Supplementary Material (ESI) for Chemical Communications

Pyridyl thioureas as switchable anion receptors.

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ELECTRONIC SUPPLEMENTARY INFORMATION:

a) NMR titration data for **1** with TBA acetate in CD_3CN
b) NMR titration data for **3d** with TBA bromide in CD_3CN
c) NMR titration data for **3d** with TBA chloride in CD_3CN
d) NMR titration data for **4a** with TBA bromide in CD_3CN
e) NMR titration data for **4a** with TBA chloride in CD_3CN
f) Crystal structure of **3a**
g) Crystal structure of **3b**

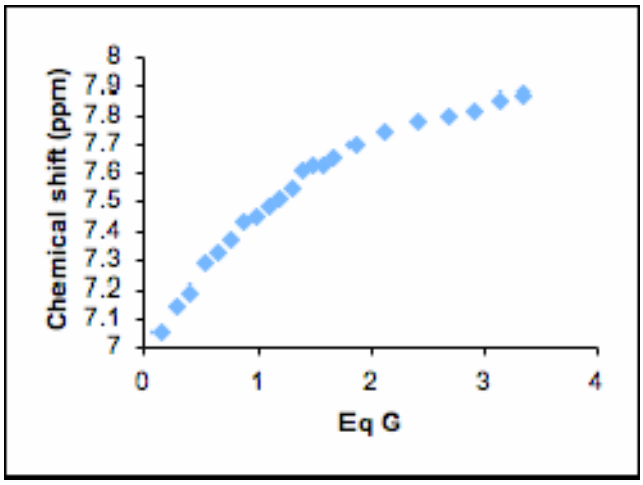
Supplementary Material (ESI) for Chemical Communications

a) NMR titration data for **1** with TBA acetate in CD_3CN

Thiourea **1** with TBAOAc

[H]=0.00873 [G] =0.07349

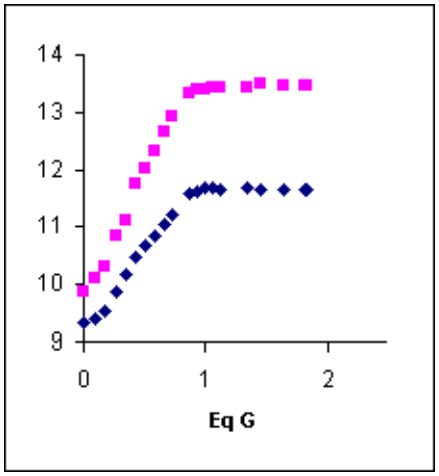
No	Vol	[[G]	EqG	CHpy4
1	10	0.001204754	0.138001615	7.052
2	20	0.002370645	0.271551565	7.146
3	30	0.003499524	0.400861834	7.19
4	40	0.004593125	0.526131157	7.291
5	50	0.005653077	0.647546039	7.324
6	60	0.006680909	0.765281683	7.37
7	70	0.00767806	0.879502829	7.433
8	80	0.008645882	0.990364531	7.454
9	90	0.009585652	1.098012849	7.482
10	100	0.010498571	1.202585502	7.515
11	110	0.011385775	1.304212445	7.548
12	120	0.012248333	1.403016418	7.61
13	130	0.01308726	1.499113433	7.63
14	140	0.013903514	1.592613232	7.635
15	150	0.014698	1.683619702	7.66
16	170	0.016225065	1.85854123	7.7
17	200	0.0183725	2.104524628	7.75
18	240	0.020997143	2.405171003	7.78
19	280	0.023383182	2.67848589	7.8
20	320	0.025561739	2.928034265	7.82
21	360	0.02755875	3.156786942	7.853
22	400	0.029396	3.367239404	7.87

