# Anion-Dependent Spin Crossover in Solution for an Iron(II) Complex of a 1*H*-pyrazolyl Ligand

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## Electronic Supplementary Information

**Experimental details**

**Figure S1** Variable temperature magnetic susceptibility data for three salts $[Fe(3\text{-bpp})_2]X_2$ ($X^- = I^-$, $BF_4^-$ and $PF_6^-$) as reported by Goodwin *et al.*.

**Figure S2** $^1$H NMR spectra of five $[Fe(3\text{-bpp})_2]X_2$ (**1X$_2$**) salts in 9:1 v/v $(CD_3)_2CO$:$D_2O$ at 298 K, showing the variation in the isotropic shifts with the anion present.

**Table S1** Experimental details for the single crystal structure determinations of solvates of $[Fe(3\text{-bpp})_2][BF_4]_2$.

**Figure S3** Comparison of the solvent dependence of the $^1$H isotropic shifts of $[Fe(3\text{-bpp})_2]X_2$ (**1X$_2$**) on the anion $X^-$, in four different solvents (Table S1).

**Figure S4** Variable temperature magnetic susceptibility data for **1X$_2$** in neat $(CD_3)_2CO$.

**Figure S5** Variable temperature magnetic susceptibility data for **1[BPh$_4$]$_2$** in 9:1 v/v $(CD_3)_2CO$:$D_2O$, in the presence of $[NBu_4]Br$.

**Figure S6** Dependence of $T_{½}$ on bromide ion concentration for **1[BPh$_4$]$_2$** in the presence of *y* equivalents of $[NBu_4]Br$.

**Figure S7** UV/vis spectra of five of the compounds in this work.

**References**

**Experimental**

Reaction of $Fe[BF_4]_2 \cdot 6H_2O$ (0.20 g, 0.59 mmol) by 3-bpp[1] (0.25 g, 1.18 mmol) in nitromethane (25 $cm^3$) at room temperature rapidly afforded a yellow-brown solution. This was filtered, concentrated to 5 $cm^3$. Slow diffusion of diethyl ether vapour into the filtered solution yielded large brown blocks, that decompose to yellow solvent-free **1[BF$_4$]$_2$** when dried *in vacuo*.

A similar complexation of $FeBr_2 \cdot 4H_2O$ (0.17 g, 0.59 mmol) and 3-bpp (0.25 g, 1.18 mmol) in methanol (25 $cm^3$) gave an orange solution, that yielded the methanol solvate of **1Br**$_2$ as an orange-brown powder following the work-up as above.

The other salts of $[Fe(3\text{-bpp})_2]^{2+}$ (**1**$^{2+}$) were prepared by warming a mixture of $FeCl_2 \cdot 4H_2O$ (0.12 g, 0.59 mmol) and 3-bpp (0.25 g, 1.18 mmol) in water (50 $cm^3$), until all the ligand had dissolved. Adding excess $NaBPh_4 \cdot H_2O$, $NaCF_3SO_3$, KNCS or $NaNO_3$ to the filtered brown solutions immediately yielded an orange or brown precipitate, which was collected, washed with water and dried *in vacuo*. Recrystallisation by slow diffusion of diethyl ether vapour into a solution of the compounds in nitromethane ($X^-$ = $BPh_4^-$ or $CF_3SO_3^-$), or methanol ($X^-$ = $NCS^-$, $NO_3^-$) gave the pure complexes as brown solids.

For **1[BPh$_4$]$_2$**$\cdot$½$H_2O$:[3] found C, 74.9; H, 5.15; N, 12.6 %. Calcd. for $C_{70}H_{58}B_2FeN_{10} \cdot$½$H_2O$ C, 75.7; H, 5.28; N, 12.4 %.

For **1[BF$_4$]$_2$**:[4,5] found C, 40.5; H, 3.05; N, 21.4 %. Calcd. for $C_{22}H_{18}B_2F_8FeN_{10}$ C, 40.5; H, 2.78; N, 21.5 %.

For **1[CF$_3$SO$_3$]$_2$**$\cdot H_2O$:[6] found C, 36.1; H, 2.50; N, 17.3 %. Calcd. for $C_{24}H_{18}F_6FeN_{10}O_6S_2 \cdot H_2O$ C, 36.3; H, 2.54; N, 17.6 %.

