Supplementary Information:

Systematic structural analysis of a series of anion receptor complexes

Contents:

1) Experimental

a. Synthesis

1,3-Bis(4-nitrophenyl)urea, **1**, was synthesised according to literature procedures.[1] 4-Nitrophenylisocyanate (0.38 g, 2.40 $x10^{-3}$ moles, 1.6 eq) was dissolved in dichloromethane (50 mL). 4-Nitroaniline (0.20 g, 1.50 $x10^{-3}$ moles, 1.0 eq) was added followed by triethylamine (0.50 mL, 1.60 $x10^{-3}$ moles, 1.0 eq) and the solution stirred overnight. The resulting solid was isolated by filtration and washed with dichloromethane, and the solid was recrystallised from acetonitrile. This resulted in a yellow powder (0.078 g, 2.50 $x10^{-4}$ moles, 17 %). MP > 300 ºC (literature value 310 ºC)[1]. ^{1}H NMR (300 MHz, d_6-DMSO) 7.73 ppm (d, 9.4 Hz, 4H, CH), 8.22 ppm (d, 9.0 Hz, 4H, CH), 9.66 ppm (br. s., 2H, NH) (consistent with literature reference)[2]

1,3-Bis(3-nitrophenyl)urea, **2**, was synthesised according to literature procedures.[1] 3-Nitrophenylisocyanate (0.36 g, 2.40 $x10^{-3}$ mol, 1.5 eq) was dissolved in dichloromethane (50 mL). 3-Nitroaniline (0.20 g, 1.50 $x10^{-3}$ mol, 1.0 eq) was added followed by triethylamine (0.50 mL, 1.60 $x10^{-3}$ mol, 1.0 eq) and the solution stirred overnight. The resulting solid was isolated by filtration and washed with dichloromethane, and the solid was recrystallised from chloroform and hexane. This resulted in a yellow solid (0.37 g, 1.20 $x10^{-3}$ moles, 80 %). MP = 250-252ºC (literature value 256-258ºC)[3] ^{1}H NMR (300 MHz, d_6-DMSO) 7.59 ppm (t, 8.3 Hz, 2H, CH), 7.77 ppm (d, 6.8 Hz, 2H, CH), 7.85 ppm (d, 6.8 Hz, 2H, CH), 8.55ppm (t, 2.0 Hz, 2H, CH), 9.75 ppm (br. s., 2H, NH) (consistent with literature reference)[3]

1,3-Bis(3,5-di-nitrophenyl)urea, **3**, was synthesised according to literature procedures.[4] 3,5-Dinitrophenylisocyanate (0.12 g, 5.50 $x10^{-4}$ mol, 1.0 eq) was dissolved in toluene (50 mL). 3,5-Dinitroaniline (0.10 g, 5.50 $x10^{-4}$ mol, 1.0 eq) was added followed by triethylamine (2.00 mL, 1.43 $x10^{-2}$ mol, 26.0 eq). The reaction was heated at reflux overnight under a nitrogen atmosphere. A precipitate formed and this was isolated by filtration to yield a pale yellow solid (0.098 g, 2.50 $x10^{-4}$ mol, 45%). MP: >270°C (decomposition) (consistent with literature value of 306°C in acetone)[5]. ^{1}H NMR (300 MHz, d_6-DMSO): 8.46 ppm (t, 1.8 Hz, 2H, CH), 8.80 ppm (d, 1.8 Hz, 4H, CH), 10.13 ppm (s, 2H, NH) ^{13}C NMR: (75 MHz, d_6-DMSO): 111.5 ppm (CH, +DEPT), 118.4 ppm (CH, +DEPT), 141.5 ppm (q, Ar C), 148.2 ppm (q, Ar C), 152.3

ppm (q, C=O) LR ESI$^-$: m/z: 391.0 $[M-H]^-$ (100%), 392.2 $[M-H]^-$ (^{13}C isotope 12%)

2) Proton NMR titration studies

a. Methodology

Proton NMR titration experiments of the receptors with the acetate, chloride and fluoride anions were performed to investigate the dynamics of the solution state binding of the receptors. The tetramethylammonium acetate salt was used however due to difficulties in the solubility of the tetramethylammonium chloride and fluoride salts in the 0.5% d_6-DMSO-H_2O solvent system, in these cases the tetrabutylammonium halide salts were used. Titrations with tetrabutylammonium hydroxide with receptors **1** and **3** were conducted to characterise the deprotonation of these receptors in solution.

Proton NMR (300 MHz) were determined on a Bruker AV300 spectrometer with chemical shifts reported in parts per million (ppm), calibrated to the solvent peak.

1.5 mL of a 0.01 M solution of the receptor was prepared. Of this solution, 0.5 mL was added to an NMR tube, which was then sealed with an air tight suba seal. The remaining 1 mL of the receptor solution was used to make a 0.15 M solution of the desired guest. The anion/receptor solution was titrated into the NMR tube in small aliquots and a ^{1}H NMR spectrum was recorded after each addition. This resulted in an increasing concentration of guest throughout the experiment while the receptor concentration was kept constant.

