Capsule-like Assemblies in Polar Solvents

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Supporting Information

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For all synthetic details about the syntheses of the calix[4]arene halfspheres, see Supporting Information of:
R. Zadmard, T. Schrader, T. Grawe, A. Kraft, *Org. Lett.* **2002**, *4*, 1687 - 1690.

Calix[6]arenes:

NMR titration of macrocycle **28** vs. calix[6]arenehexaphosphonate **22**:

Host **28** solution: 3.79 mg in 7.0 mL D₂O; guest solution: 19.77 mg **22** in 1.04 mL D₂O.

Sample	Host soln. μL	Guest soln. μL	(Ar-H) in 28 ppm	(Ar-CH ₂ -) in 28 ppm
1	700	0	7,4448	4,2705
2	700	10	7,4271	4,2506
3	700	20	7,3895	4,2053
4	700	30	7,3718	4,1335
5	700	40	7,3773	4,1003
6	700	50	7,3718	4,0683
7	700	60	7,3707	4,0661
8	700	80	7,3652	4,0539
9	700	120	7,3541	4,0252

Job plot experiment between calix[6]arene phosphonate **22 and macrocycle **28**:**

Solution A: 3.11 mg **28** in 1040 μL D_2O ; solution B: 3.83 mg **22** in 7000 μL D_2O .

Content 28 [%]	(CH_2Ar in 28) ppm
20	4.0152
33	4.0440
42	4.0561
50	4.0594
55	4.0871
60	4.1147
66	4.1633
75	4.2197
83	4.2573
100	4.3269

Job plot experiment between calix[6]arene sulfonate **27** and azacrown **29**:

Solution A: 3.9 mg **27** in 4510 μL D_2O ; solution B: 1.2 mg **29** in 3700 μL D_2O .

Content 27 [%]	(CH_2N in 29) ppm	(Ar- CH_2 in 27) ppm	(Ar-H in 27) ppm
10	3.157	3.981	-
20	3.133	3.981	7.533
30	2.349	4.094	7.665
40	2.326	4.080	7.624
50	2.318	4.048	7.572
60	2.284	3.998	7.547
70	2.261	3.991	7.553
80	2.171	3.973	7.550
90	2.113	3.966	7.527

Inclusion of *N*-methylpyrazinium iodide and *N*-methylnicotinamide inside the rigid tetrphosphonate anionic halfsphere:

NMR titration: Calix[4]arenetetraphosphonate **15** vs. 1-methylnicotinamide iodide in methanol- d_4 .

Guest solution: 3.26 mg (2.95×10^{-3} mol) calix[4]arenetetraphosphonate **15** in 6 mL MeOD;
Host solution: 1.51 mg (5.71×10^{-3} mol) 1-methylnicotinamide iodide in 0.61 ml MeOD.

Sample	Host soln. μL	Guest soln. μL	(1) [ppm]	1 [ppm]	(2) [ppm]	2 [ppm]
1	600	0	0,0000	7,3097	0,0000	3,9985
2	600	10	0,0064	7,3161	0,0326	4,0311
3	600	20	0,0101	7,3198	0,0564	4,0549
4	600	30	0,0128	7,3225	0,0706	4,0691
5	600	40	0,0147	7,3244	0,0774	4,0759
6	600	50	0,0151	7,3248	0,0810	4,0795
7	600	60	0,0160	7,3257	0,0834	4,0819
8	600	80	0,0165	7,3262	0,0871	4,0856
9	600	120	0,0183	7,3280	0,0894	4,0879
10	600	200	0,0192	7,3289	0,0889	4,0874

NMR titration: Calix[4]arenetetraphosphonate **15** vs. 1-methylpiperazinium iodide in methanol- d_4 .

Guest solution: 3.79 mg (3.43×10^{-3} mol) calix[4]arenetetraphosphonate **15** in 6 mL MeOD;
Host solution: 1.33 mg (5.98×10^{-3} mol) methylpiperazinium iodide in 0.61 mL MeOD.

Sample	Host soln. μL	Guest soln. μL	(1) [ppm]	1 [ppm]
1	600	0	0,0000	1,0984
2	600	10	0,0210	1,1164
3	600	20	0,0409	1,1393
4	600	30	0,0487	1,1471
5	600	40	0,0818	1,1802
6	600	50	0,0630	1,1614
7	600	60	0,0652	1,1636
8	600	80	0,0674	1,1658
9	600	120	0,0697	1,1681
10	600	200	0,0697	1,1681