ESI for

A rotaxane host system containing integrated triazole C–H hydrogen bond donors for anion recognition

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Details of instrumentation

Routine NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^{1}H NMR operating at 300 MHz, ^{13}C at 75.5 MHz, ^{19}F at 283 MHz, and ^{31}P at 122 MHz. Some compounds were too poorly-soluble, or not enough compound was synthesized to allow ^{13}C NMR spectra to be recorded on the 300 MHz spectrometer. In these cases, the spectra were collected on a Bruker AVII 500 spectrometer with a 5 mm $^{13}C(^{1}H)$ dual cryoprobe with ^{13}C operating at 126 MHz and ^{1}H operating at 500 MHz.

High resolution ESI mass spectra were recorded on a Bruker μTOF spectrometer. High resolution EI mass spectra were recorded on a Waters GCT Classic spectrometer. Low resolution ESI mass spectra were recorded on a Walters LCT premier spectrometer.

NMR Spectra of new compounds

NMR Spectra of 2

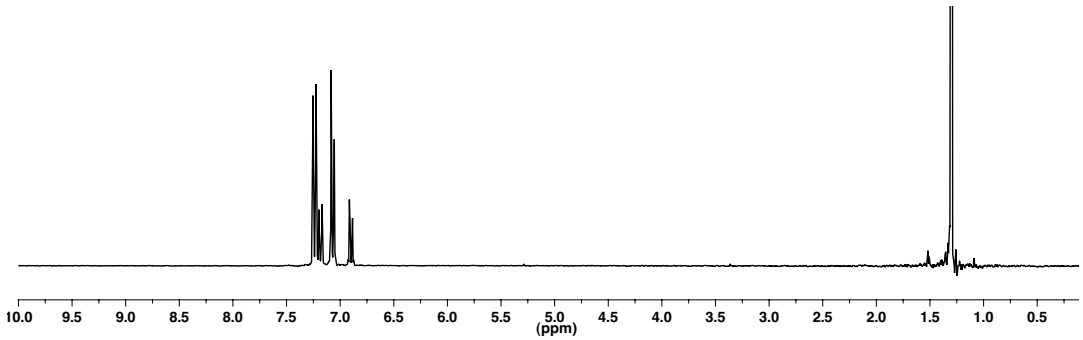

Figure S1. ^{1}H NMR spectrum of **2** ($CDCl_3$, 293 K, 300 MHz).

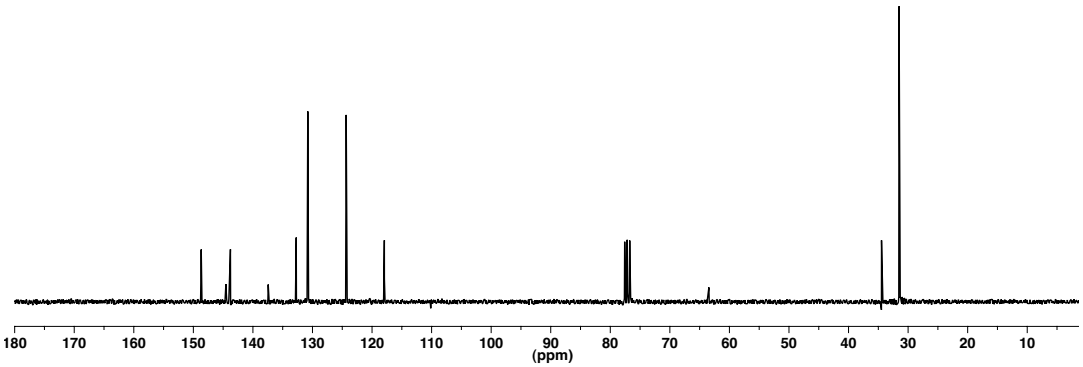

Figure S2. ^{13}C NMR spectrum of **2** ($CDCl_3$, 293 K, 300 MHz).

NMR Spectra of 4

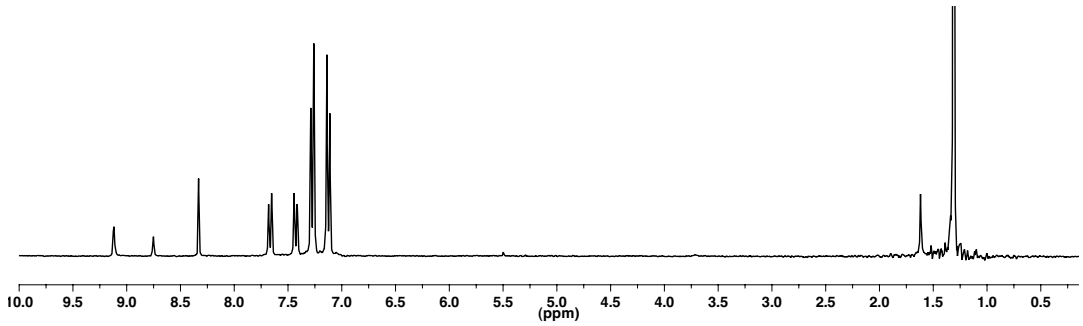

Figure S3. ^{1}H NMR spectrum of **4** ($CDCl_3$, 293 K, 300 MHz).