The binding constants were obtained using the WinEQNMR[6] software.

b. Stack Plot and Fit Plot for receptor **1** with TMA acetate

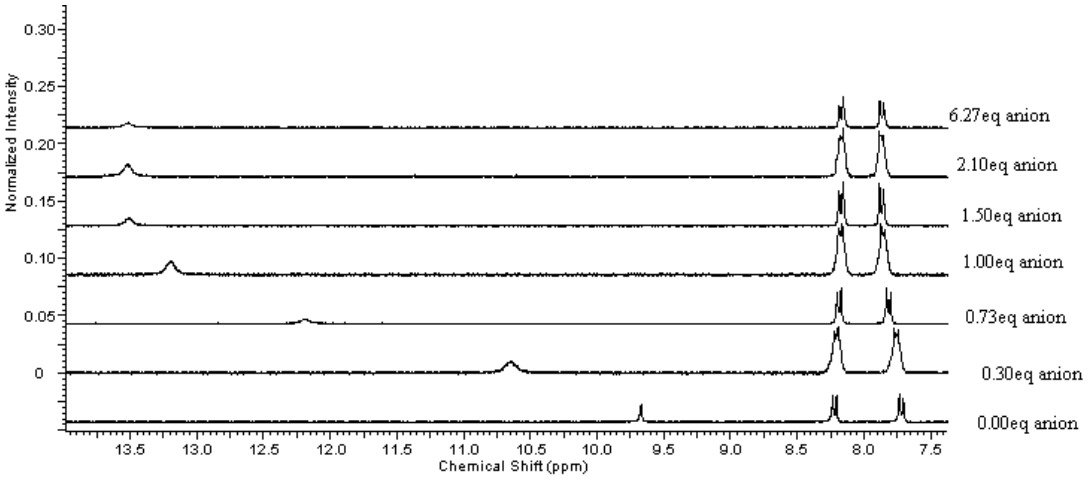
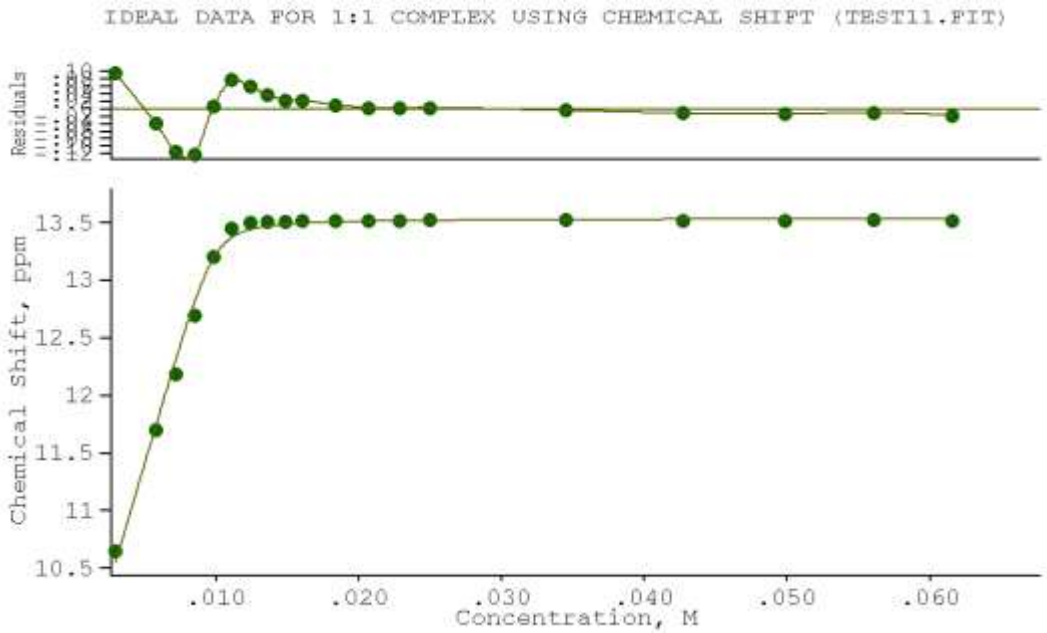


Figure S2: Stack Plot of titration of receptor **1** with TMA acetate



$K_1 > 10^4\ M^{-1}$, Error N. A.

