Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Factors influencing the formation of polybromide monoanions in solutions of ionic liquid bromide salts

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Additional DFT Data

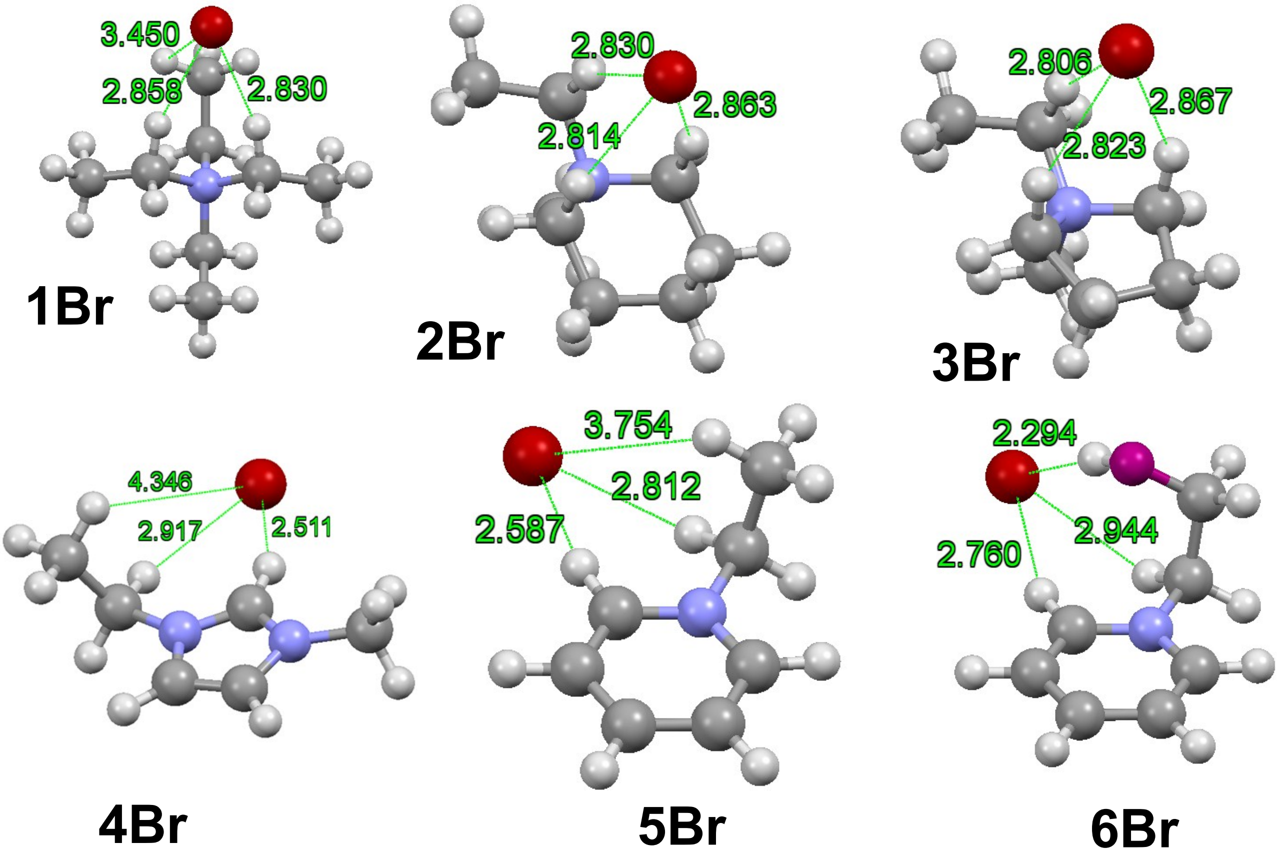
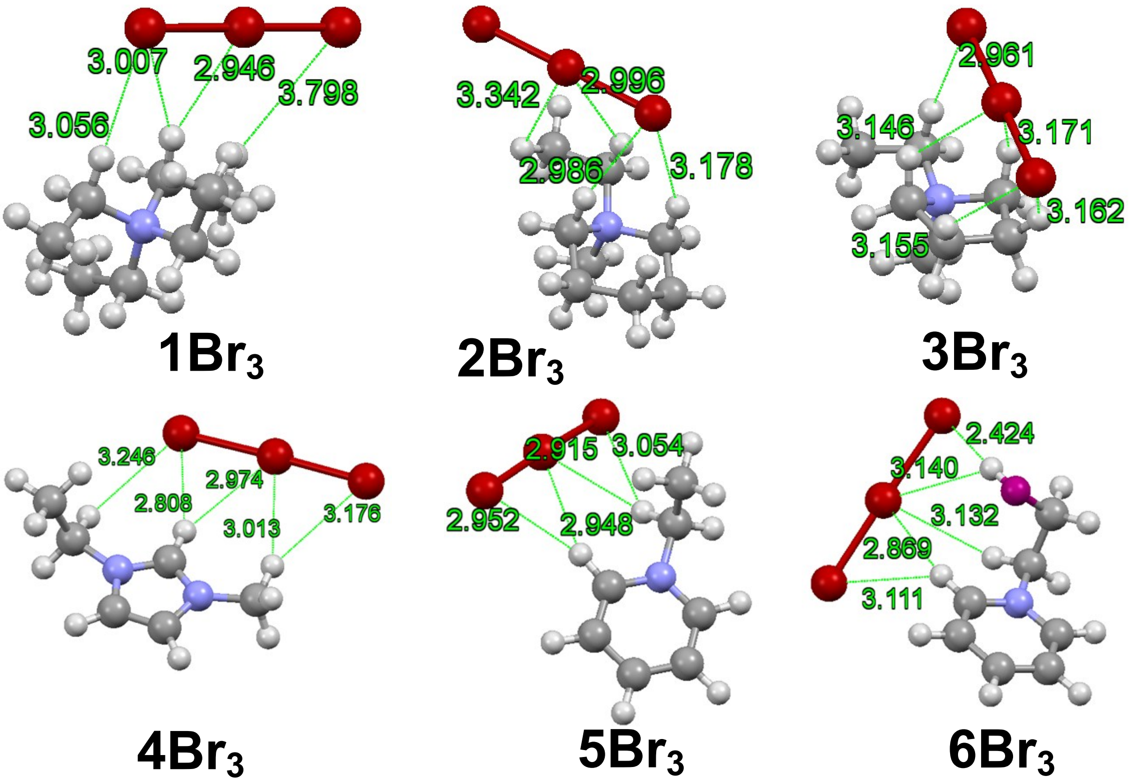