For **1[NCS]$_2$**$\cdot H_2O$:[7] found C, 46.4; H, 3.15; N, 27.2 %. Calcd. for $C_{24}H_{18}FeN_{12}S_2 \cdot H_2O$ C, 47.1; H, 3.29; N, 27.4 %.

For **1[NO$_3$]$_2$**$\cdot 2H_2O$:[8] found C, 41.4; H, 3.35; N, 26.4 %. Calcd. for $C_{22}H_{18}FeN_{12}O_6 \cdot 2H_2O$ C, 41.4; H, 3.47; N, 26.3 %.

For **1Br**$_2 \cdot CH_3OH$: found C, 41.2; H, 3.05; N, 20.7 %. Calcd. for $C_{22}H_{18}Br_2FeN_{10} \cdot CH_3OH$ C, 41.2; H, 3.31; N, 20.9 %. This salt has been previously reported as its pentahydrate and anhydrous solid forms.[8]

**Other measurements**

UV/visible spectra were obtained with a Perkin-Elmer Lambda 900 spectrophotometer operating between 200–1,500 nm, in 1 cm quartz cells. Paramagnetic $^1$H NMR spectra were measured with a Bruker DPX300 spectrometer operating at 300.2 MHz. Magnetic susceptibility measurements in solution were obtained by Evans method using Bruker DRX500 or Bruker Avance500 spectrometers operating at 500.13 MHz.[9] Duplicate measurements on both spectrometers were performed to confirm their temperature calibration was consistent. Tetramethylsilane was added to all the solutions as an internal standard. A diamagnetic correction for the sample,[10] and a correction for the variation of the density of the solvent with temperature,[11] were applied to these data. All magnetochemical data manipulation and graph plotting was carried out using *SIGMAPLOT*.[12]

Each Evans method measurement was performed at a concentration of 10±1 mM. The UV/vis spectra required lower concentrations, of 0.16-0.20 mM.

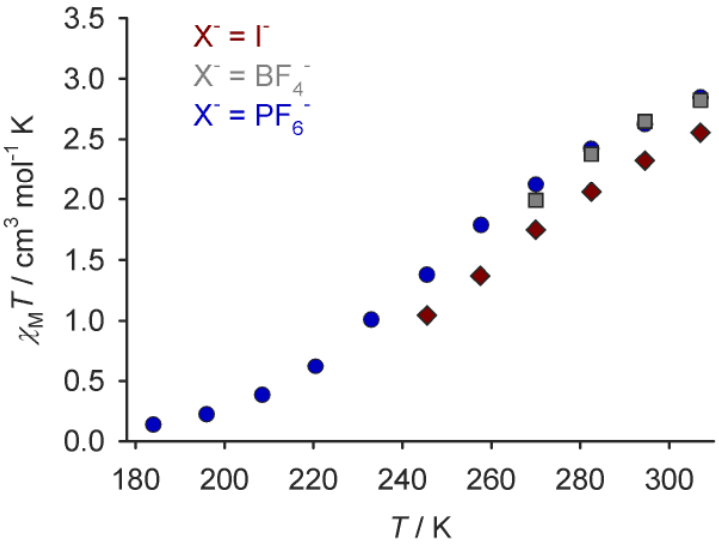


**Fig. S1** Variable temperature magnetic susceptibility data for $[Fe(3\text{-bpp})_2]X_2$ (**1X$_2$**; $X^- = I^-$, $BF_4^-$ and $PF_6^-$), as reported by Goodwin *et al.*[8] The data have been converted from $\mu_{eff}$ to $\chi_M T$, and replotted.

These measurements were performed in "acetone containing a few drops of water", and in the presence of excess 3-bpp ligand. The excess ligand has no apparent influence on the results, based on the similarity between the data for **1[BF$_4$]$_2$** in the Figure, and in this study.