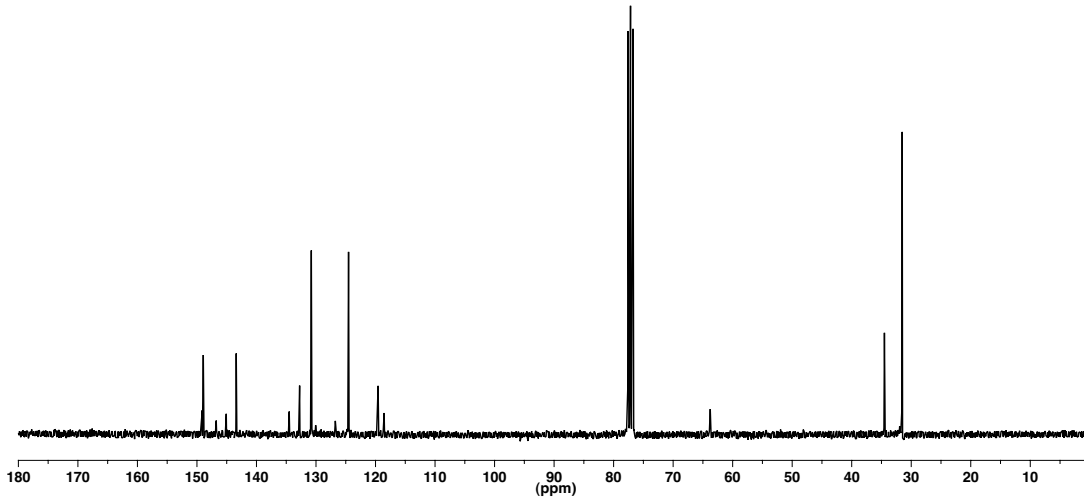

Figure S4. ^{13}C NMR spectrum of **4** ($CDCl_3$, 293 K, 300 MHz).

NMR Spectra of 5·PF_6

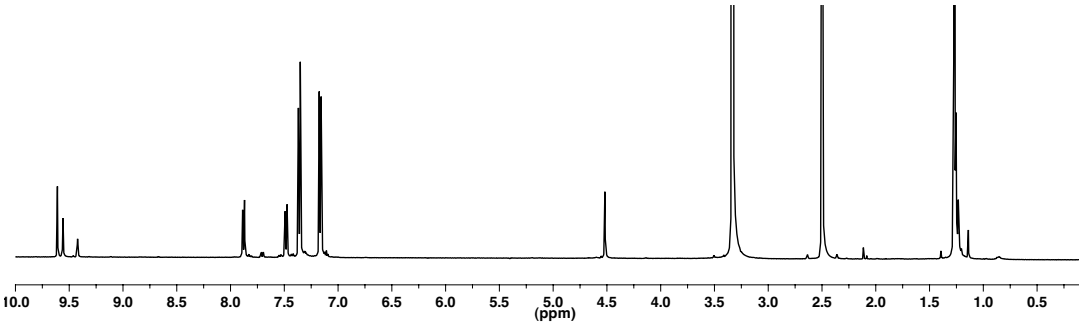

Figure S5. ^{1}H NMR spectrum of **5·PF_6** (d_6-DMSO, 293 K, 500 MHz).

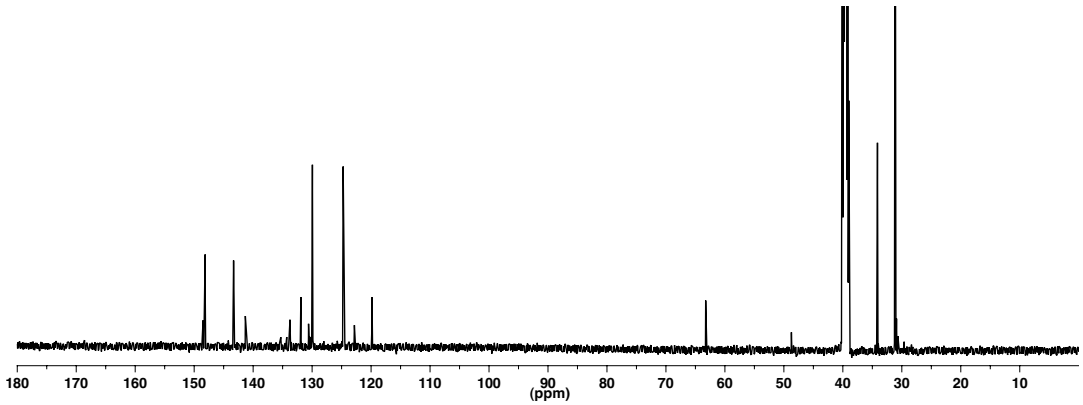

Figure S6. ^{13}C NMR spectrum of **5·PF_6** (d_6-DMSO, 293 K, 500 MHz).

