Supporting Information

Different Metal-Ion-Induced Dimeric Self-Assembling Cavities Based on Thiacalix[4]benzocrown-4 Isomers

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ESI(+)-MS for the complexation of compounds **1** and **2** with Ag^+

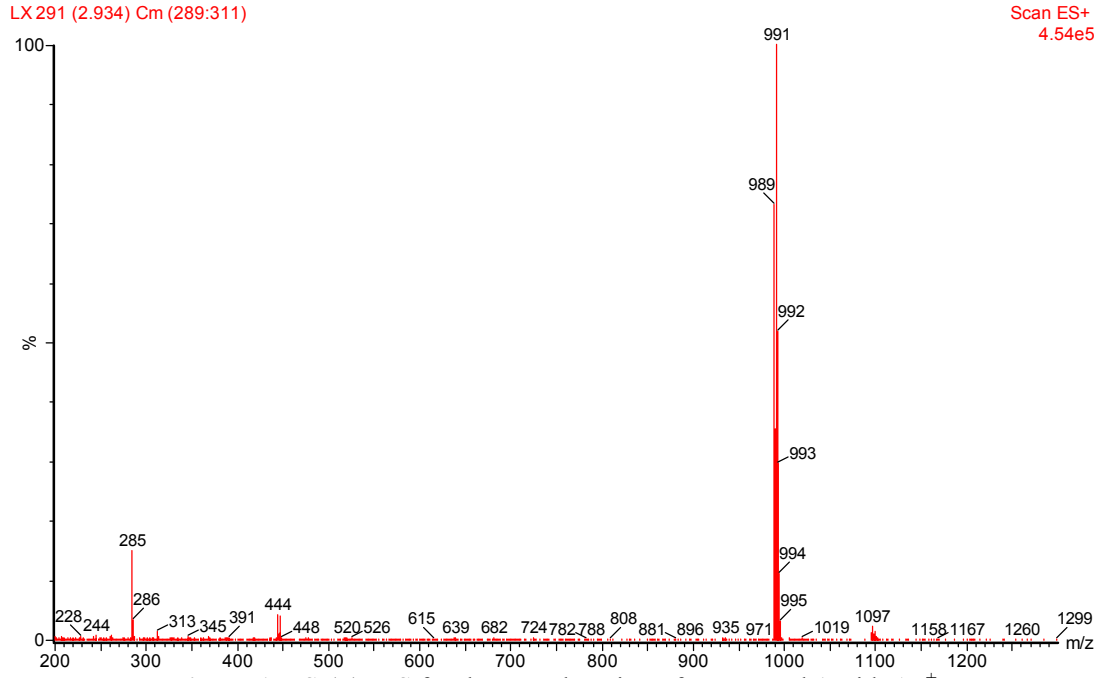

Figure 1. ESI(+)-MS for the complexation of compound **1** with Ag^+

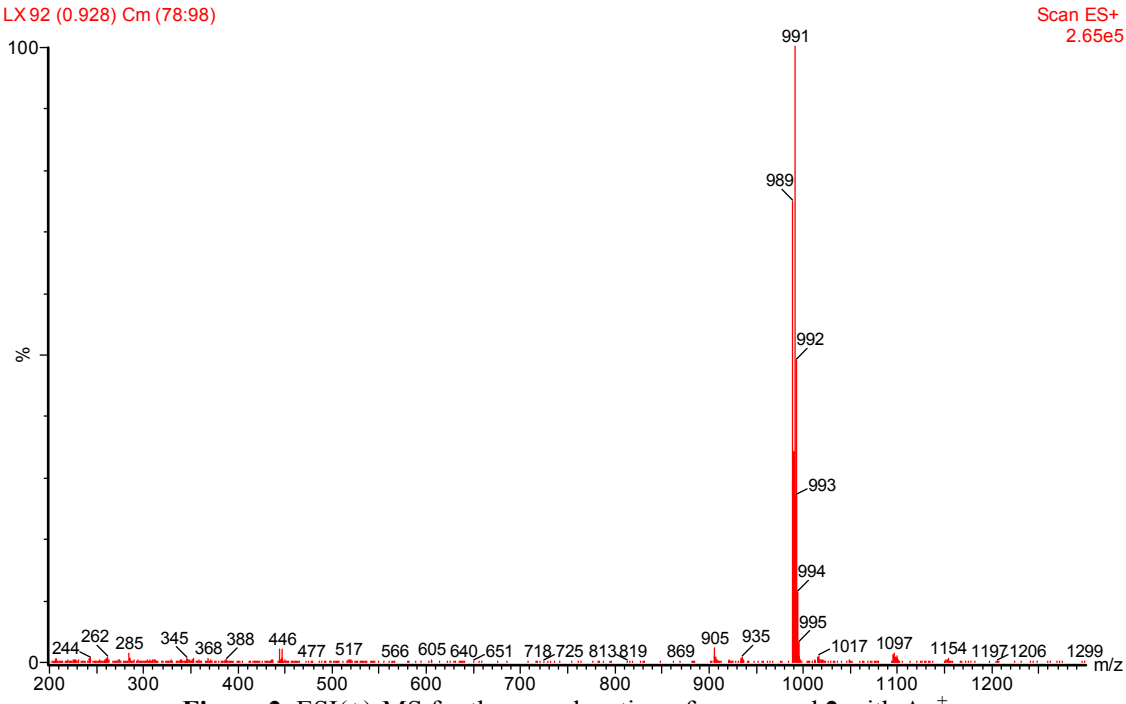

Figure 2. ESI(+)-MS for the complexation of compound **2** with Ag^+

Job plot experiment between thiacalix[4]arene **1** and AgPic
Solution A: 18.1 mg **1** in 10 mL CDCl3: CD_3OD (10:1 v/v)
Solution B: 6.7 mg AgPic in 10 mL $CDCl_3$: CD_3OD (10:1 v/v)