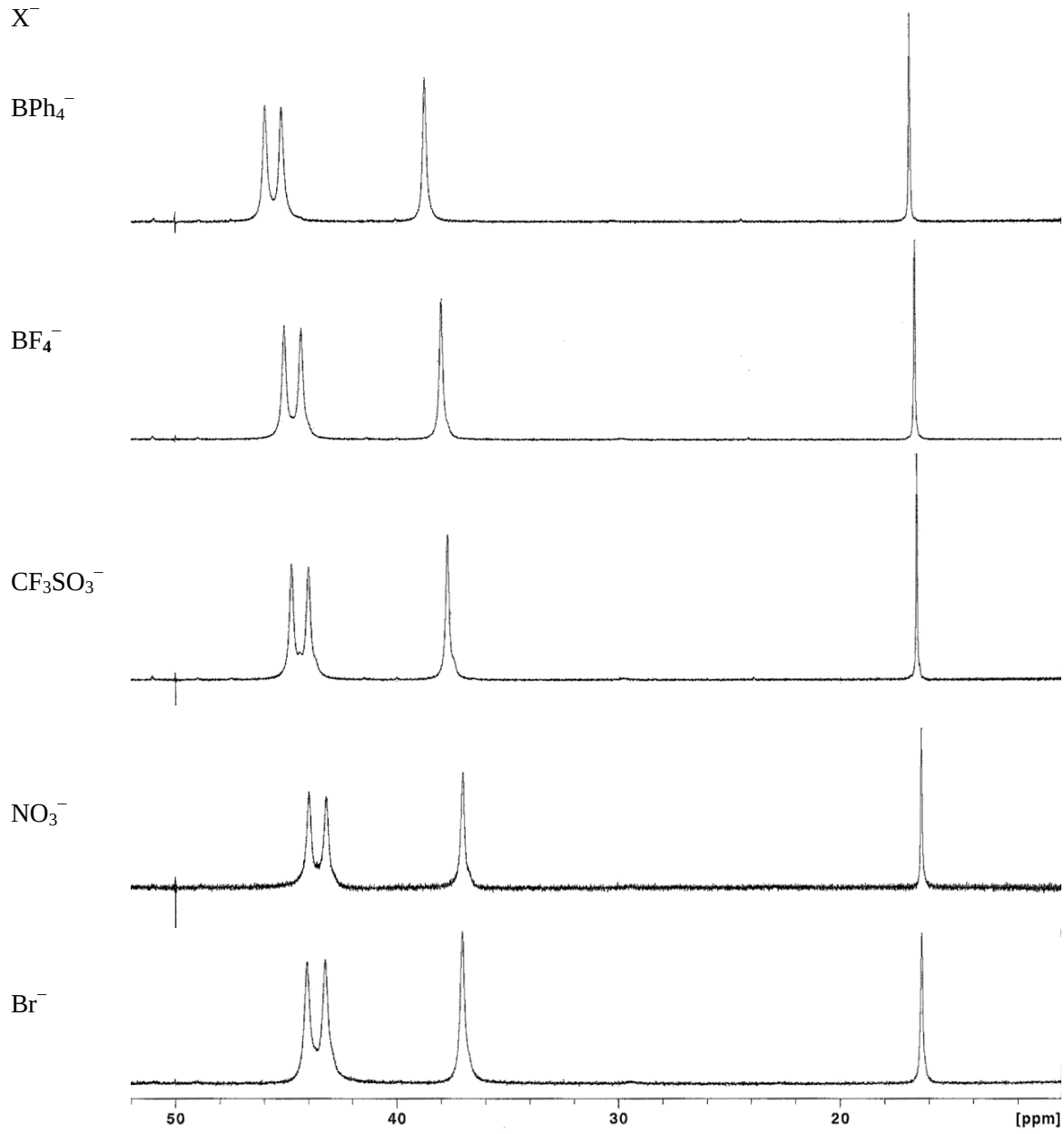


**Fig. S2** $^{1}$H NMR spectra of five $[Fe(3\text{-bpp})_2]X_2$ (**1X$_2$**) salts in 9:1 v/v $(CD_3)_2CO$:$D_2O$ at 298 K, showing the variation in the isotropic shifts with the anion present. See Table S1 for the assignment of these resonances.