Figure S1. DFT energy-minimized structures for the bromide salts of the studied cations: $[N_{2,2,2,2}]Br$, **1Br**; $[C_2MPip]Br$, **2Br**; $[C_2MPyrr]Br$, **3Br**; $[C_2Mim]Br$, **4Br**; $[C_2Py]Br$, **5Br**; $[C_2OHPy]Br$, **6Br**.



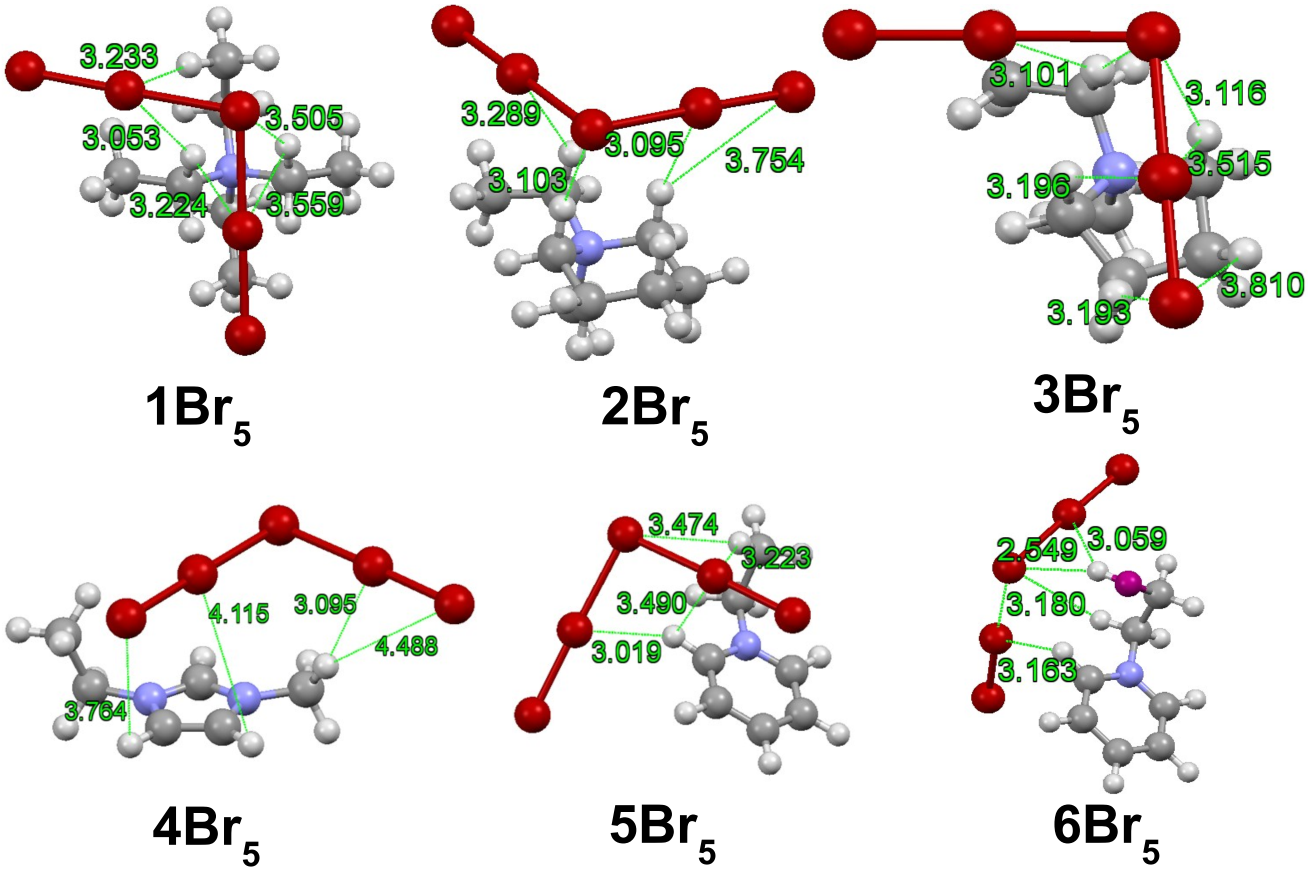
$1Br_3$ **$2Br_3$** **$3Br_3$**

$4Br_3$ **$5Br_3$** **$6Br_3$**

Figure S2. DFT energy-minimized structures for the tribromide salts of the studied cations: $[N_{2,2,2,2}]Br_3$, **$1Br_3$**; $[C_2MPip]Br_3$, **$2Br_3$**; $[C_2MPyrr]Br_3$, **$3Br_3$**; $[C_2Mim]Br_3$, **$4Br_3$**; $[C_2Py]Br_3$, **$5Br_3$**; $[C_2OHPy]Br_3$, **$6Br_3$**.