A solution /*u*L	Mole fraction of add AgPic	B solution /*u*L	δ due to *one pair* opposite phenyl rings on the TC[4]A moiety /ppm	$\Delta\delta\times[H]_t$ /ppm
1000	0	0	7.154	0
900	0.1	100	7.166	2.07164E-5
800	0.2	200	7.178	3.78486E-5
700	0.3	300	7.191	5.13297E-5
600	0.4	400	7.204	5.96529E-5
500	0.5	500	7.215	6.1268E-5
400	0.6	600	7.224	5.58822E-5
300	0.7	700	7.241	5.23206E-5
200	0.8	800	7.252	3.93514E-5
100	0.9	900	7.265	2.21595E-5

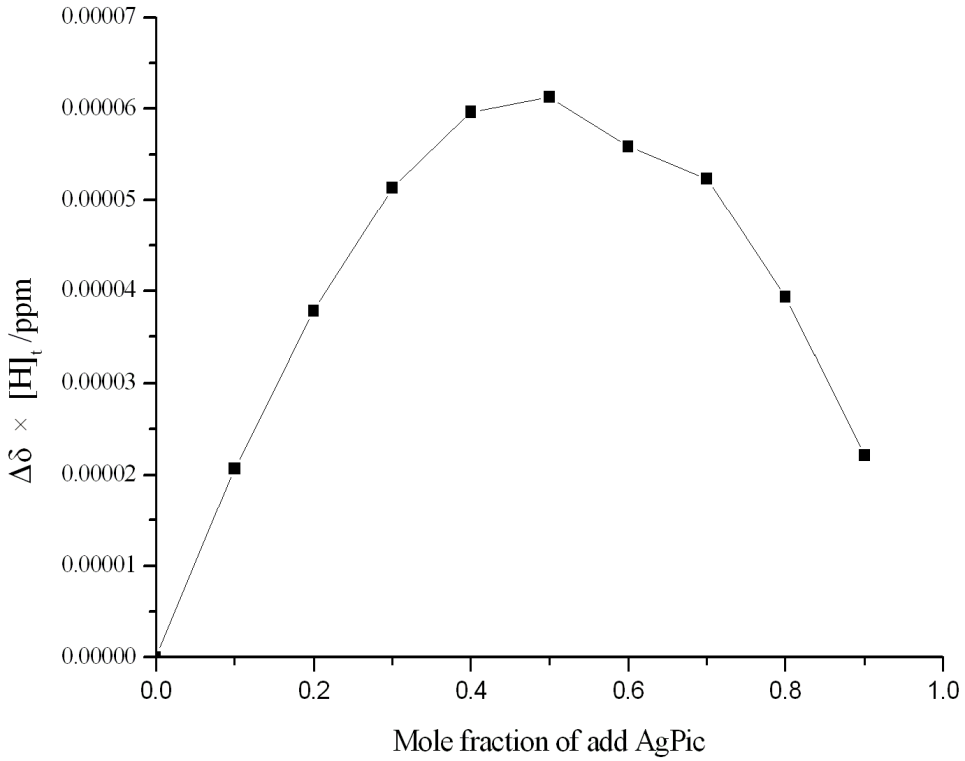

Figure 3. Job' s plot based on ^{1}H NMR for ligand **1** with Ag^+.

Job plot experiment between thiacalix[4]arene **2** and AgPic
Solution A: 18.1 mg **1** in 10 mL $CDCl_3$: CD_3OD (10:1 v/v)
Solution B: 6.7 mg AgPic in 10 mL $CDCl_3$: CD_3OD (10:1 v/v)

A solution /*u*L	Mole fraction of add AgPic	B solution /*u*L	δ due to a singlet representing one set of aromatic protons on the crown ring /ppm	$\Delta\delta\times[H]_t$ /ppm
1000	0	0	7.452	0
900	0.1	100	7.491	7.07561E-5
800	0.2	200	7.535	1.33561E-4
700	0.3	300	7.579	1.77659E-4
600	0.4	400	7.622	2.03713E-4
500	0.5	500	7.672	2.1987E-4
400	0.6	600	7.717	2.11642E-4
300	0.7	700	7.743	1.74672E-4
200	0.8	800	7.786	1.33663E-4
100	0.9	900	7.802	7.00099E-5