Figure S3: Fit Plot for titration of receptor **1** with TMA acetate

c. Stack Plot and Fit Plot for receptor **1** with TBA chloride

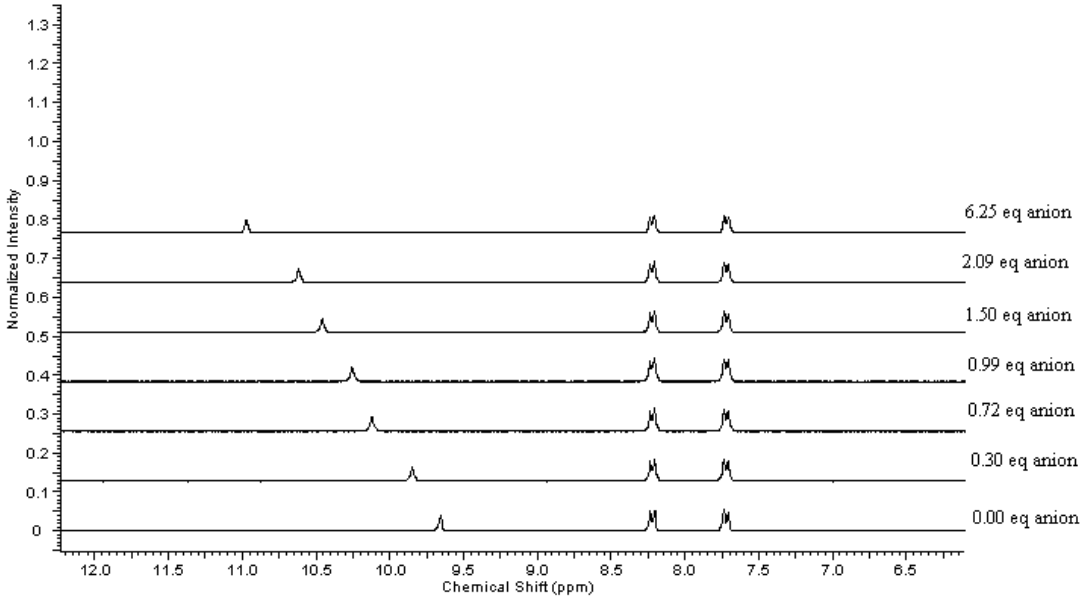
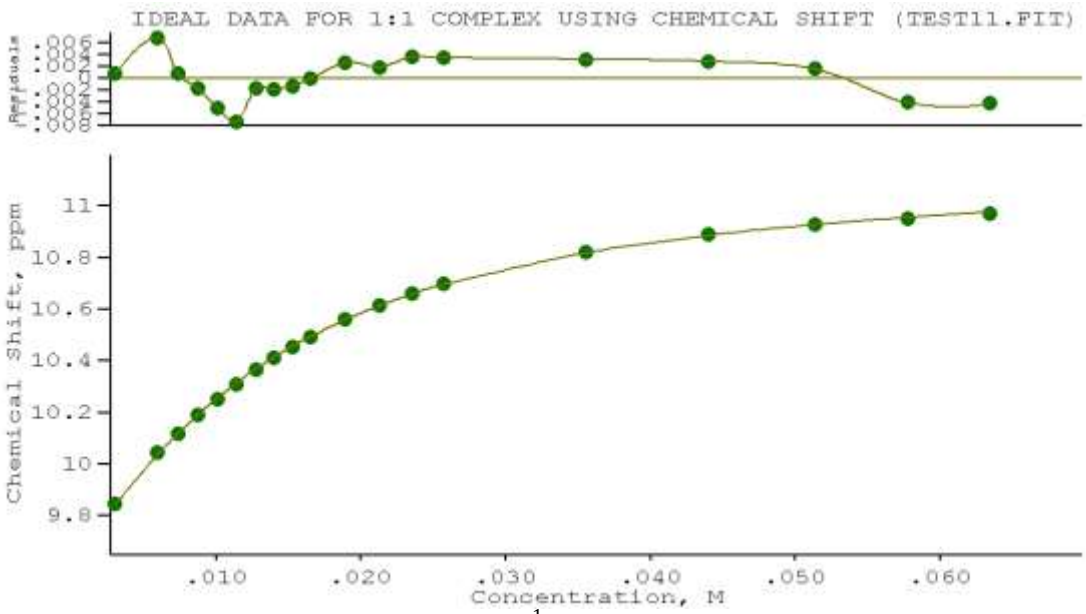