Table S1. Summary of data derived from modelling the ion-pairing step between an IL cation and a bromide anion (solvent-separated) by DFT methods

	shortest H···Br contact (H1, Å)	**2nd shortest H···Br contact (H2, Å)**	**3rd shortest H···Br contact (H3, Å)**
1 $[N_{2,2,2,2}]$	2.830	2.858	3.450
2 $[C_2MPip]$	2.814	2.830	2.863
3 $[C_2MPyrr]$	2.806	2.823	2.867
4 $[C_2MIm]$	2.511	2.917	4.345
5 $[C_2Py]$	2.587	2.812	3.754
6 $[C_2OHPy]$	2.294	2.760	2.944



$1Br_5$ $2Br_5$ $3Br_5$ $4Br_5$ $5Br_5$ $6Br_5$

Figure S3. DFT energy-minimized structures for the pentabromide salts of the studied cations where: $[N_{2,2,2,2}]Br_5$, **$1Br_5$**; $[C_2MPip]Br_5$, **$2Br_5$**; $[C_2MPyrr]Br_5$, **$3Br_5$**; $[C_2Mim]Br_5$, **$4Br_5$**; $[C_2Py]Br_5$, **$5Br_5$**; $[C_2OHPy]Br_5$, **$6Br_5$**.

Table S2. Computed NBO charges on hydrogen atoms of IL cations $[Q]^+$

	Charge on H1	Charge on H2	Charge on H3
1 $[N_{2,2,2,2}]$	0.278	0.278	0.256
2 $[C_2MPip]$	0.275	0.274	0.276
3 $[C_2MPyrr]$	0.276	0.276	0.275
4 $[C_2MIm]$	0.299	0.277	0.253
5 $[C_2Py]$	0.296	0.281	0.255
6 $[C_2OHPy]$	0.505	0.294	0.282

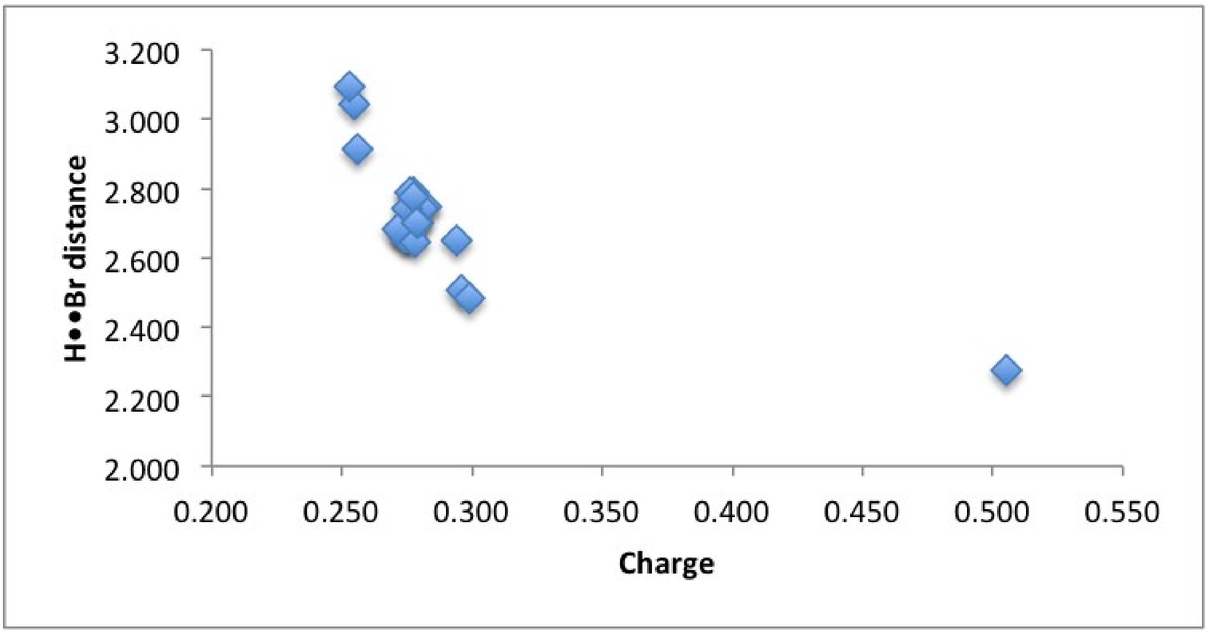


Figure S4. Relationship between H···Br distance in [Q][Br] ion pair and charge on the relevant hydrogen atom in isolated $[Q]^+$calculated from energy-minimized structures (see Computational Details for further information) for the studied [Q][Br] ion pairs.