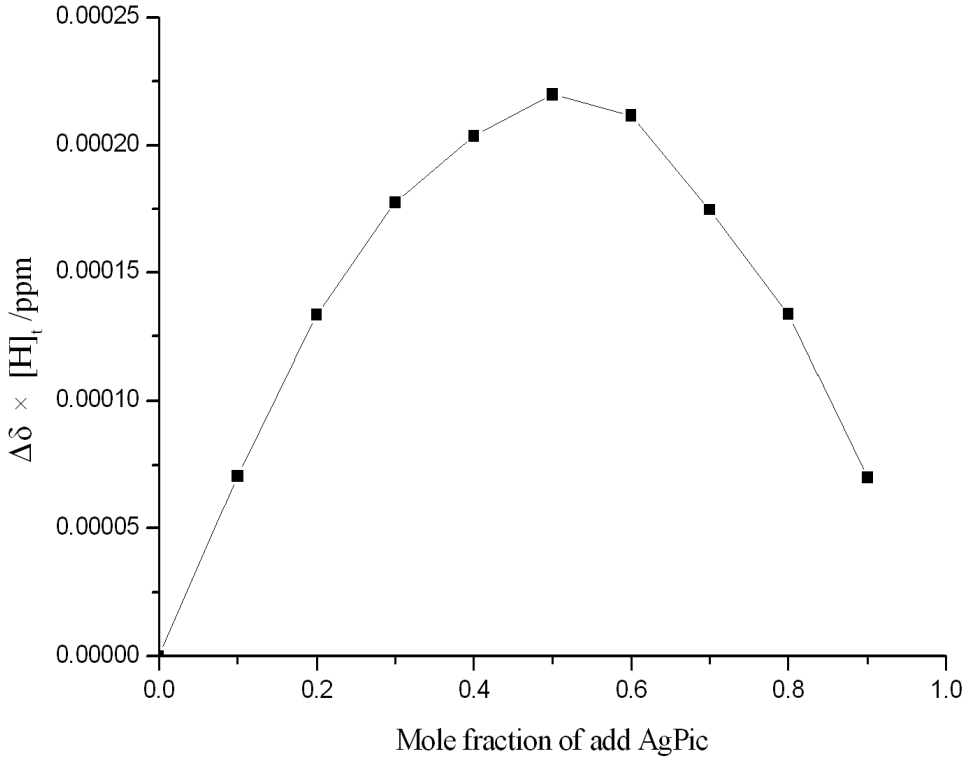

Figure 4. Job' s plot based on ^1H NMR for ligand **1** with Ag^+.

NMR titration: thiacalix[4]arene **1** *vs* and AgPic in $CDCl_3$: CD_3OD (10:1 v/v)
Solution A: 19.9 mg **1** in 10 mL $CDCl_3$
Solution B: 739.1 mg AgPic in 10 mL CD_3OD

A solution /*u*L	Mol equiv. of added AgPic	B solution /*u*L	Added CD_3OD	δ due to *one pair* opposite phenyl rings on the TC[4]A moiety /ppm	$\Delta\delta$ /ppm
1000	0	0	100	7.154	0
1000	0.5	5	95	7.200	0.046
1000	1	10	90	7.253	0.099
1000	1.5	15	85	7.285	0.130
1000	2	20	80	7.311	0.157
1000	2.5	25	75	7.336	0.182
1000	3	30	70	7.359	0.205
1000	3.5	35	65	7.376	0.222
1000	4	40	60	7.389	0.235
1000	4.5	45	55	7.396	0.242
1000	5	50	50	7.414	0.260
1000	5.5	55	45	7.422	0.268
1000	6	60	40	7.430	0.276
1000	7	70	30	7.441	0.287
1000	8	80	20	7.449	0.295
1000	9	90	10	7.459	0.305
1000	10	100	0	7.470	0.316

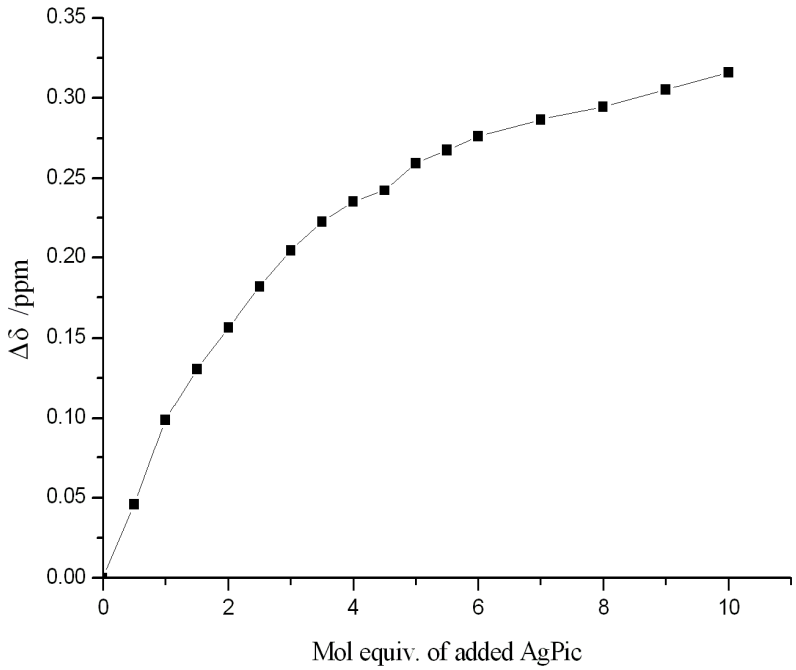

Figure 5. ^{1}H NMR titration of **1** with AgPic in $CDCl_3$: CD_3OD (10:1 v/v).

NMR titration: thiacalix[4]arene **2** *vs* and AgPic in $CDCl_3$: CD_3OD (10:1 v/v)
Solution A: 19.9 mg **1** in 10 mL $CDCl_3$
Solution B: 739.1 mg AgPic in 10 mL CD_3OD

A solution /*u*L	Mol equiv. of added AgPic	B solution /*u*L	Added CD_3OD	δ due to a singlet representing one set of aromatic protons on the crown ring /ppm	$\Delta\delta$ /ppm
1000	0	0	100	7.452	0
1000	0.5	5	95	7.583	0.131
1000	1	10	90	7.649	0.197
1000	1.5	15	85	7.698	0.246
1000	2	20	80	7.738	0.286
1000	2.5	25	75	7.770	0.318
1000	3	30	70	7.802	0.350
1000	3.5	35	65	7.825	0.373
1000	4	40	60	7.845	0.393
1000	4.5	45	55	7.862	0.410
1000	5	50	50	7.877	0.424
1000	5.5	55	45	7.890	0.437
1000	6	60	40	7.903	0.451
1000	7	70	30	7.913	0.461
1000	8	80	20	7.918	0.466
1000	9	90	10	7.959	0.507
1000	10	100	0	7.965	0.513