Figure S4: Stack plot of titration of receptor **1** with TBA chloride



K_1 = 118 M^{-1} Error = 1.5%

Figure S5: Fit plot of titration of receptor **1** with TBA chloride

d. Stack Plot for receptor **1** with TBA fluoride

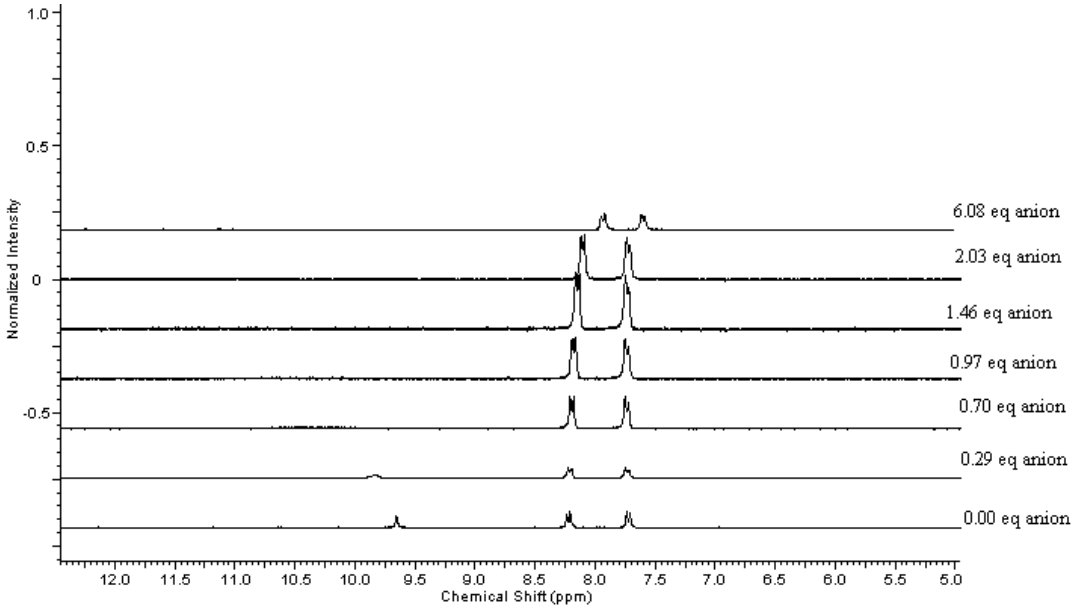


Figure S6: Stack plot of titration of receptor **1** with TBA fluoride

e. Stack Plot for receptor **1** with TBA hydroxide

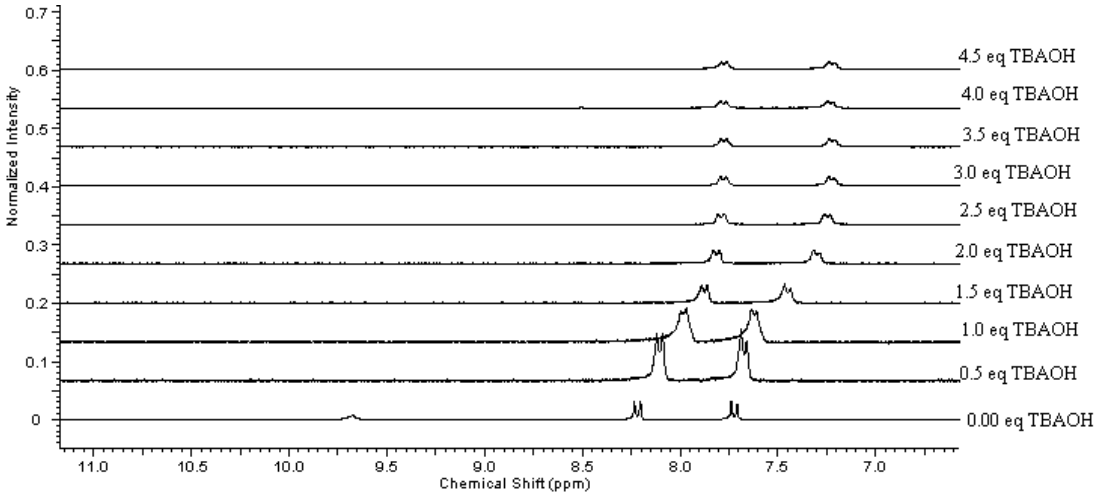


Figure S7: Stack plot of titration of receptor **1** with TBA hydroxide

f. Stack Plot and fit plot for receptor **2** with TMA acetate

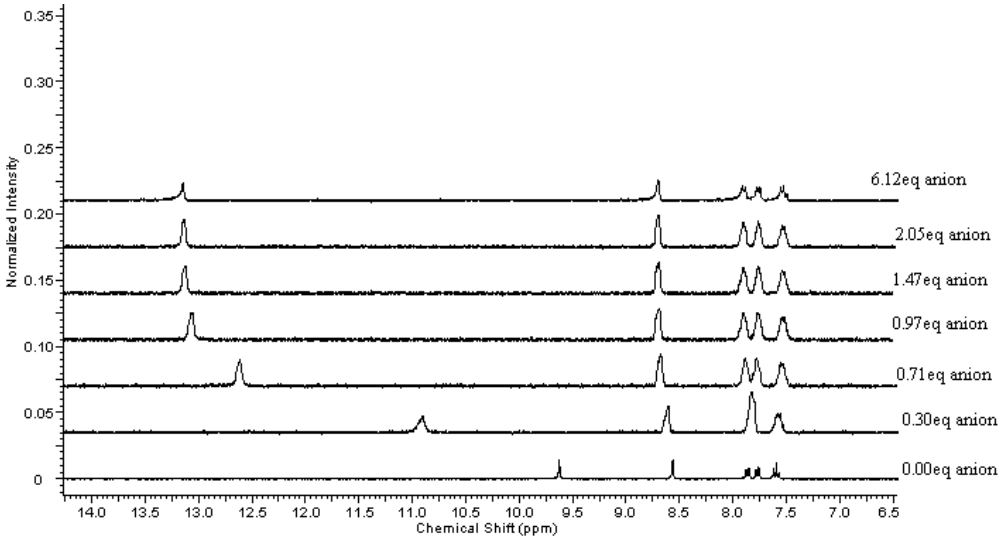
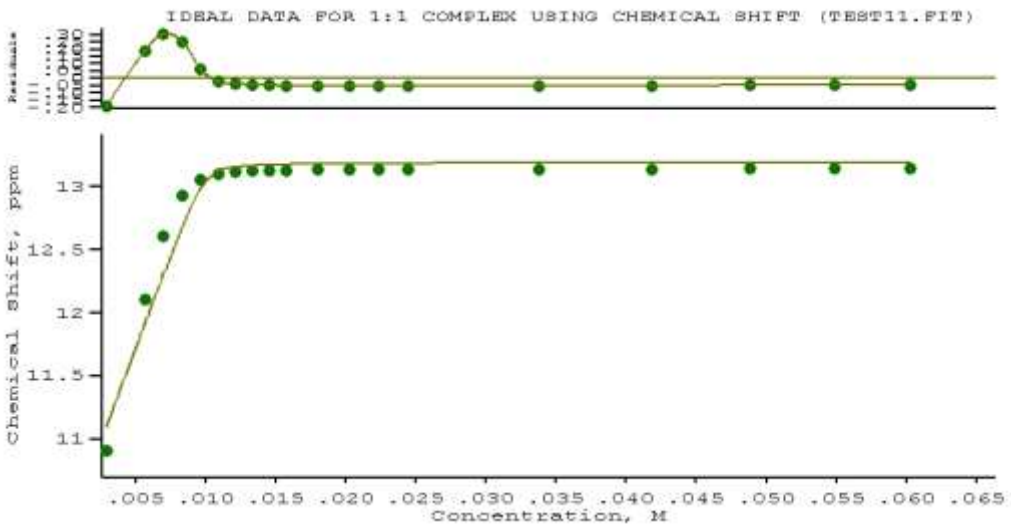


Figure S8: Stack plot of titration of receptor 2 with TMA acetate



$K_1 > 10^4\ M^{-1}$, Error N. A.