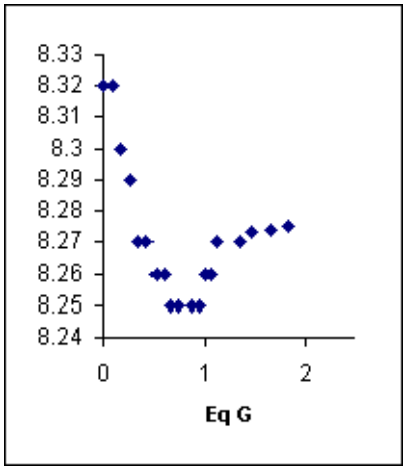


b) NMR titration data for **3d** with TBA bromide in CD_3CN

[G] = 0.0383
[H] = 0.00681

No	Vol	[G]	[G]/[H]	NH1	NH2	Hpy2
1	0	0	0	9.35	9.88	8.32
2	10	0.000628	0.092198	9.39	10.1	8.32
3	20	0.001235	0.181422	9.54	10.31	8.3
4	30	0.001824	0.267813	9.86	10.85	8.29
5	40	0.002394	0.351505	10.16	11.11	8.27
6	50	0.002946	0.432622	10.46	11.75	8.27
7	60	0.003482	0.51128	10.69	12.02	8.26
8	70	0.004001	0.587591	10.86	12.32	8.26
9	80	0.004506	0.661657	11.05	12.65	8.25
10	90	0.004996	0.733576	11.22	12.94	8.25
11	110	0.005934	0.871337	11.57	13.34	8.25
12	120	0.006383	0.937347	11.62	13.39	8.25
13	130	0.006821	1.001549	11.67	13.39	8.26
14	140	0.007246	1.064016	11.67	13.42	8.26
15	150	0.00766	1.124816	11.64	13.42	8.27
16	190	0.009211	1.352627	11.67	13.42	8.27
17	210	0.00993	1.458095	11.65	13.5	8.273
18	250	0.011265	1.654142	11.65	13.45	8.274
19	290	0.01248	1.832566	11.65	13.46	8.275

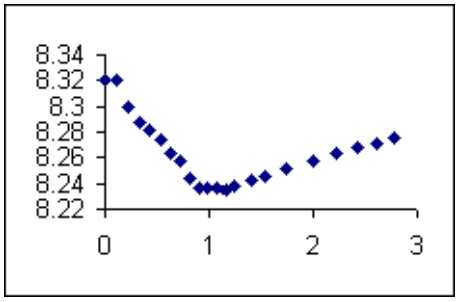


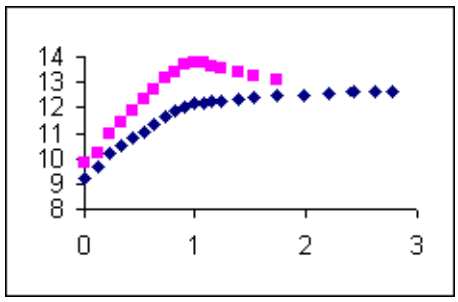


c) NMR titration data for **3d** with TBA chloride in CD_3CN

[G] = 0.0438 [H] = 0.00631

No	Vol	[G]	[G]/[H]	NH1	NH2	Hpy1
1	0	0	0	9.833	9.248	8.32
2	10	0.000719	0.114012	10.235	9.706	8.32
3	20	0.001416	0.224346	10.995	10.196	8.3
4	30	0.00209	0.331177	11.453	10.509	8.288
5	40	0.002743	0.43467	11.84	10.789	8.281
6	50	0.003376	0.534979	12.305	11.036	8.274
7	60	0.003989	0.632247	12.698	11.356	8.263
8	70	0.004585	0.726613	13.131	11.668	8.257
9	80	0.005163	0.818203	13.391	11.841	8.244
10	90	0.005724	0.907138	13.68	12.038	8.237
11	100	0.006269	0.993532	13.75	12.164	8.237
12	110	0.006799	1.077492	13.76	12.186	8.236
13	120	0.007314	1.15912	13.606	12.244	8.235
14	130	0.007815	1.238512	13.542	12.278	8.238
15	150	0.008777	1.390944	13.38	12.35	8.243
16	170	0.009689	1.535458	13.224	12.39	8.246
17	200	0.010971	1.738681	13.067	12.446	8.252
18	240	0.012538	1.987064	br	12.518	8.258
19	280	0.013963	2.212866	br	12.55	8.264
20	320	0.015264	2.419034	br	12.61	8.268
21	360	0.016457	2.608021	br	12.64	8.271
22	400	0.017554	2.781889	br	12.64	8.276