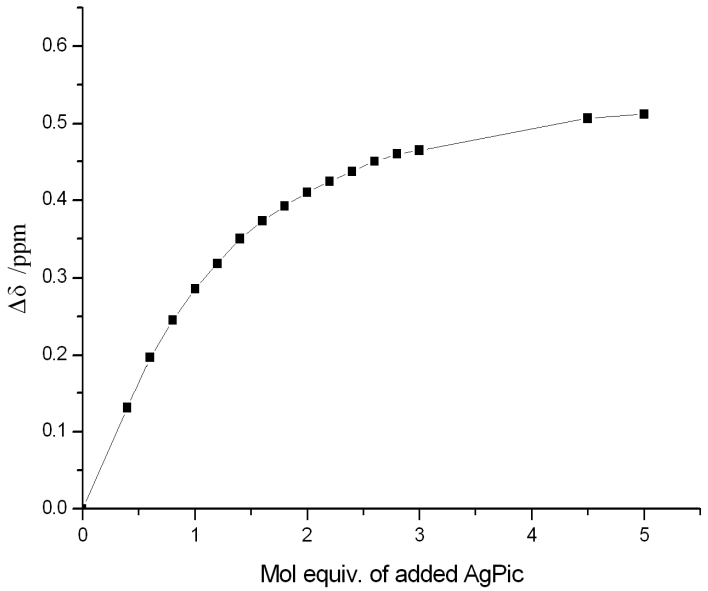

Figure 6. ^1H NMR titration of **1** with AgPic in $CDCl_3$: CD_3OD (10:1 v/v)

NMR diffusion experiments of ligands (**1, 2)** and their Ag^+ coplexes (**1**•Ag^+, **2**•$Ag^{+)}$)

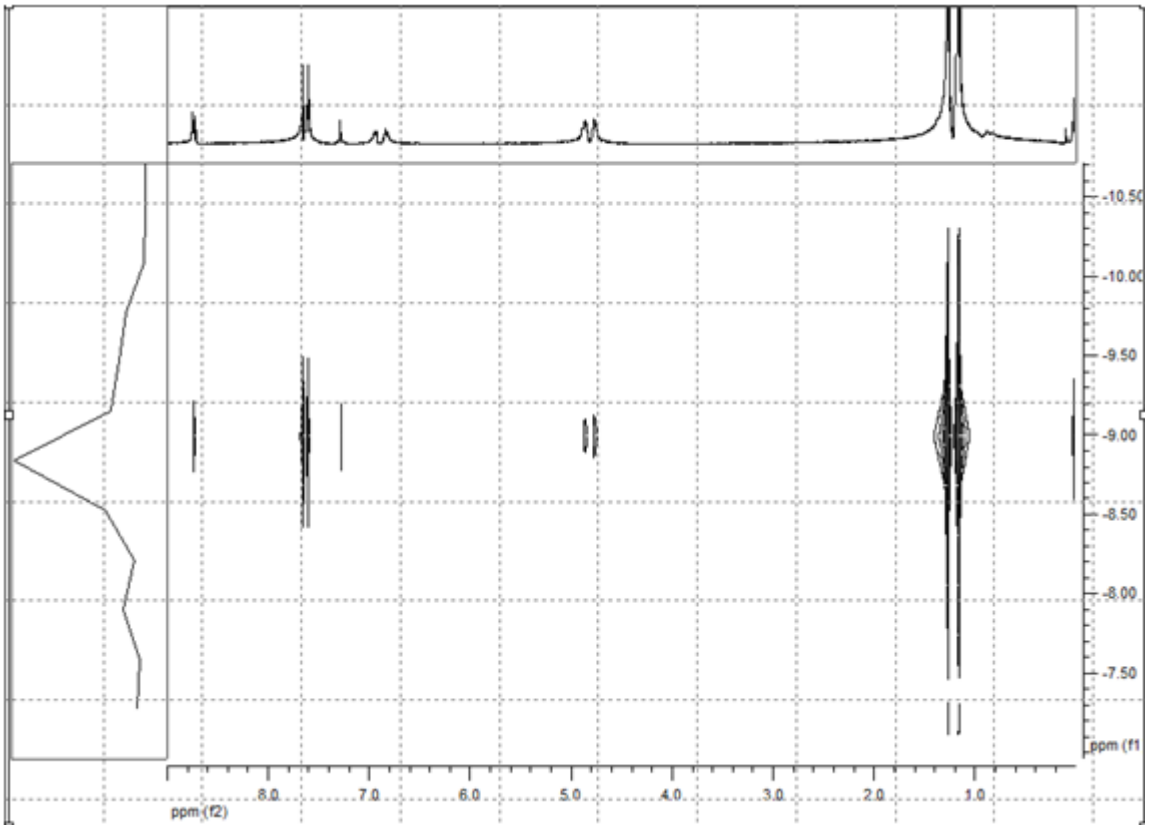

Figure 7 2D-DOSY spectra of recorded in $CDCl_3$, at 300 K mixture of thiacalix[4]arene **1** and AgPic in a 1:1 ratio showing the presence of a single species diffusing in solution with $D = 0.99\times10^{-9}$ cm^2 s^{-1}.