Figure S9: Fit plot of titration of receptor **2** with TMA acetate

g. Stack Plot and fit plot for receptor **2** with TBA chloride

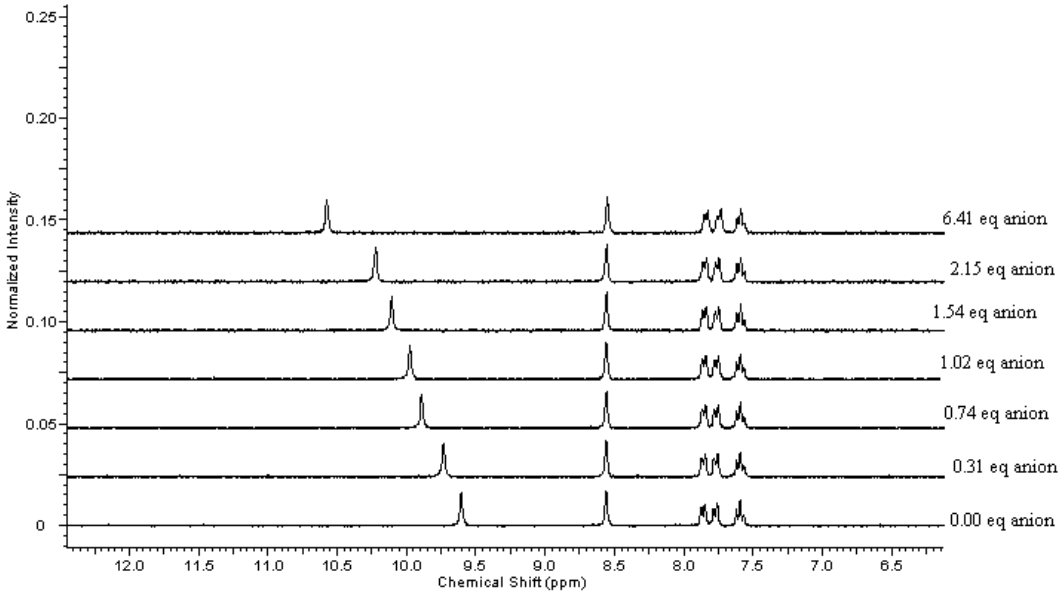
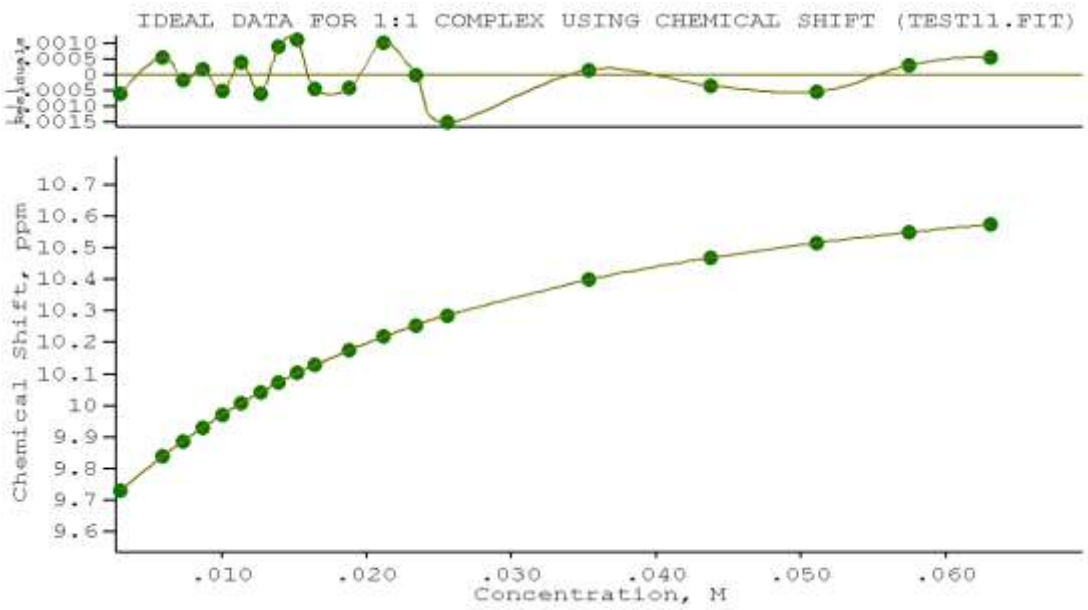


Figure S10: Stack plot of titration of receptor **2** with TBA chloride



K_1 = 56 M^{-1} Error = 0.4%

Figure S11: Fit plot of titration of receptor **2** with TBA chloride

h. Stack Plot and fit plot for receptor **3** with TMA acetate

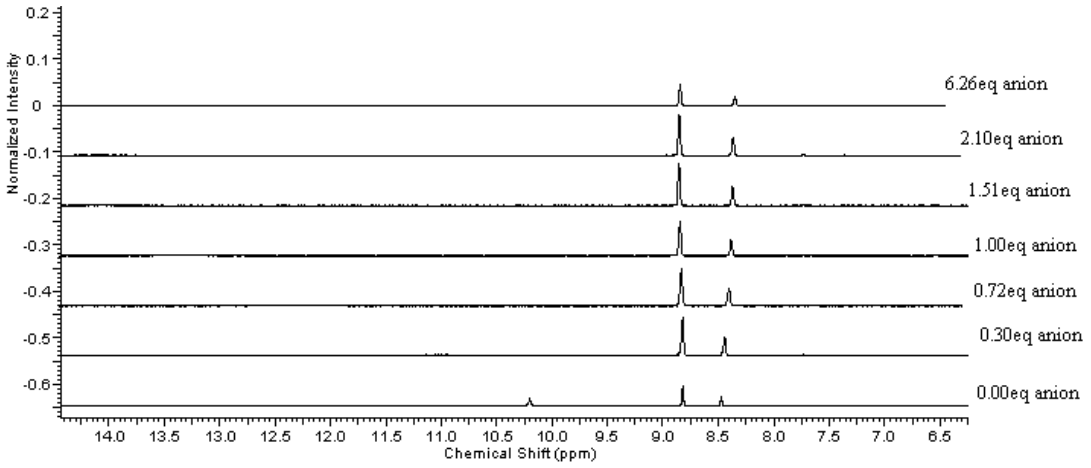
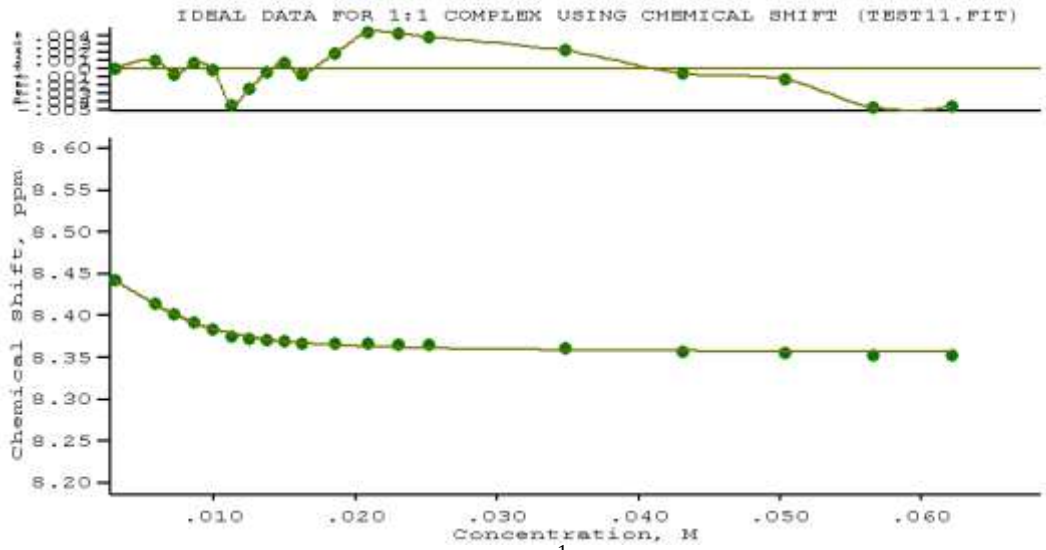