Reduced isotropic shifts imply the sample contains a smaller high-spin population at room temperature,[13] which would be consistent with an increased spin-crossover $T_{½}$ value. These isotropic shifts do not depend on concentration, all other things being equal.[13]

**Table S1** $^1$H NMR data for [Fe(3-bpp)$_2$]X$_2$ (**1X$_2$**) in different solvents at 298 K, at a concentration of 15 mmol dm$^{-3}$. These data are plotted in Fig. S1.

| Solvent | $X^-$ | $\beta^{N}$ [14] | Py $H^4$ | N$H$ | Py $H^{3/5}$ | Pz $H^4$ & Pz $H^5$ |
|---|---|---|---|---|---|---|
| $CD_3CN$ | $BPh_4^-$ | 0 | 18.6 | 32.7 | 45.5 | 53.1, 53.8 |
| | $BF_4^-$ | 0.69 | 18.5 | 32.8 | 45.5 | 53.0, 53.8 |
| | $CF_3SO_3^-$ | 0.74 | 18.2 | 32.6 | 44.6 | 52.0, 52.8 |
| $(CD_3)_2CO$ | $BPh_4^-$ | 0 | 18.6 | 33.4 | 44.5 | 51.8, 52.5 |
| | $BF_4^-$ | 0.69 | 18.1 | 33.2 | 43.4 | 50.5, 51.8 |
| | $CF_3SO_3^-$ | 0.74 | 17.7 | 32.7 | 42.4 | 49.2, 50.2 |
| $CD_3OD$ | $BPh_4^-$ | 0 | 18.3 | – | 42.5 | 49.9, 49.9 |
| | $BF_4^-$ | 0.69 | 18.3 | – | 42.3 | 49.5, 49.7 |
| | $CF_3SO_3^-$ | 0.74 | 18.3 | – | 42.2 | 49.4, 49.8 |
| | $NCS^-$ [a] | 0.78 | 18.2 | – | 42.0 | 49.2, 49.6 |
| | $NO_3^-$ [b] | 0.86 | 18.2 | – | 42.0 | 49.2, 49.6 |
| | $Br^-$ [b] | 0.93 | 18.3 | – | 42.2 | 49.5, 49.8 |
| 9:1 v/v $(CD_3)_2CO$:$D_2O$ | $BPh_4^-$ | 0 | 16.9 | – | 38.7 | 45.2, 45.9 |
| | $BF_4^-$ | 0.69 | 16.6 | – | 38.0 | 44.3, 45.2 |
| | $CF_3SO_3^-$ | 0.74 | 16.6 | – | 37.7 | 44.0, 44.8 |
| | $NCS^-$ [b] | 0.78 | 16.3 | – | 37.0 | 43.2, 43.9 |
| | $NO_3^-$ [b] | 0.86 | 16.4 | – | 37.0 | 43.2, 44.0 |
| | $Br^-$ [b] | 0.93 | 16.3 | – | 37.0 | 43.2, 44.0 |

[a]Spectrum also contains broad peaks assignable to free 3-bpp at 6.9, 7.6, 7.7 and 7.8 ppm with a 2:2:2:1 integral ratio. This species has a 40 % integral ratio compared to the main, paramagnetic complex. This is evidence for substantial dissociation of the complex in this solvent, probably from displacement of 3-bpp by the nucleophilic $NCS^-$ ion.

[b]Spectrum contains free 3-bpp (see above), with a 6-10 % integral ratio compared to the main, paramagnetic complex. This is evidence for a small degree of dissociation of the complex in this solvent (the integral of the diamagnetic free ligand will be overestimated compared to the paramagnetic complex, because of line-broadening in the contact-shifted peaks).

The $\beta^{N}$ parameter is a measure of the hydrogen-bond acceptor character of an anion, derived from a $^1$H NMR measurement of its association with the 1-butyl-3-methylimidazolium ([Bmim]$^+$) cation in $CD_2Cl_2$.[14]

The relationship between $\delta$ and the different solvents used, for a given anion $X^-$, has been reported in ref. [5].

