Supplementary Information File For Manuscript:

Synthesis, X-ray Characterization and DFT Studies of bis-N-imidazolylpyrimidine salts: the prominent role of hydrogen bonding and anion–π interactions

by

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Aggregation study of compound 1.

The X-ray structure of compound **1** shows the formation of an assembly dominated by H-bonding interactions where two *bimipyr*H_2 cations are present (See Fig. S1).

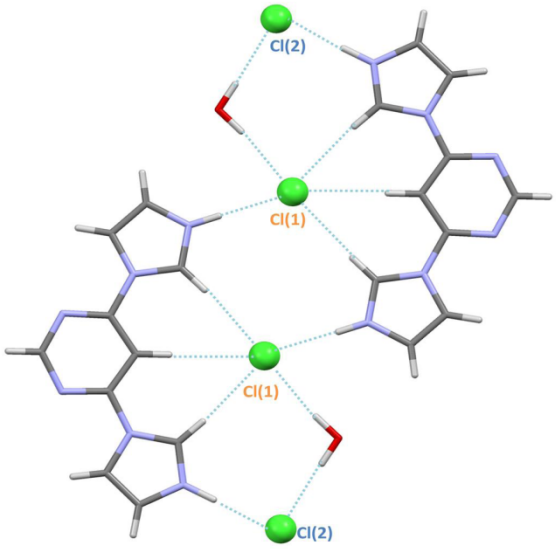

Fig. S1 Assembly observed in the solid state structure of compound 1.

We have performed the ESI-HRMS analysis of a solution of **1** and the spectrum shows the existence of species with two and three bimipyr moieties. That is: $[(bimipyrH)_2 + Cl]^+$ (exact mass for $C_{20}H_{18}N_{12}Cl$: experimental 461.1477; calculated

461.1466) and [(*bimipyr*H)$_2$ + *bimipyr*H +Cl]$^+$ (exact mass for $C_{30}H_{26}N_{18}Cl$: exp. 673.2303; calc. 673.2276).

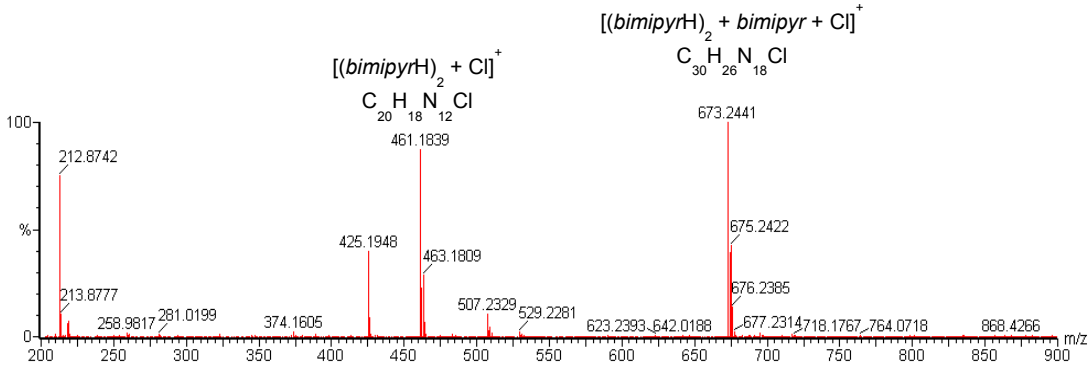

Fig. S2 Mass spectrum of compound 1

Since we have detected both in the gas and solid phase the assembly where two *bimipyr*H$_2$ cations are connected by chloride anions, it is interesting to study the existence of these species in solution. We have performed several dilution experiments, following the behaviour by NMR spectroscopy in DMSO-d$_6$ and a concentration range from $4 \cdot 10^{-4}$ M and $1.4 \cdot 10^{-2}$ M (two orders of magnitude). Some representative spectra are shown in Fig. S3 and a clear movement of all signals is observed (being all of them down shifted) upon increasing the concentration.