Figure S12: Stack plot of titration of receptor **3** with TMA acetate



K_1 = 1239 M^{-1} Error = 2%

Figure S13: Fit plot of titration of receptor 3 with TMA acetate

i. Stack Plot for receptor **3** with TBA hydroxide

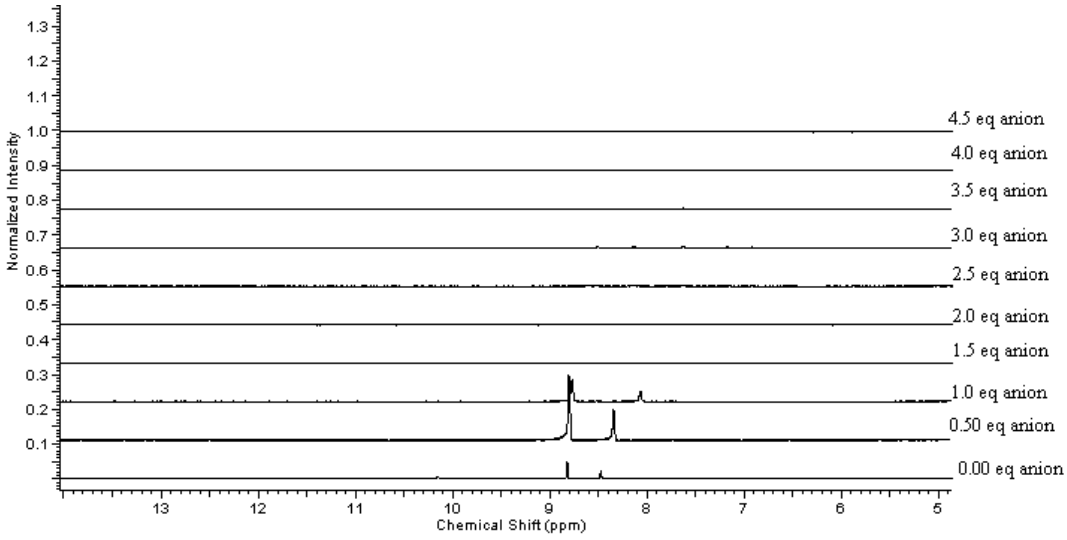


Figure S14: Stack plot of titration of receptor **3** with TBA hydroxide

3) Free ligand of 1,3-bis(2-nitrophenyl)urea

a. Structure of 1,3-bis(2-nitrophenyl)urea

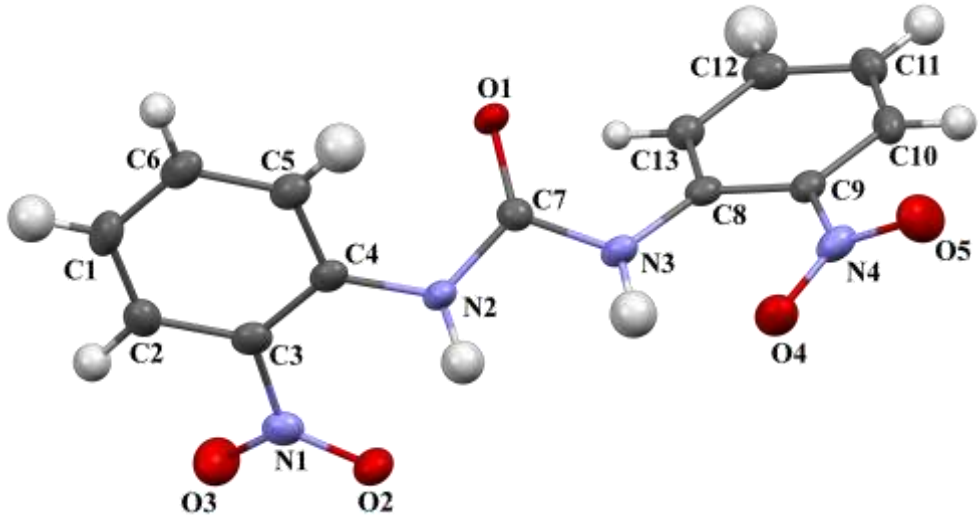


Figure S15: Structure of free ligand of 1,3-bis(2-nitrophenyl)urea drawn with ellipsoids at the 50% probability level. Crystallised from dichloromethane, isopropanol and acetonitrile.

