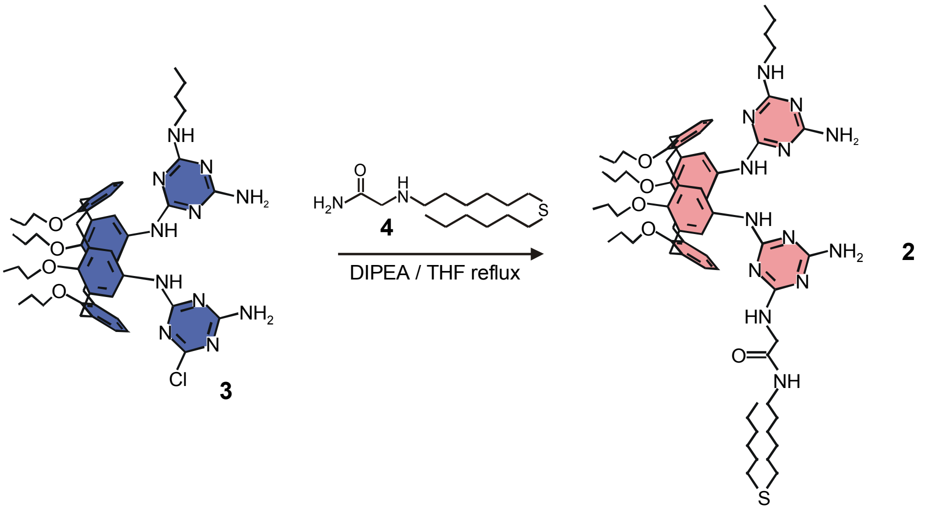
Supplementary data

Growth of Individual Hydrogen-Bonded Nanostructures on Gold Monolayers

Juan J. Garcia-Lopez,[a] Szczepan Zapotoczny,[b] Peter Timmerman,[a] Frank C. J. M. van Veggel,[a] G. Julius Vancso,[b] Mercedes Crego-Calama,*[a] and David N. Reinhoudt*[a]

[a]Supramolecular Chemistry and Technology, MESA$^+$ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands. Fax: +31534894645; Tel: +31534892980; E-mail: D.N.Reinhoudt@ct.utwente.nl
[b]Materials Science and Technology of Polymers, MESA$^+$ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Asymmetrically substituted calix[4]arene dimelamine **2** was obtained from the coupling of calix[4]arene dimelamine **3**[1] and sulfide derivative **4**.



Scheme 1

Calix[4]arene dimelamine 2. A solution of calix[4]arene dimelamine **3** (0.234 g, 0.25 mmol), sulfide derivative **4** (0.140 g, 0.50 mmol) and diisopropyl ethyl amine (DIPEA) (0.450 mL, 2.5 mmol) was refluxed in anhydrous THF (5 mL) under Ar atmosphere for

3 days. The solvent was removed under low pressure. Column chromatography (eluent: methanol-chlorofom 1:20) gave compound **2** as a white solid. Yield 0.270 gr (92%). M.p. 120 - 123 ºC. ^{1}H NMR: δ_H($CDCl_3$, 300 MHz) 7.07 (m, 4H, ArH), 6.88 (m, 2H, ArH), 6.80-6.10 (m, 8H, 4 NH, 4 *o*-NHArH), 5.20- 4.90 (m, 5H, 2 NH_2, NH), 4.46 (2 ABq, 4H, 2 $ArCH_2Ar$), 4.00 (m, 6H, 2 OCH_2, CH_2CO), 3.68 (m, 4H, 2 OCH_2), 3.31 (q, 2H, ^3J (H,H) = 6.7 Hz, CH_2), 3.14 (m, 6H, 2 $ArCH_2Ar$, CH_2), 2.50 (t, 4H, ^3J (H,H) = 7.5 Hz, SCH_2), 2.47 (t, 4H, ^3J (H,H) = 7.5 Hz, SCH_2), 2.10 – 1.80 (m, 8H, 4 CH_2), 1.65 – 1.20 (m, 24H, 12 CH_2), 1.15 – 1.05 (m, 6H, 2 CH_3), 1.01 – 0.86 (m, 12H, 4 CH_3); ^{13}C-NMR: δ($CDCl_3$, 75 MHz) 169.8, 165.8, 163.6, 157.5, 151.6, 151.3, 136.3, 133.1, 132.9, 131.8, 128.3, 121.0, 39.9, 38.8, 31.7, 31.5, 31.3, 30.9, 30.6, 29.2, 29.0, 28.7, 28.1, 28.0, 26.0, 23.0, 22.5, 22.0, 19.6, 13.5, 13.4, 10.3, 9.3; FAB-MS: *m/z*: 1154.7 ([M^+], calcd. for $C_{64}H_{91}N_{13}O_5S$: 1154.69).