Table S3. Computed Raman absorptions for tri- and pentabromide species (cm-1)

	Calculated	After Standard Scale Factor	Experimental
$[Br_3]^-$	181, 201	170, 188	163, 190
$[Br_5]^-$	223, 260	209, 244	210, 253

Supporting Raman Spectra

Raman spectra for each bromide salt solution are provided below in Figures S4*a-f*, revealing the polybromide fingerprint region (inset) and other Raman absorption signals up to 3500 cm^{-1}. No observable influence of bromine addition on the Raman active absorption bands belonging to the solvent system (methanol nor acetonitrile) or the IL cation can be seen in these spectra.

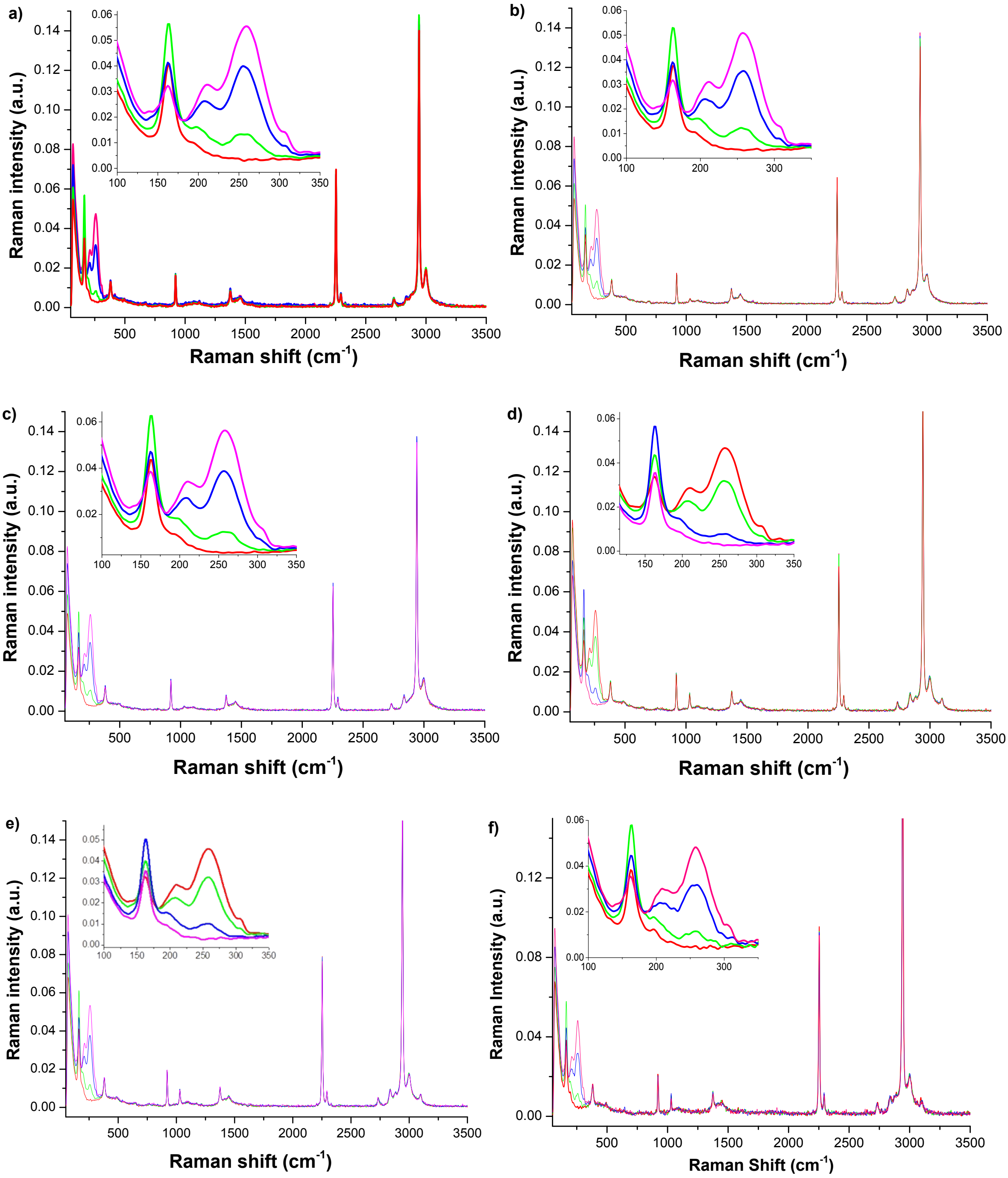


Figure S4) Complete Raman spectra for: a) [$N_{2,2,2,2}$]Br_5, **1Br$_5$** b) [C_2MPip]Br_5; c) **2Br$_5$**; [C_2MPyrr]Br_5, **3Br$_5$**; d) [C_2Mim]Br_5, **4Br$_5$**; e) [C_2Py]Br_5, **5Br$_5$**; f) [C_2OHPy]Br_5, **6Br$_5$** showing the Raman absorption regions outside of the fingerprint region for polybromide compounds.

Procedure for Dimerization Modelling

The NMR dimerization modelling method is nearly identical to that of Weber, et al.[1] Thus, the following is reproduced from the Supporting Information of that work for ease of reference:

Titration curves were fit to the dimerization model in equation (S1).

$$2[\mathrm{IP}] \rightleftharpoons [\mathrm{D}] \qquad \text{(S1)}$$

where [IP] is the concentration of ion pairs and [D] is the concentration of dimers. K_a, the association equilibrium constant for the dimerization, would be given by equation (S2):