b. Table of hydrogen bonding parameters

Bond	D−H (Å)	H···A (Å)	D···A (Å)	∠ DHA (°)
N(2)−H(2A)···O(1)$^{\#}$	0.88	2.04	2.844(4)	151.8
N(2)−H(2A)···O(2)	0.88	2.18	2.643(5)	112.2
N(3)−H(3A)···O(1)$^{\#}$	0.88	2.16	2.915(4)	144.1
N(3)−H(3A)···O(4)	0.88	2.18	2.665(5)	114.2

$^{\#}$ Symmetry transformations used to generate equivalent atoms x, y+1, z

4) Hirshfeld surface plots

a. Hirshfeld surface and fingerprint plot of receptor in **4**

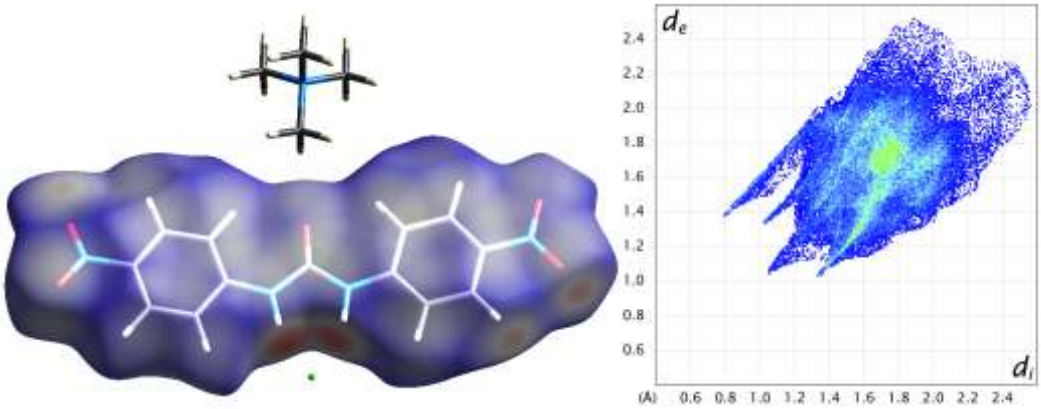


Figure S16: Hirshfeld surface plot and Fingerprint for receptor molecule of **4**.

b. Hirshfeld surface and fingerprint plot of receptor in **5**

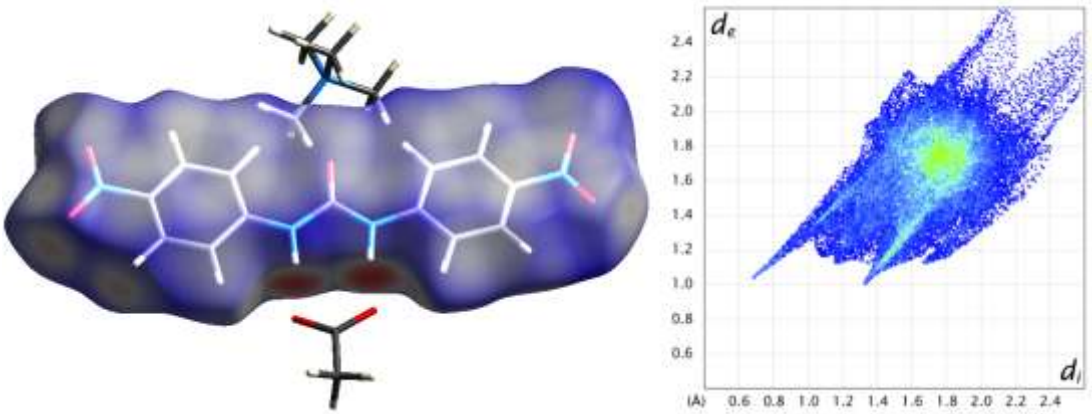


Figure S17: Hirshfeld surface plot and Fingerprint for receptor molecule of **5**.

c. Hirshfeld surface and fingerprint plot of receptor in **6**

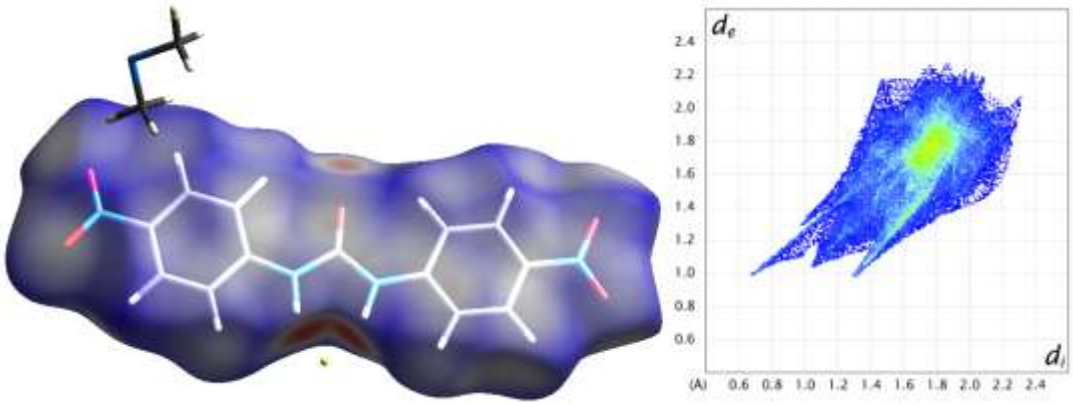


Figure S18: Hirshfeld surface plot and Fingerprint for receptor molecule of **6**.