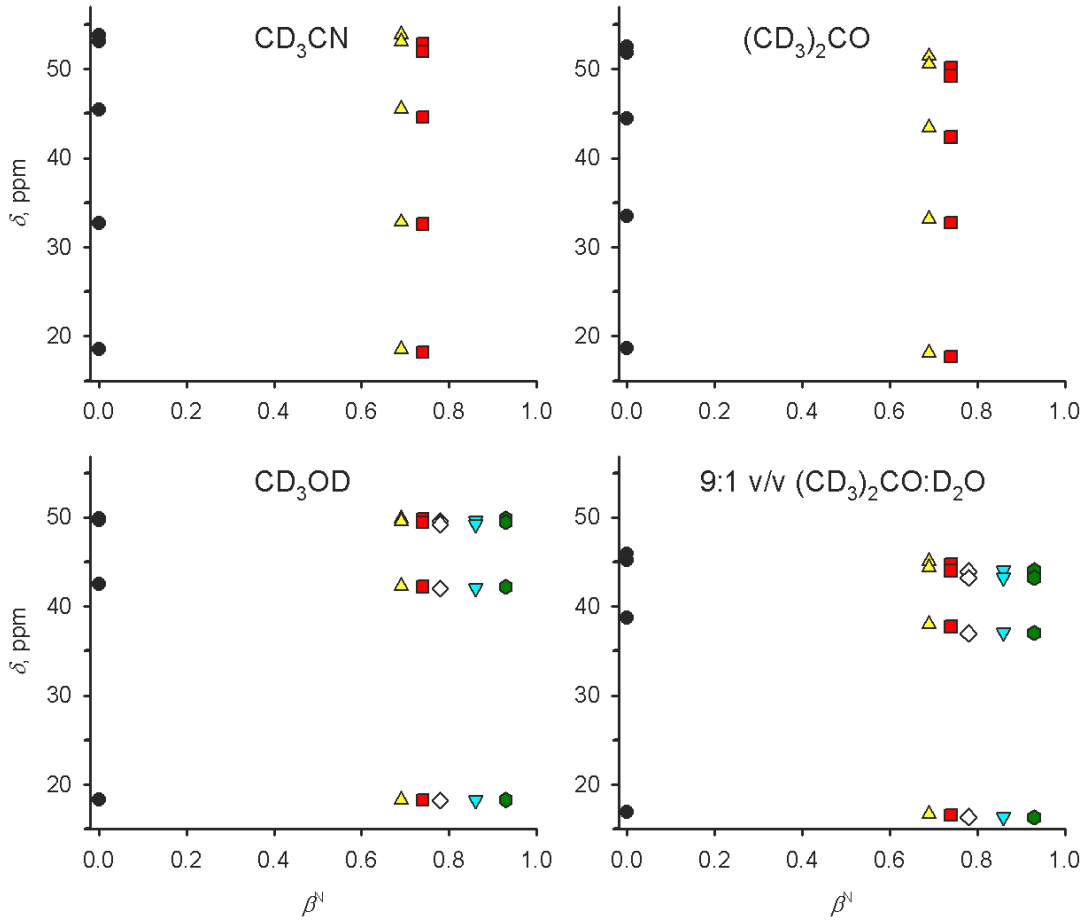


**Fig. S3** Comparison of the solvent dependence of the $^{1}$H isotropic shifts of $[Fe(3\text{-bpp})_2]X_2$ (**1X₂**) on the anion $X^-$, in three different solvents (Table S1). Colour code: $X^-$ = $BPh_4^-$ (black), $BF_4^-$ (yellow), $CF_3SO_3^-$ (red), $NCS^-$ (white), $NO_3^-$ (cyan), $Br^-$ (green).

There is a small but consistent decrease in the isotropic shifts ($\delta$) in $CD_3CN$ and $(CD_3)_2CO$ when $X^- = CF_3SO_3^-$, compared to $BPh_4^-$ and $BF_4^-$. A comparable trend was also seen for all the salts in the acetone/water mixed solvent. That implies that salts of the complex with more associating anions have a slightly greater low-spin population at room temperature. This was subsequently confirmed by the Evans method study described in the main article.

No comparable relationship between $\delta$ and $X^-$ was observed in $CD_3OD$, implying that hydrogen bonding between $\mathbf{1}^{2+}$ and $X^-$ is weaker in that solvent, as expected.