$$K_a = \frac{[D]}{[IP]^2} \qquad \text{(S2)}$$

The total concentration of ions is given by:

$$[\mathrm{C}] = [\mathrm{IP}] + 2[\mathrm{D}] \qquad \text{(S3)}$$

Rearranging equation (S2) and substituting into (S3) yields:

$$[\mathrm{C}] = [\mathrm{IP}] + 2[\mathrm{IP}]^2K_a$$

This can be further simplified through the following steps:

$$\frac{[C]}{2K_a} = \frac{[IP]}{2K_a} + [IP]^2$$

$$\frac{[C]}{2K_a} = ([IP] + \frac{1}{4K_a})^2 - \frac{1}{16K_a^2}$$

$$[IP] + \frac{1}{4K_a} = \frac{\sqrt{1 + 8K_a[C]}}{4K_a}$$

Hence

$$[IP] = \frac{-1 + \sqrt{1 + 8K_a[C]}}{4K_a} \qquad (S4)$$

Directly from equation (S3) it can be obtained that:

$$[D] = \frac{[C] - [IP]}{2} \qquad (S5)$$

Finally the observed chemical shift can be treated as a weighted average of the dimeric and monomeric chemical shift environments:

$$\delta_{obs} = \frac{[IP]}{[C]}\delta_{ip} + \frac{2[D]}{[C]}\delta_d \qquad (S6)$$

The titration curves obtained from the NMR spectra were correspondingly fit using the Origin 8.5 non-linear least squares fitting program to equation (S6) using equations (S4) and (S5) as constraints.

This was repeated for at least 9 different ^{1}H NMR environments and the average of these values, weighted by $|\delta_d - \delta_{ip}|$ for each environment, was reported.

The fits and titration curves are all shown in Figure S5. All R^2 values exceed 0.99.