The capability of calix[4]arene dimelamine **2** to form the double rosette assembly $\mathbf{2}_3$•$(DEB)_6$ and the ability of this assembly to mix with assembly $\mathbf{1}_3$•$(DEB)_6$[2] were studied in solution. Figure 1 shows the characteristic peaks at 15.0 – 13.0 ppm for the hydrogen bonded imide hydrogens of the DEB upon formation of the homogeneus assemblies $\mathbf{1}_3$•$(DEB)_6$, $\mathbf{2}_3$•$(DEB)_6$, and the heterogeneous mixture of assemblies $\mathbf{1}_3$•$(DEB)_6$, $\mathbf{1}_2$•**2**•$(DEB)_6$, **1**•$\mathbf{2}_2$•$(DEB)_6$ and $\mathbf{2}_3$•$(DEB)_6$, upon mixing a solution of $\mathbf{1}_3$•$(DEB)_6$ (1 mM, toluene) and a solution of $\mathbf{2}_3$•$(DEB)_6$ (1 mM, toluene)[3].

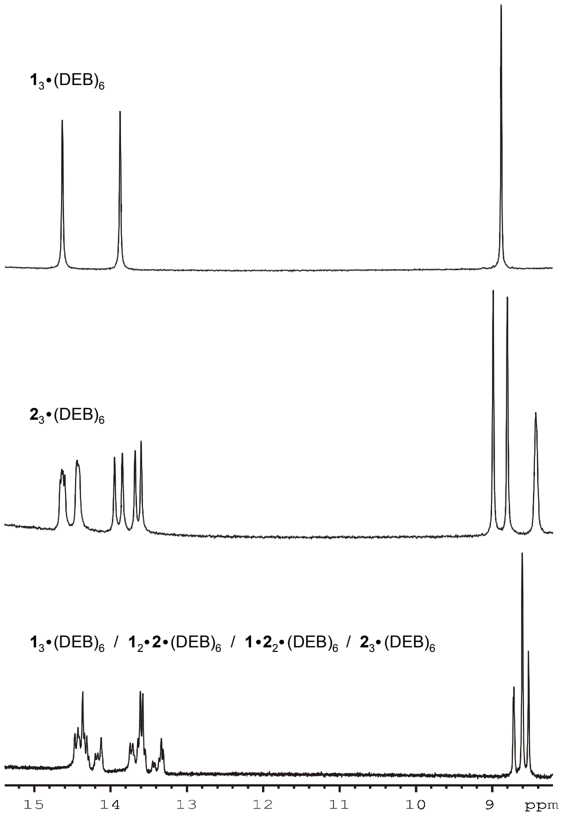


Figure 1

Procedure for the preparation of adsorbate solution $\mathbf{1}_3$•(DEB)$_6$ (50 μM, toluene). Typically, a solution of calix[4]arene dimelamine **1** (1 equiv.) and barbiturate derivative DEB (2 eq) in toluene (50 mL) was stirred and sonicated until no remaining solid was present in solution.

Growth of the Hydrogen-Bonded Assemblies on the monolayer. Hexanethiol monolayers were placed into a calix[4]arene dimelamine **2** solution (50 and 20 μM CH_2Cl_2) for one hour at room temperature. After the adsorption time, the samples were rinsed with CH_2Cl_2 (50 mL), sonicated in CH_2Cl_2 for one minute and rinsed extensively again with CH_2Cl_2. Finally, they were dried under a stream of dry N_2. Hexanethiol monolayers and monolayers containing inserted molecules of calix[4]arene dimelamine **2** were placed into a solution of the assembly $\mathbf{1}_3$•(DEB)$_6$ (50 μM, toluene) for one hour at room temperature. After the exposure, the samples were rinsed with toluene (50 mL) and sonicated for 1 minute in a flask containing toluene. Finally, they were rinsed extensively again with toluene and dried under a stream of dry N_2. When the calix[4]arene dimelamine **2** was not present in the monolayers, no features corresponding to the assembly $\mathbf{1}_3$•(DEB)$_6$ were imaged (figure 2). This blank experiment rules out physisorption and demonstrate that the features observed in the images corresponding to the hexanethiol monolayers containing the calix[4]arene **2** are due to the growth of the assemblies $\mathbf{1}_2$•2•(DEB)$_6$ in the monolayer.

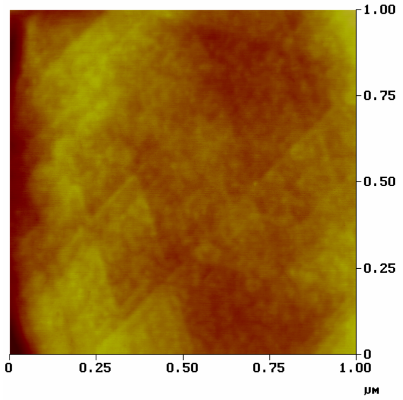


Figure 2. TM-AFM image (1 x 1 μm, height profile) of a hexanethiol monolayer after treatment with a solution of assembly $\mathbf{1}_3$•(DEB)$_6$. Color scale from dark to yellow: Z = 10 nm.

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[2] Timmerman, P.; Vreekamp, R. H.; Hulst, R.; Verboom, W.; Reinhoudt, D. N.; Rissanen, K.; Udachin, K. A.; Ripmeester, J. *Chem. Eur. J.* **1997**, *3*, 1823-1832.

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