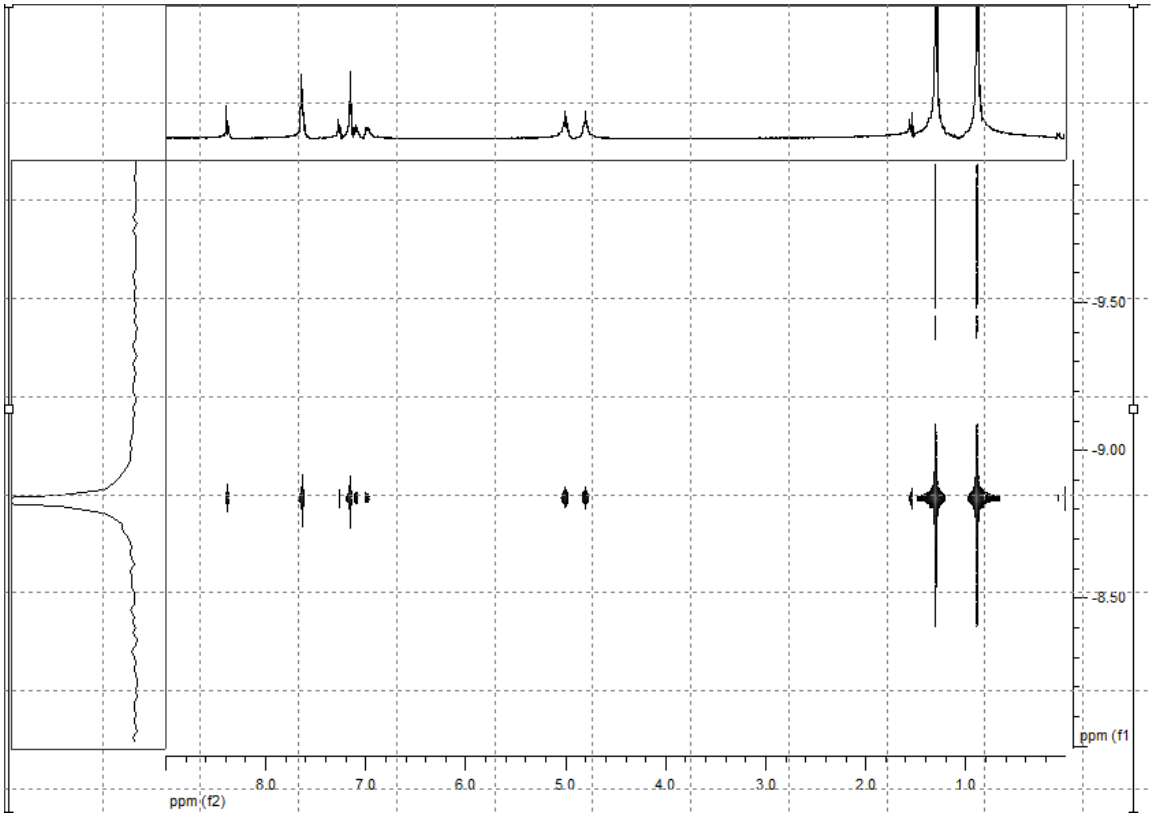

Figure 8 2D-DOSY spectra of recorded in $CDCl_3$, at 300 K solution of thiacalix[4]arene **1** showing the presence of a single species diffusing in solution with $D = 1.39\times10^{-9}$ cm^2 s^{-1}