d. Hirshfeld surface and fingerprint plot of receptor in **7**

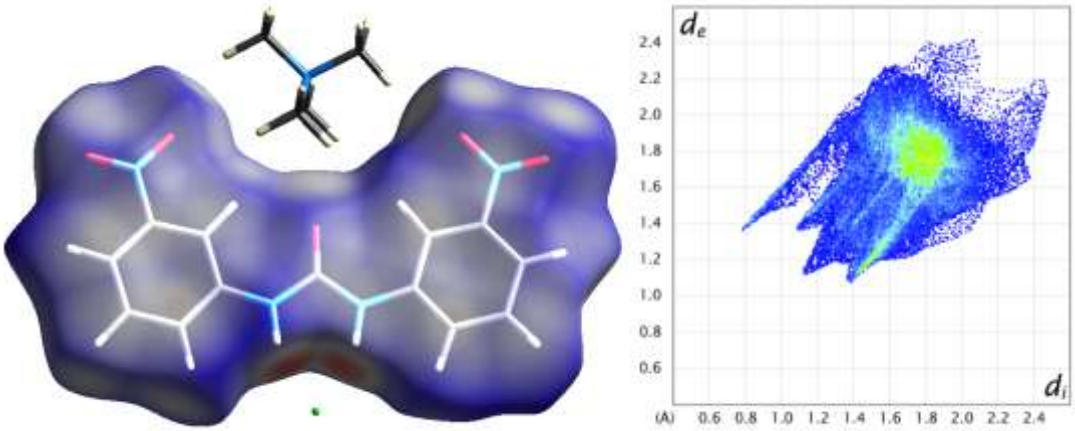


Figure S19: Hirshfeld surface plot and Fingerprint for receptor molecule of **7**.

e. Hirshfeld surface and fingerprint plot of receptor in **8**

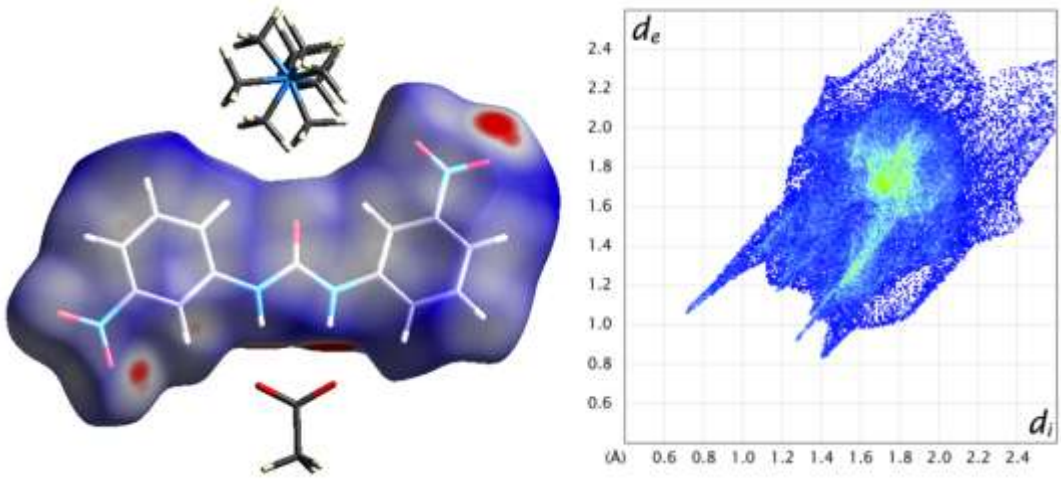


Figure S20: Hirshfeld surface plot and Fingerprint for receptor molecule of **8**.

f. Hirshfeld surface and fingerprint plot of receptor in **9**

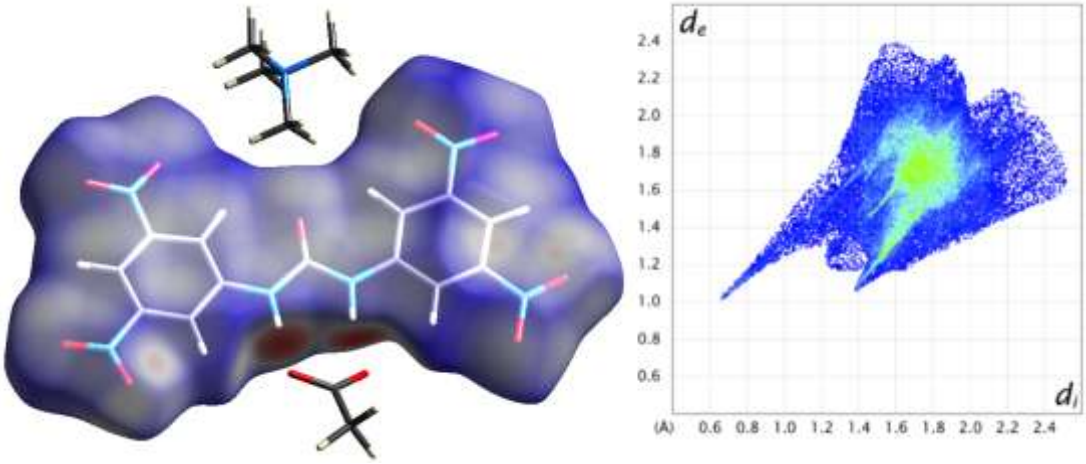


Figure S21: Hirshfeld surface plot and Fingerprint for receptor molecule of **9**.

5) References

1. S. Perveen, S. M. Abdul Hai, R. A. Khan, K. M. Khan, N. Afza and T. B. Sarfaraz, *Synth. Commun.*, 2005, **35**, 1663.
2. M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507.
3. M. C. Etter, Z. Urbanczyk-Lipkowska, M. Zia-Ebrahimi and T. W. Panunto, *J. Am. Chem. Soc.*, 1990, **112**, 8415.
4. M. Miyahara, *Chem. Pharm. Bull.*, 1986, **34**, 1950.
5. J. J. Blanksma and G. Verberg, *Recl. Trav. Chim. Pays-Bas*, 1934, **53**, 1037.
6. M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.