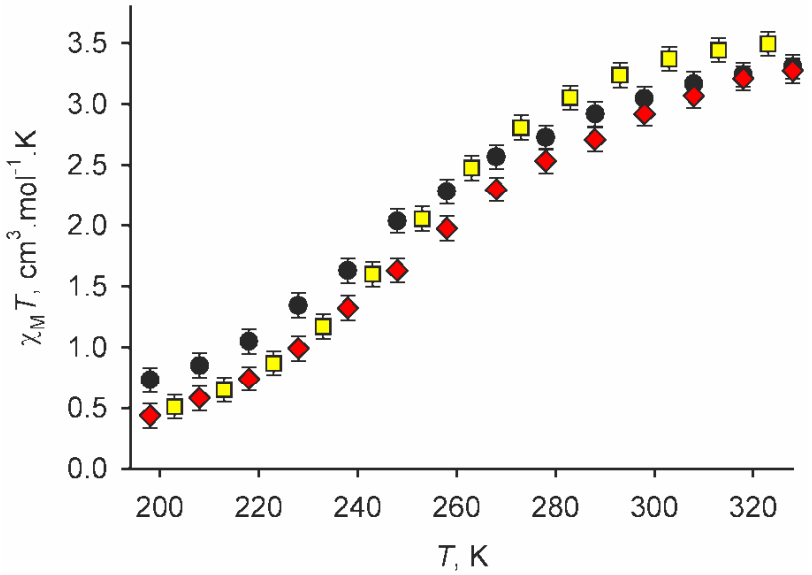


**Fig. S4** Variable temperature magnetic susceptibility data for **1X$_2$** in neat $(CD_3)_2CO$, with $X^-$ = $BPh_4^-$ (black circles), $BF_4^-$ (yellow squares) and $CF_3SO_3^-$ (red diamonds).

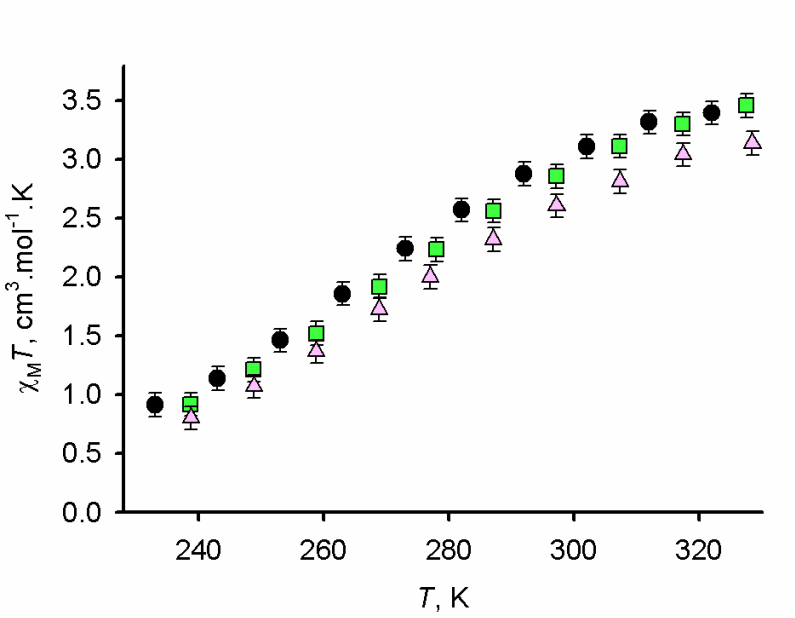


**Fig. S5** Variable temperature magnetic susceptibility data for **1[BPh$_4$]$_2$** in 9:1 v/v $(CD_3)_2CO$:$D_2O$, in the presence of *y* equivalents of [NBu$_4$]Br: *y* = 0 (black circles), *y* = 0.78 (green squares) and *y* = 1.71 (pink triangles).