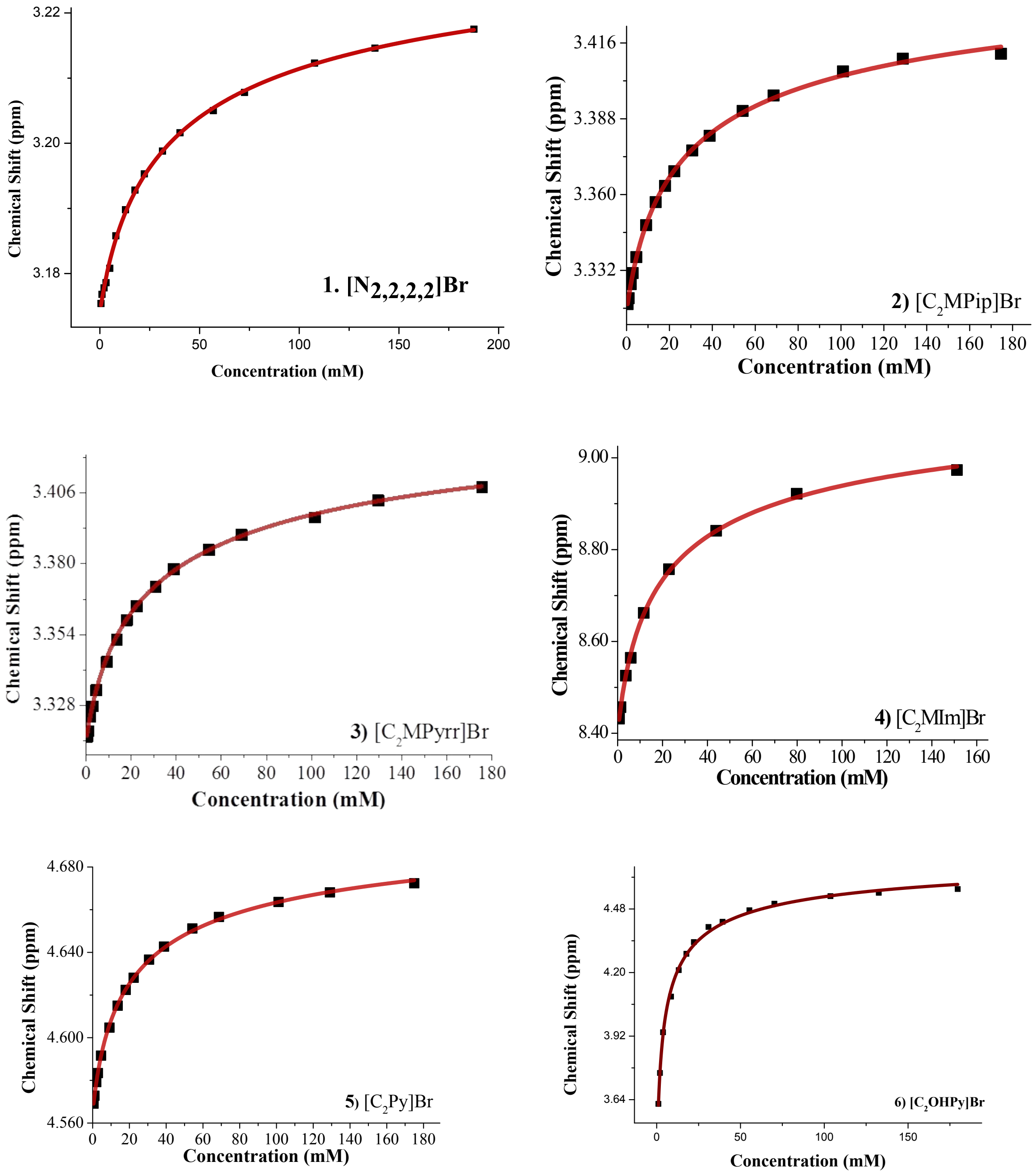


Figure S5. Fits of dimerization data obtained in the ^{1}H NMR dilution titration, where chemical shift refers to that of the cation's C2 proton.

References

[1] C. C. Weber, A. F. Masters, T. Maschmeyer, *Journal of Physical Chemistry B* **2012**, *116*, 1858-1864.