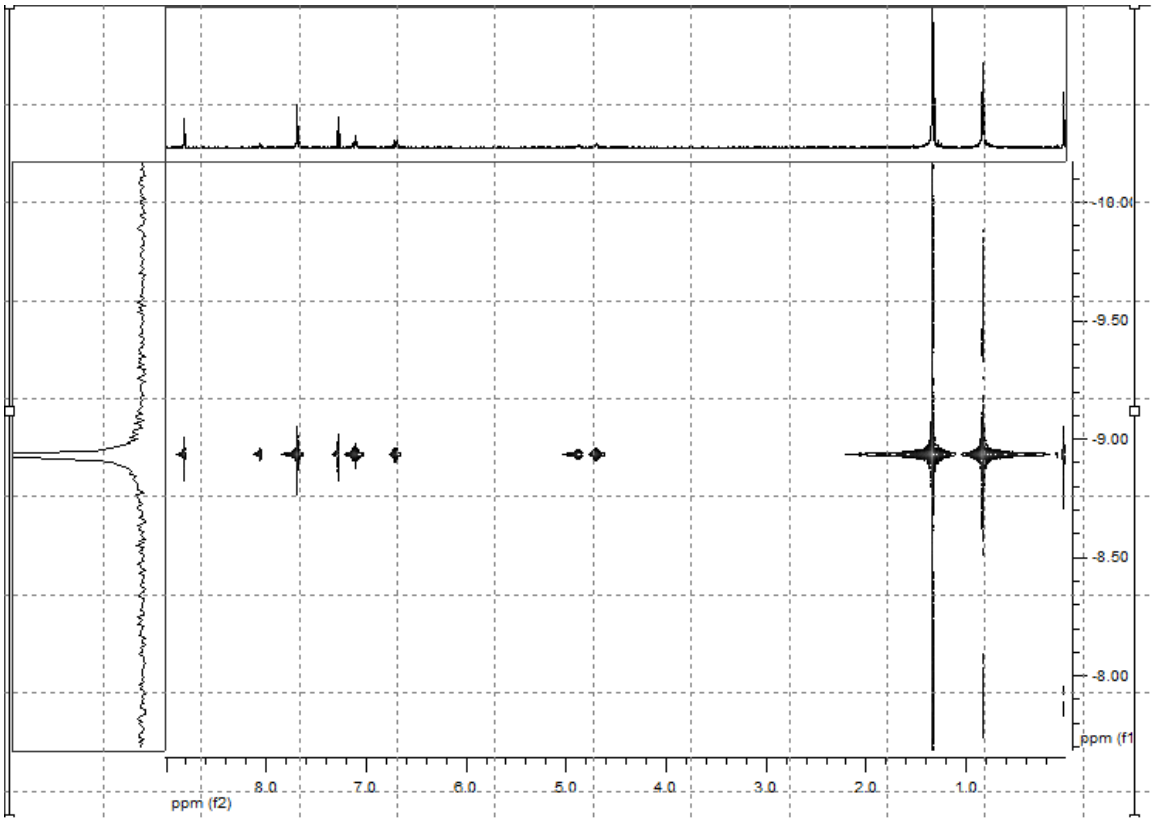

Figure 9 2D-DOSY spectra of recorded in $CDCl_3$, at 300 K mixture of thiacalix[4]arene **2** and AgPic in a 1:1 ratio showing the presence of a single species diffusing in solution with $D = 1.13 \times 10^{-9}$ cm^2 s^{-1}.

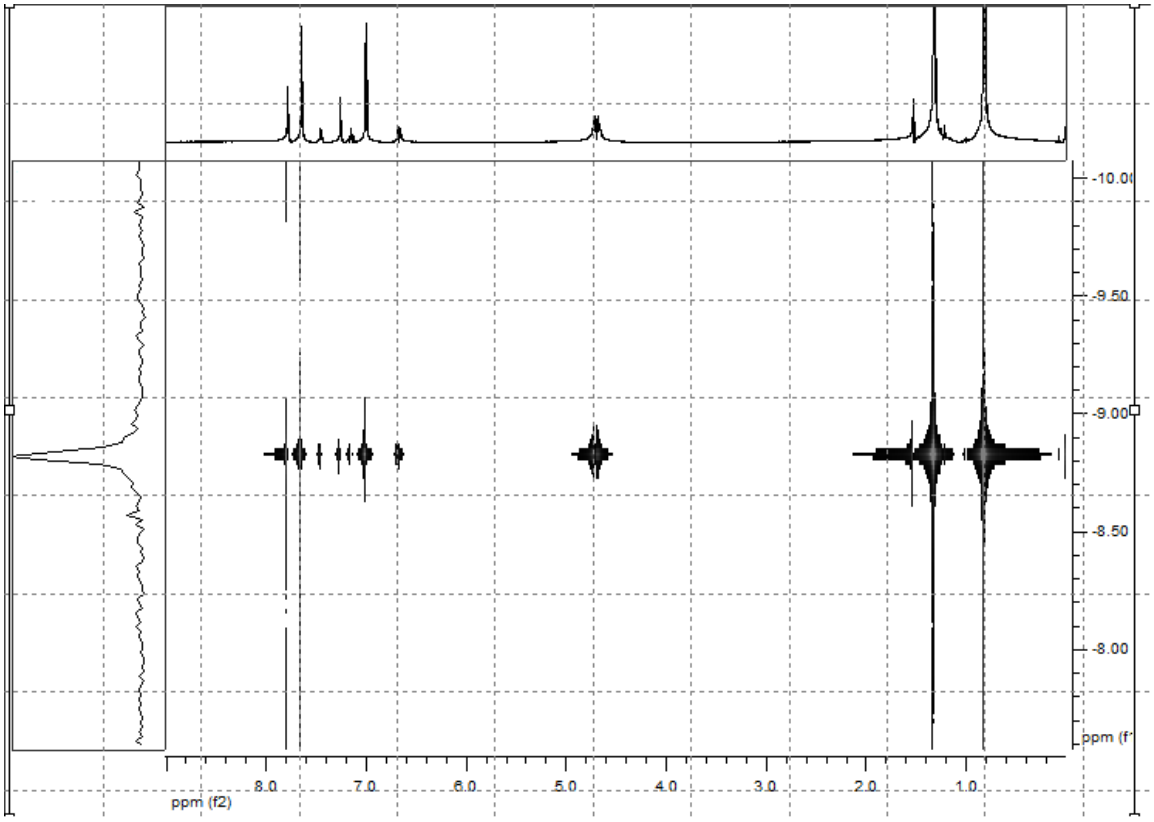

Figure 10 2D-DOSY spectra of recorded in $CDCl_3$, at 300 K solution of thiacalix[4]arene **2** showing the presence of a single species diffusing in solution with $D = 1.48 \times 10^{-9}$ cm^2 s^{-1}.

Ortep plots of the structures for ligands (**1, 2**) and their AgPic complexes (**1**·AgPic and **2**·AgPic)