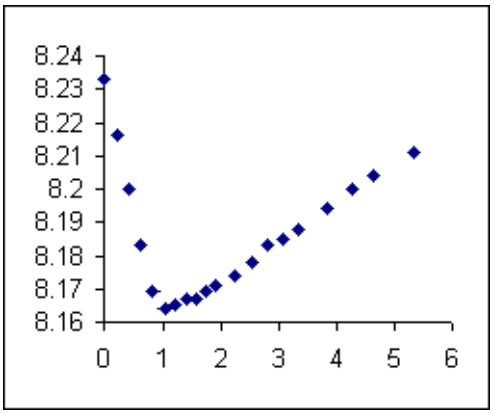


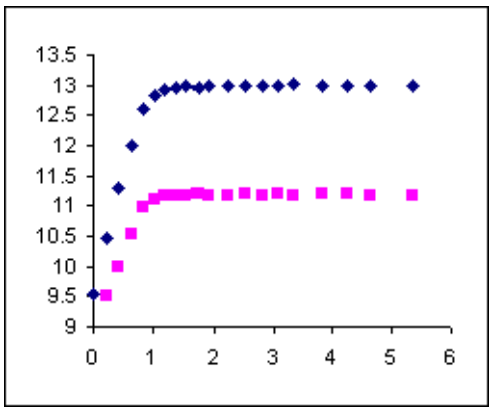


d) NMR titration data for **4a** with TBA bromide in CD_3CN

[G] = 0.0843
[H] = 0.00631

No	Vol	[G]	[G]/[H]	NH1	NH2	Hpy1
1	0	0	0	9.558	8.888	8.233
2	10	0.001382	0.219028	10.469	9.501	8.216
3	20	0.00272	0.430991	11.293	9.993	8.2
4	30	0.004015	0.636225	12.008	10.524	8.183
5	40	0.005269	0.835046	12.597	10.975	8.169
6	50	0.006485	1.027749	12.832	11.107	8.164
7	60	0.007664	1.214612	12.941	11.161	8.165
8	70	0.008808	1.395897	12.96	11.165	8.167
9	80	0.009918	1.571851	12.99	11.161	8.167
10	90	0.010996	1.742704	12.97	11.187	8.169
11	100	0.012044	1.908676	12.99	11.18	8.171
12	120	0.014051	2.226789	12.99	11.174	8.174
13	140	0.01595	2.527706	13	11.195	8.178
14	160	0.017749	2.812786	12.98	11.182	8.183
15	180	0.019455	3.083246	12.99	11.187	8.185
16	200	0.021077	3.340183	13.01	11.181	8.188
17	240	0.024087	3.817352	12.99	11.189	8.194
18	280	0.026825	4.251142	12.99	11.189	8.2
19	320	0.029324	4.647211	12.99	11.161	8.204
20	400	0.033722	5.344293	12.99	11.165	8.211