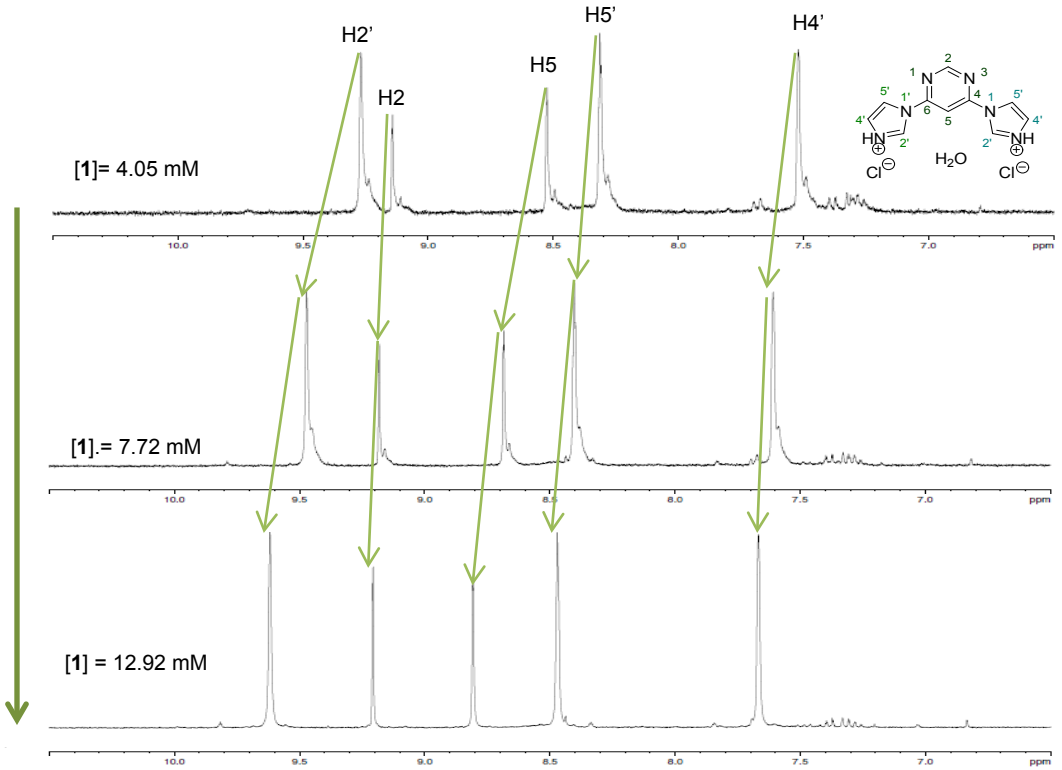

Fig. S3 1H-NMR spectra at different concentrations of **1** in DMSO

The signal of the H2' proton has a maximum displacement of +0.65 ppm and H5 is displaced +0.47 ppm, which indicates the presence of H-bonding interactions and consequently the formation of aggregates in solution. In table S1 a summary of the dis

Tale S1. Chemical displacement of **1** at different concentrations:

Δδ (ppm)	**H2**	**H5**	**H2'**	**H4'**	**H5'**
[1] = 13.27 to [1] = 1.80 mM	+0.14	+0.47	+0.65	+0.30	+0.27
From Saturation to [1] = 1.80 mM	+0.32	+0.95	+1.22	+0.51	+0.51

This study suggests the existence of a dynamic process of aggregation in solution. We have performed an adjustment of the experimental data using a dimerization model:

$$2A \rightleftharpoons A_2 \qquad A = [(bimipyrH_2)^{2+}\cdot 2Cl^-]\cdot x\ nH_2O$$

The nonlinear multi-regression analysis of the experimental data using HypHNMR 2008[1,2] software shows a very good agreement between the theoretical model and the experimental data (see Fig. S4). The dimerization constant obtained by the fitting of these data is K_{dim}=250 ± 20 M^{-1}. Finally, in Fig. S5 we show the distribution of species in solution, it can be observed that at [**1**] = $1\cdot10^{-2}$ M the 60 % of A_2 is present.