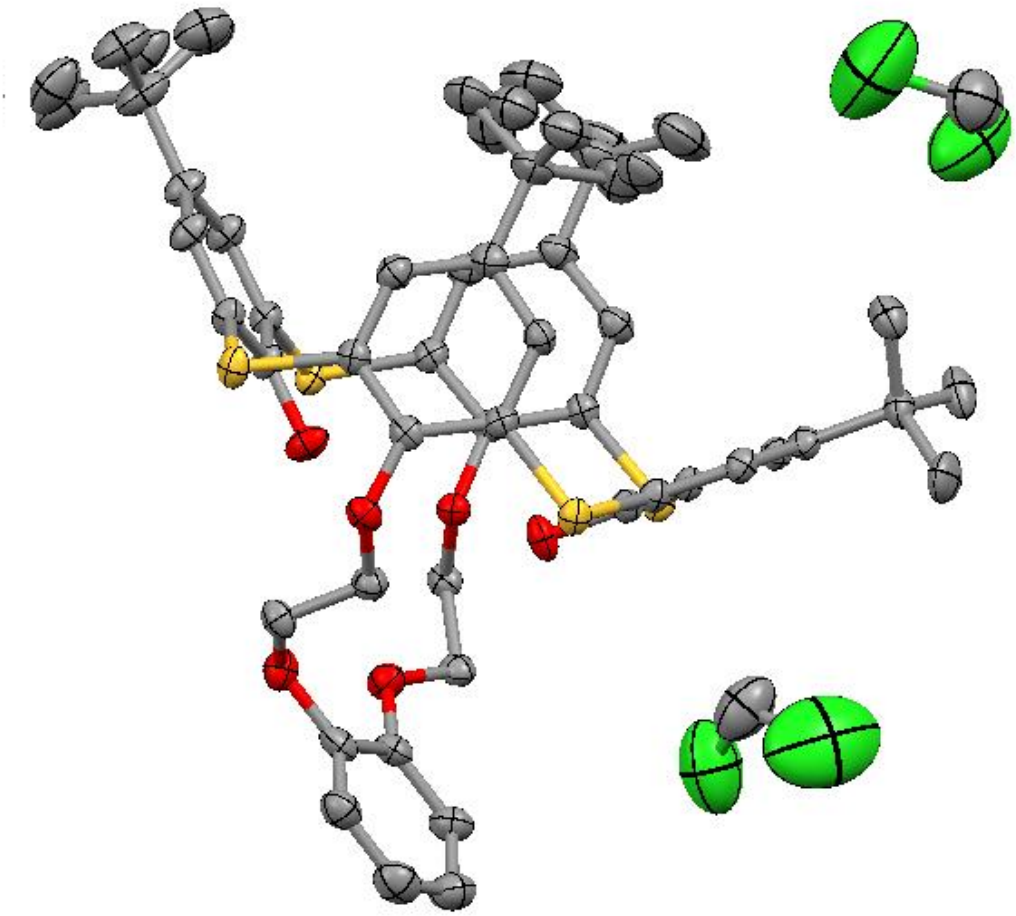

Figure 11 The molecular structure of ligand **1** (CCDC-740901). Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

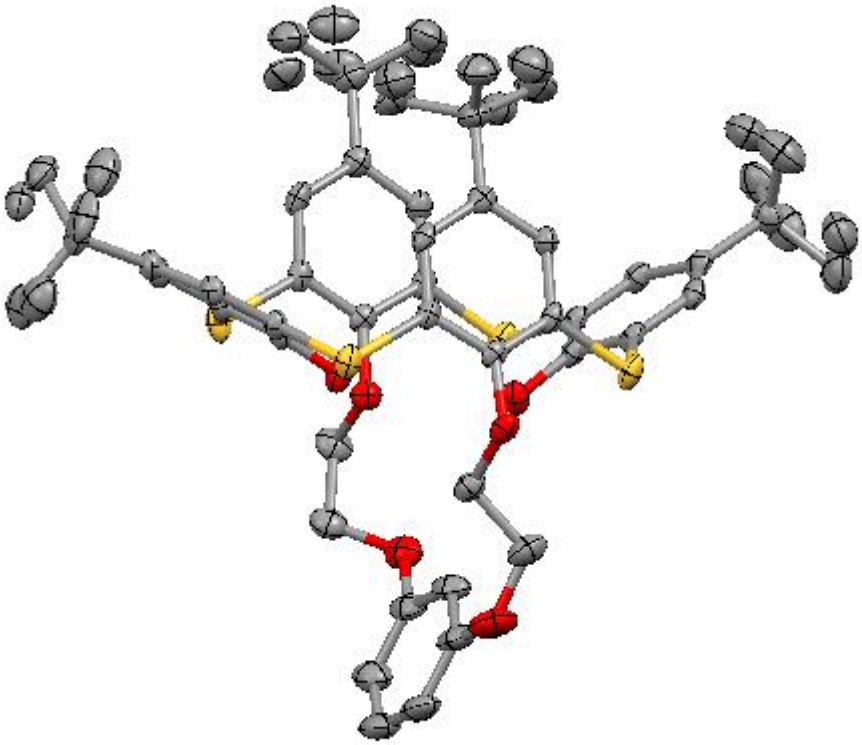

Figure 12 The molecular structure of ligand **2** (CCDC-740900). Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

