloroform as a function of contained ion-pair formation constants ($K_1$ or $K'_1$) when modelling only NMR data ($\chi_{\text{NMR}}$) or both NMR and DRS data ($\chi_{\text{DRS+NMR}}$).
Figure S5. DRS spectra for (a) Qu in DCM, (b) Qu in THF, (c) PhQu in CHCl₃, (d) PhQu in DCM, and (e) PhQu in THF. The imine concentration is kept constant at 0.1 mol L⁻¹ in all samples. The data shown in panel a) are taken from ref. 1. Symbols correspond to experimental spectra, solid lines show fits of eq S2 to the data.
Figure S6. Concentration of multimers and ion-pairs (symbols) as extracted from the DRS experiments together with the concentration of all species (solid lines) according to the fitted equilibria (eqs 3 & 4, main manuscript) for (a) Qu in DCM, (b) Qu in THF, (c) PhQu in CHCl₃, (d) PhQu in DCM, and (e) PhQu in THF. Error bars are calculated assuming the error of the relaxation strengths to 2% of $\varepsilon_s$. 
Figure S7. Comparison of the fit quality ($\chi_{\text{NMR+DRS}}$) for simultaneously fitting the NMR and DRS data. Blue columns correspond to fits taking DPP dimerization into account (eqs 3-4), while red columns show fits based on free DPP monomers in solution.

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