^{1}H NMR Spectrum of 7·PF_6

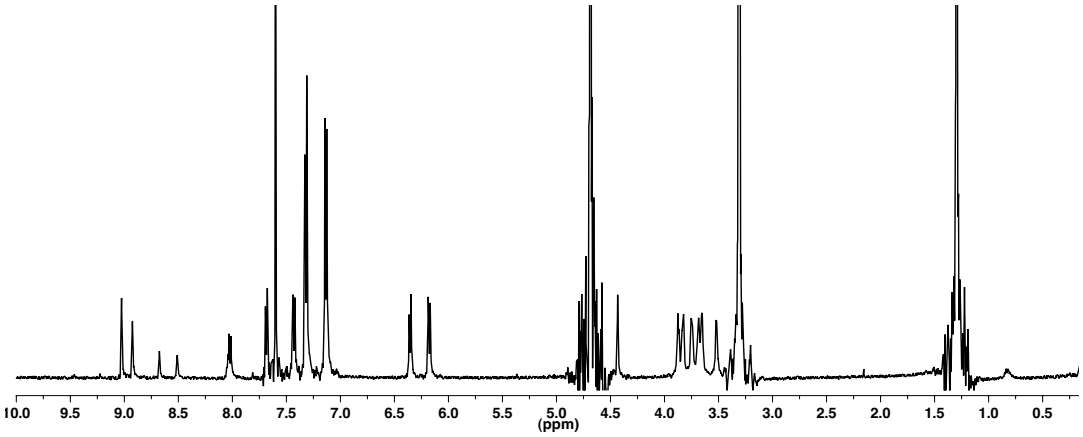

Figure S7. ^{1}H NMR spectrum of **7·PF_6** (1:1 $CDCl_3$:CD_3OD, 293 K, 500 MHz).

Insufficient material was prepared to obtain a useful ^{13}C NMR spectrum of this compound.

NMR Spectra of 9·PF_6

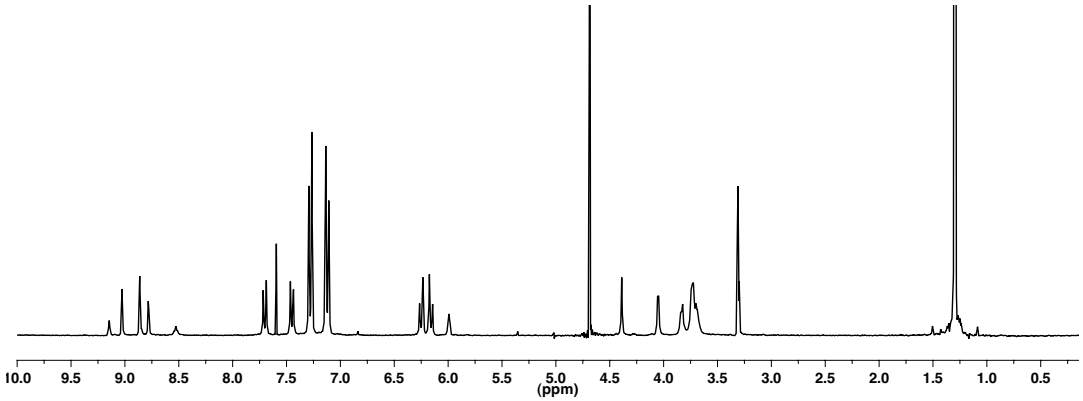

Figure S8. ^{1}H NMR spectrum of **9·PF_6** (1:1 $CDCl_3$:CD_3OD , 293 K, 500 MHz).