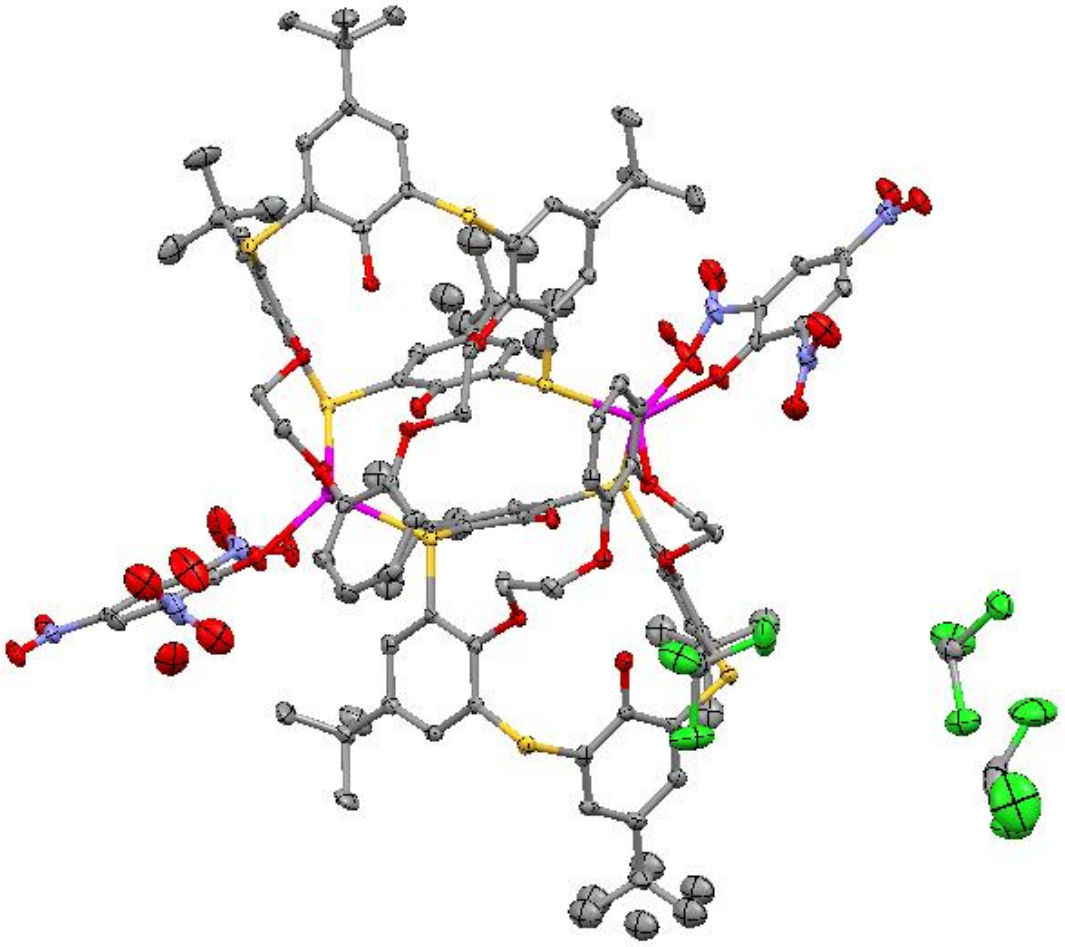

Figure 13 The molecular structure of complex **1**·AgPic (CCDC-740899). Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

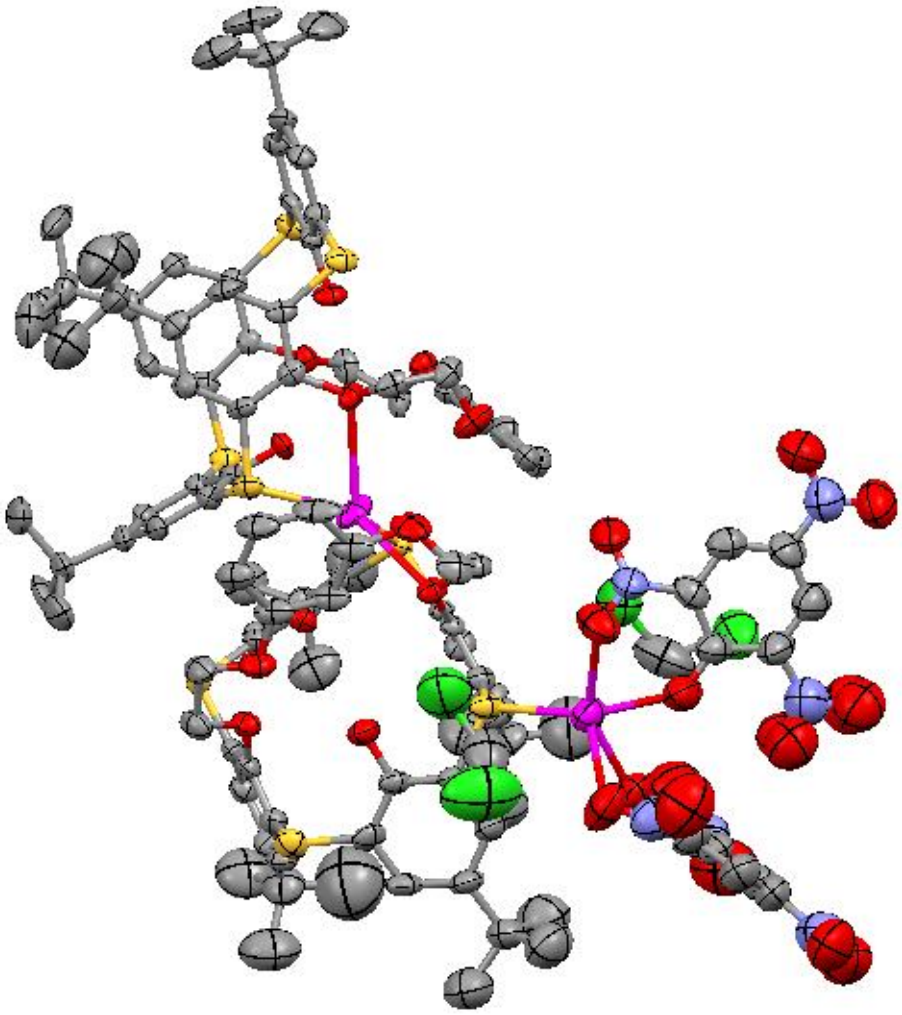

Figure 14 The molecular structure of complex **2**·AgPic (CCDC-740898). Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.