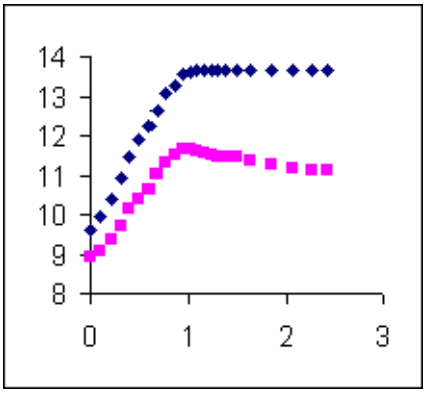


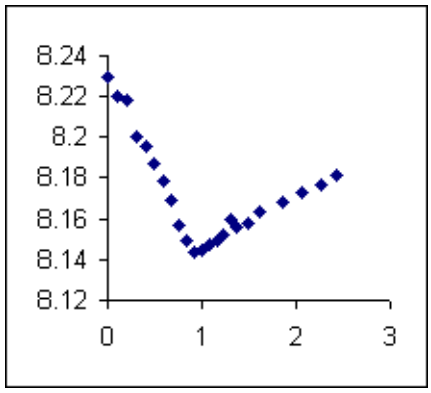


e) NMR titration data for **4a** with TBA chloride in CD_3CN

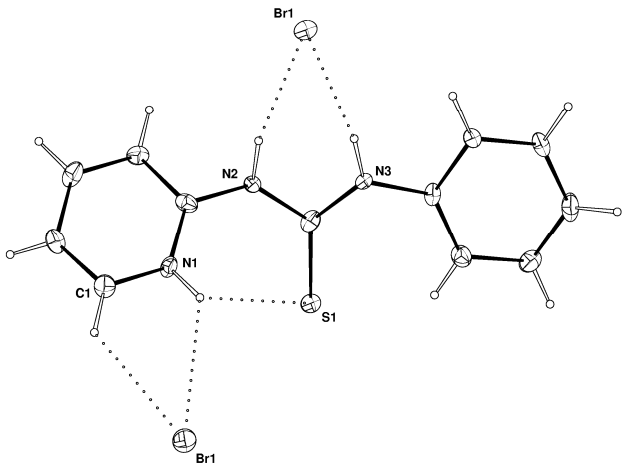
[G] = 0.04349 [H] = 0.006706

No	Vol	[G]	[G]/[H]	NH1	NH2	Hpy1
1	0	0	0	9.6	8.91	8.23
2	10	0.000713	0.106315	9.95	9.08	8.22
3	20	0.001403	0.209201	10.39	9.36	8.218
4	30	0.002071	0.308821	10.93	9.7	8.2
5	40	0.002718	0.405327	11.45	10.13	8.196
6	50	0.003345	0.498864	11.89	10.41	8.187
7	60	0.003954	0.589567	12.25	10.65	8.179
8	70	0.004544	0.677562	12.64	11.03	8.169
9	80	0.005116	0.762969	13.07	11.3	8.157
10	90	0.005673	0.8459	13.29	11.51	8.149
11	100	0.006213	0.926462	13.58	11.67	8.144
12	110	0.006738	1.004755	13.63	11.67	8.145
13	120	0.007248	1.080873	13.65	11.63	8.147
14	130	0.007745	1.154905	13.66	11.54	8.149
15	140	0.008228	1.226937	13.66	11.5	8.152
16	150	0.008698	1.297047	13.66	11.47	8.16
17	160	0.009156	1.365313	13.66	11.46	8.156
18	180	0.010036	1.496593	13.66	11.45	8.158
19	200	0.010873	1.621309	13.66	11.39	8.163
20	240	0.012426	1.852925	13.66	11.25	8.168
21	280	0.013838	2.063485	13.66	11.18	8.173
22	320	0.015127	2.255735	13.65	11.11	8.177
23	360	0.016309	2.431964	13.65	11.1	8.181



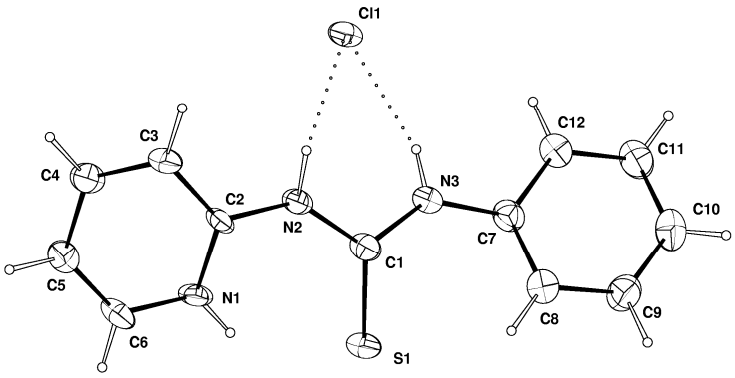


f) Crystal structure of 3a



Crystal data for 3a: $C_{12}H_{12}N_3SBr$, M = 310.22, colourless block, 0.2 x 0.15 x 0.08 mm^3, monoclinic, space group $P2_1/c$, a = 7.2182(15), b = 13.451(4), c = 13.041(4) Å, β = 97.126(18)°, V = 1256.4(6) $Å^3$, Z = 4, D_c = 1.640 g/cm^3, F_{000} = 624, $2\theta_{max}$ = 54.96º, 12582 reflections collected, not merged. Final *GooF* = 1.076, *R1* = 0.0629, *wR2* = 0.1450, *R* indices based on 12587 reflections with I >2sigma(I), 155 parameters, 0 restraints, T_{min} = 0.5480, T_{max} =0.7716 , μ = 3.418 mm^{-1}. Residual electron density 0.889 $e/Å^3$. The crystal was a non-merohedral twin (180° rotation about the 00-1 reciprocal lattice vector) CCDC deposition number 603099.

f) Crystal structure of 3b



Crystal data for 3b: $C_{12}H_{12}N_3SCl$, M = 265.76, colourless plate, 0.18 x 0.08 x 0.01 mm^3, monoclinic, space group $P2_1$, a = 4.8778(10), b = 8.0177(16), c = 16.085(3) Å, β = 90.43(3)°, V = 629.0(2) $Å^3$, Z = 2, D_c = 1.403 g/cm^3, F_{000} = 276, $2\theta_{max}$ = 54.94º, 7779 reflections collected, 2745 unique (R_{int} = 0.106). Final *GooF* = 1.097, *R1* = 0.0736, *wR2* = 0.1778, *R* indices based on 2745 reflections with I >2sigma(I), 154 parameters, 1 restraints. , T_{min} = 0.9234, T_{max} =0.9978 μ = 0.45 mm^{-1}. Residual electron density 0.922 e/$Å^3$, absolute structure parameter = 0.28(15). CCDC deposition number 603098.