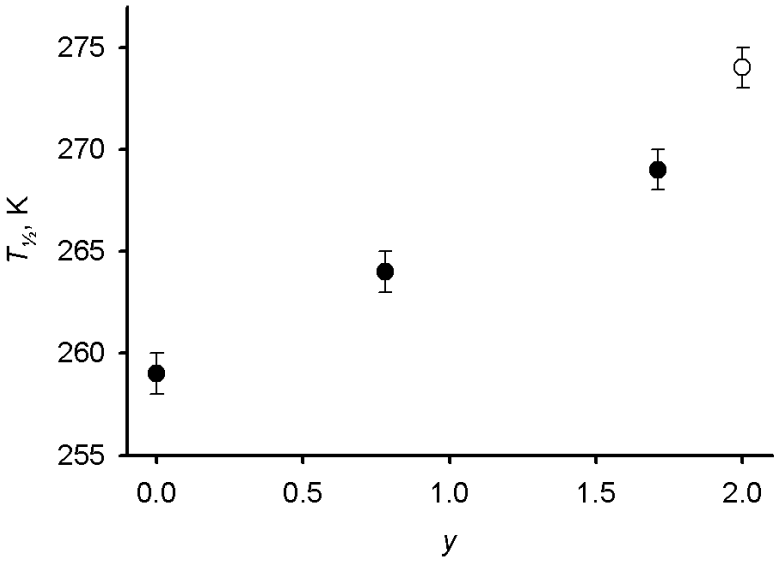


**Fig. S6** Dependence of $T_{½}$ on bromide ion concentration for **1[BPh$_4$]$_2$** in the presence of *y* equivalents of [NBu$_4$]Br. The open circle is for pure **1Br$_2$** (putatively, *y* = 2).

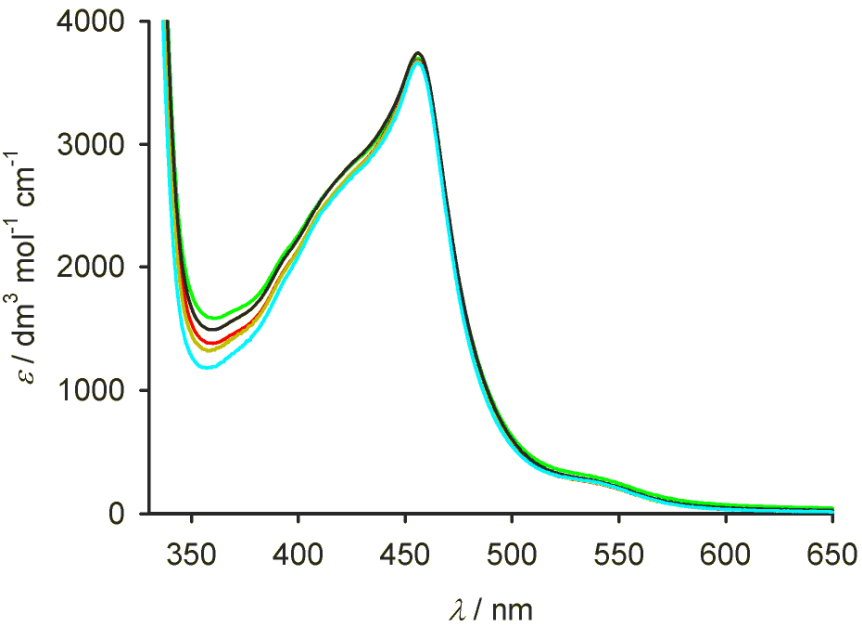


**Fig. S5** UV/vis spectra of five of the compounds in this work, in 9:1 v/v $(CH_3)_2CO$:$H_2O$ at 293 K: **1[BPh$_4$]$_2$** (black), **1[BF$_4$]$_2$** (yellow), **1[CF$_3$SO$_3$]$_2$** (red), **1[NO$_3$]$_2$** (cyan) and **1Br$_2$** (green).

The differing depth of the trough against the solvent shoulder, near 360 nm, reflects small differences in the concentrations of the samples, which were between 1.6-2.0 x$10^{-4}$ mol $dm^{-3}$. Otherwise, these spectra are identical within experimental error, and are consistent with those reported previously for **1[BF$_4$]$_2$** in $(CH_3)_2CO$:$H_2O$ solvent mixtures.[5]

The invariance of these spectra with the anion present may reflect the sample concentrations used in the UV/vis measurements, which were *ca.* 50x lower than for the NMR and Evans method experiments. This lower concentration will promote dissociation of any supramolecular anion complexes of **1**$^{2+}$.

**References**


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