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Supplementary Information

The Synthesis of tetra-acrylamido-Calix[4]arene Capsules

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Mass spectra

The FAB mass spectrum of **3b** shows a molecular ion centred around *m/z* 1329 that is indicative of a monomeric structure. The ESI-mass spectrum of **3b** in methanol, recorded in the negative ion mode however, displays as its main signal a molecular ion centred around *m/z* 2689 that corresponds to the dimeric capsule **3b●3b** with one molecule of methanol included in its inner cavity (see figure 5). A second much weaker signal with 2 % of the intensity centred around [m/z] 2725 shows a dimeric capsule **3b●3b** with two molecules of methanol enclosed in the inner cavity of the capsule.

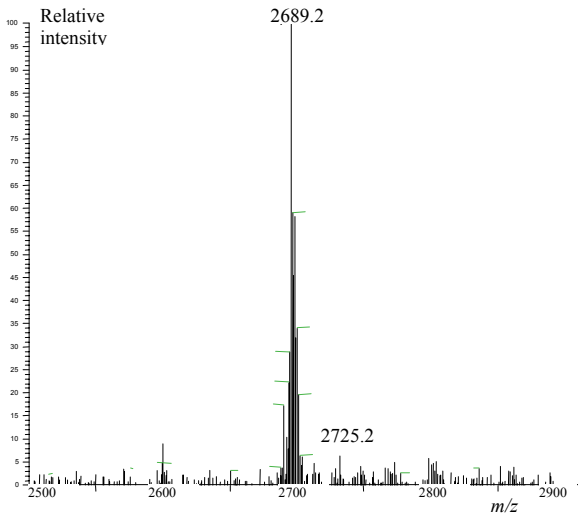

Fig. 5: Expanded region of ESI-mass spectrum of **3b●3b●MeOH** (recorded in the negative ion mode).

Stoichiometry of inclusion complex

The stoichiometry of this inclusion complex **3b●3b●4** is clearly 1:1 (one dimeric capsule to one molecule of **4**). This follows from the integration of the signals in the ^{1}H-NMR and from a molecular model that indicates complementarity in size of the inner volume of the dimeric capsule **3b●3b** and thiuram **4**. The ESI-mass spectrum of **3b●3b●4** in methanol shows as expected a weak molecular ion centred around *m/z* 2894.

NMR of heterodimer

Finally and most importantly an equimolar mixture of **3a** and **3b** in $CDCl_3$ gives rise to the formation of heterodimeric capsules. In the ^{1}H-NMR spectrum four N-H signals corresponding to the four different N-H protons of **3a●3a, 3a●3b** and **3b●3b** are observed in a statistical ratio of 1:2:1 at 8.2 mM concentration of of **3a, b** in $CDCl_3$ (see figure 6).

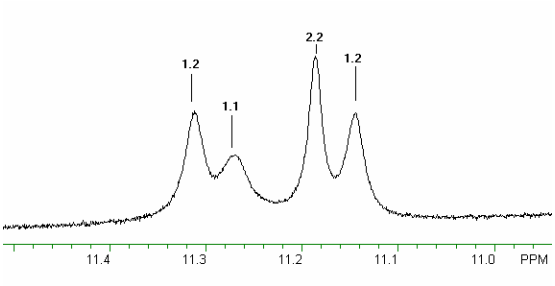

Fig. 6: Expanded 500 MHz-^{1}H-NMR spectrum in $CDCl_3$ of amide region showing four N-H signals corresponding to **3a•3a** (11.28 ppm)**, 3a•3b** (11.31 and 11.14 ppm) and **3b•3b** (11.20 ppm)

Typical Experimental (Synthesis of (3b)

5,11,17,23- Tetrakis[(*E*)-N-(4-cyanophenyl)-acrylamido]-25,26,27,28 tetra-n-butoxy acrylamido-calix[4]arene (3b)

Triethylamine (0.335ml, 0.157g, 1.56mmol) and 4-cyanophenylacrylamide **(2b)** (0.33g, 2.08mmol) was added to a stirred solution of 5,11,17,23 tetraiodocalixarene 25,26,27,28 tetra-n-*butylether* **(1)** (0.3g, 0.26 mmol) in DMF (20ml). After 10 minutes vigorous stirring at 25°C Palladium Acetate (0.0060g, 0.026 mmol) and diphenyl-phosphinopropane (0.011g, 0.026 mmol) were added and the mixture heated to 100°C and stirred for 175hrs. After addition of 50ml ether the mixture was washed with acid (3×20ml 3M HCl). The organic extract was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was further dried in a desiccator (SiO_2) under reduced pressure for 12hrs and recrystalised from methanol to give the *calix[4]arene* **(3b)** (0.19g, 55%) as off-white cubes, mp- 180-183°C; 3312 (N-H) 2228 (CN) 1686 (C=O) 1604 (C=C); δ_H(500 MHz; DMSO) 10.43 (4H, s, NH) 7.72 (8H, d, J8.8, Ar-H (benzenenitrile)) 7.61 (8H, d, J 8.8, Ar-H (Benzenenitrile)) 7.32 (4H, d, J 15.50, Ar-CH=), 6.97 (8H, s, Ar-H) 6.42(4H, d, J 15.50, Ar-CH=C*H*-C=O) 4.41 (4H, d, J 13.8, CH_AH$_B$Ar), 3.83 (8H, t, J 6.4, CH_2O), 3.19 (4H, d, J 13.8, CH$_A$$H_B$Ar), 1.90 (8H, m, C$H_2CH_2$O), 1.50-1.38 (8H,m, OCHCH$_2$CH_2), 1.00 (12H, t, J 8.3, CH_3CH_2) δ_H (500 MHz; $CDCl_3$) 11.20 (8H, s, NH) 8.21 (8H, d, J 8.7, Ar-H (benzenenitrile)) 7.72 (8H, d, J 8.7, Ar-H (Benzenenitrile)) 6.98 (4H, d, J 12.36, Ar-CH=), 6.84 (4H, s, Ar-H) 6.42(4H, d, J 15.5, Ar-CH=C*H*-C=O) 5.77 (4H, s, Ar-H) 4.22 (4H, d, J 15.5, CH_AH$_B$Ar), 3.74 (8H, dd, J 12.7 J 8.1, CH_2O), 2.63 (4H, d, J 11.8, CH$_A$$H_B$Ar), 1.92 (8H, m, C$H_2CH_2$O), 1.44-1.20 (8H,m, OCHCH$_2$CH_2), 1.00 (12H, t, J 8.3, CH_3CH_2);. δ_c(DMSO) 167.4,155.2, 139.9, 139.2, 134.6, 133.9, 127.1, 122.7, 120.3, 119.9, 116.2, 96.3, 76.6, 32.5, 33.0, 19.7, 15.08.; *m/z* (LSIMS) 1329[M+]. *m/z* (ESI, negative ion mode), 2689.2 {M_2+ CH_3OH); CHN: Found C, 75.79% H, 6.37 N, 8.29% $C_{84}H_{80}O_8N_8$ requires C, 75.88%, H, 6.06%, N, 8.43%.