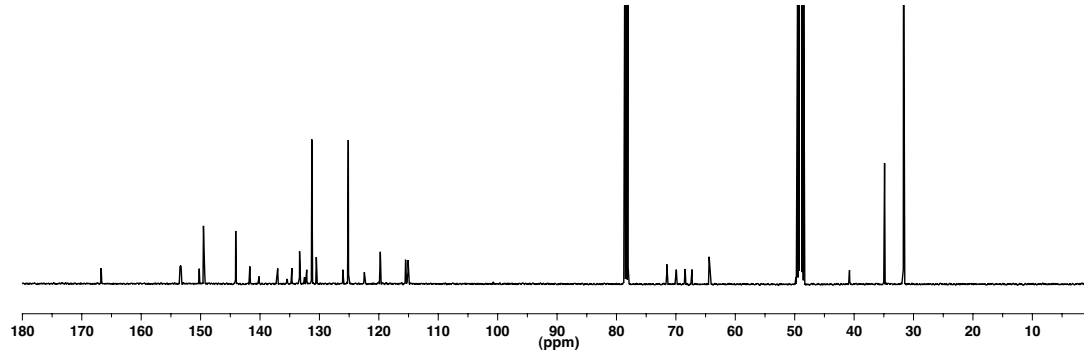

Figure S9. ^{13}C NMR spectrum of **9·PF_6** (1:1 $CDCl_3$:CD_3OD , 293 K, 500 MHz).

ROESY NMR Spectrum of 9·PF_6

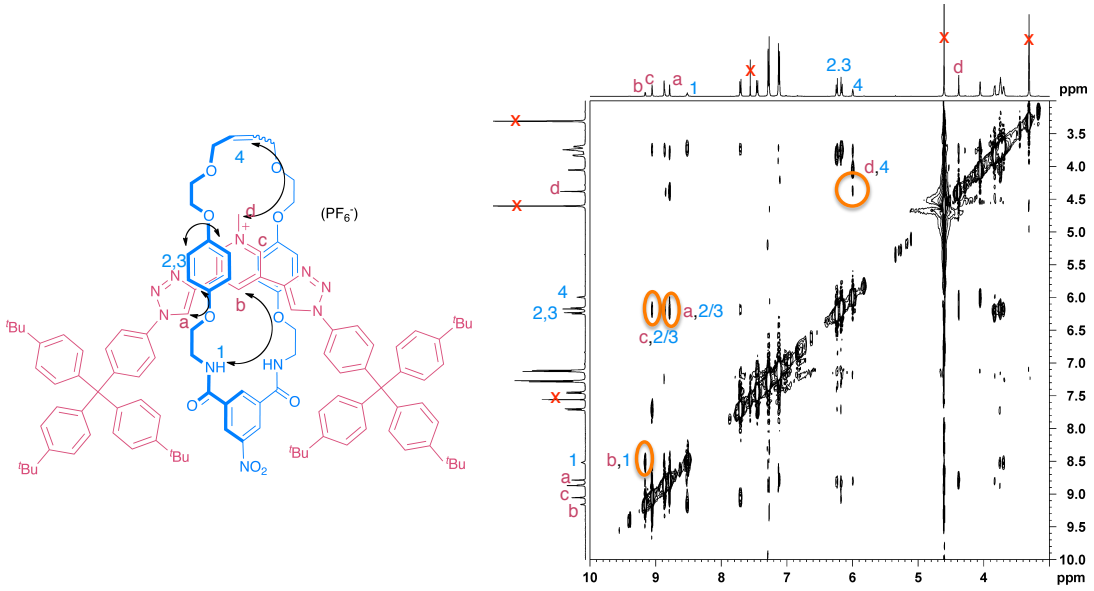

Figure S10. Truncated ROESY NMR spectrum of **9·PF_6** showing selected inter-component couplings (1:1 $CDCl_3$:CD_3OD, 293 K, 500 MHz).

Titration protocols

Spectra for ^{1}H NMR titrations were recorded at 293 K on a Varian Unity Plus 500 spectrometer with ^{1}H operating at 500 MHz. Initial sample volumes were 0.50 mL and concentrations were 2.0 mM of host. Solutions (100 mM) of anions as their tetrabutylammonium salts were added in aliquots, the samples thoroughly shaken and spectra recorded. Spectra were recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents. Stability constants were obtained by analysis of the resulting data using the WinEQNMR2[S1] computer program, monitoring the triazole C–H proton resonance in all cases.

Estimates for the association constant and the limiting chemical shifts were added to the program's input file. The parameters were refined by non-linear least-squares analysis using WINEQNMR2[S1] to achieve the best fit between observed and calculated chemical shifts. The input parameters for the final chemical shift and association constant were adjusted based on the program output until convergence was reached. Comparison of the calculated and experimental binding isotherms demonstrated that an appropriate model with an appropriate 1:1 binding stoichiometry was being used. The 1:1 stoichiometry was also confirmed using approximations of Job plots. A graph of $\Delta\delta\cdot\chi_H$ against χ_H was plotted, with a 1:1 binding stoichiometry corresponding to a maximum $\delta\cdot\chi_H$ of approximately 0.5 (χ_H = mole fraction of host, $\Delta\delta$ = change in chemical shift relative to free host).

Reference

[S1] M.J. Hynes, *J. Chem. Soc., Dalton Trans.*, **1993**, 311-312.