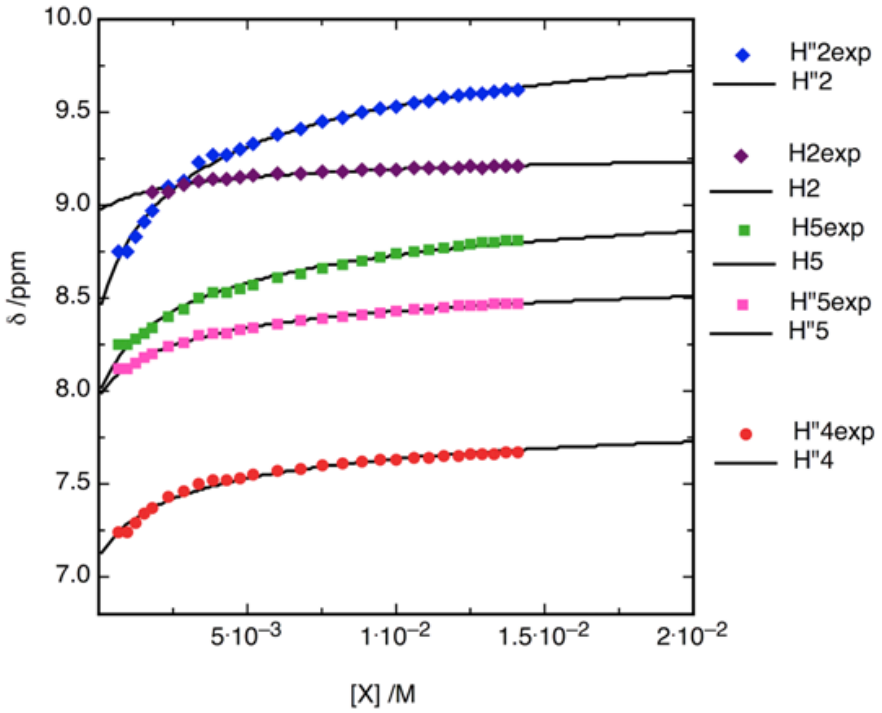

Fig. S4 Plot of the [1] vs chemical 1H-NMR shift displacement of several signals of 1 at different concentrations.

[1] C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M.S. Moruzzi, A. Vacca. Anal. Biochem. 1995, 231, 374-382.
[2] C. Frassineti, L. Alderighi, P. Gans, A. Sabatini, A.Vacca, S. Ghelli, *Anal. Bioanal. Chem.* 2003, **376**, 1041-1052.

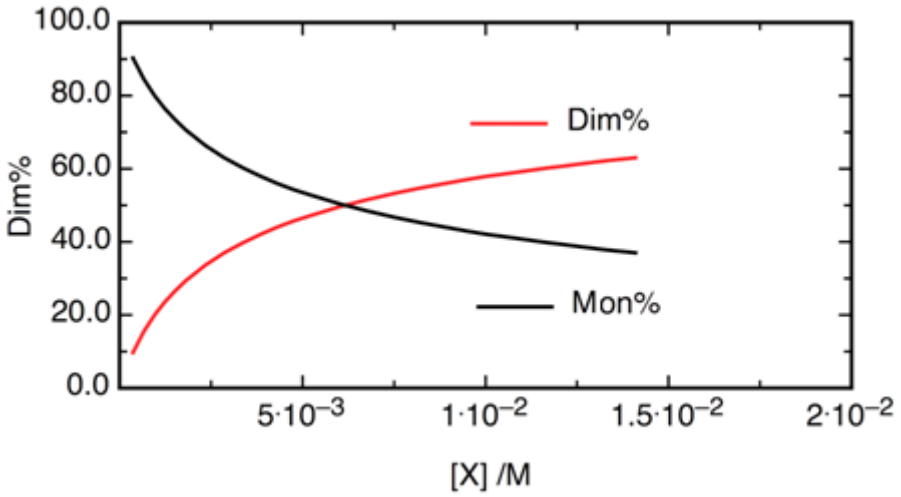

Fig. S5 Distribution of species in solution at different concentrations.