Supplementary information

Molecular modelling details

The crystal structure of *p*-phosphonic acid calix[4]arene (CSD entry code QOCCUH) was used as the input structure of the calix[4]arene. The protons at the lower rim of the calix[4]arene were substituted with C_{18} alkyl chains giving rise to **1**. The geometry of the calix[4]arene in **1** was then fixed and the energy of the structure minimized correcting for unorthodox bond lengths and angles in the alkyl chains. Replicates of **1** were then aligned to give the 'ferris wheel' shown in Figure 3 which is composed of 16 units of **1** with the C_{18} alkyl chains pointing towards the centre and the phosphonated calix[4]arenes pointing towards the outside. Four copies of the 'ferris wheel' were stacked on top of each other giving the starting geometry of the fibre. The fixed geometry constraint previously imposed on the calix[4]arene was removed allowing for flexibility within the entire structure.

The Amorphous Cell module was used to construct a periodic cell with the stacked 'ferris wheels' in a box of toluene molecules. The Forcite module was used to minimize the structure using the smart minimizer with coarse quality and the atom-based summation methods, and the PCFF Force Field. The convergence criterion of the average energy derivative was less than $2x10^{-3}$ kcal/mol. The optimized structure had a total energy of $8.52x10^{6}$ kcal/mol. To reduce the likelihood of being in a local minimum, a dynamic simulation at an elevated temperature was undertaken. The NVT ensemble was used at 298 K with a time step of 1 fs. Five hundred thousand steps were used for the simulation giving a total simulation time of 500.0 ps. The final structure from the dynamics trajectory was then optimized giving a total energy of $-4.93x10^{4}$ kcal/mol.

Dilution Studies

Originally nano-fibre formation was observed at a calix[4]arene concentration of 5ppm. A series of dilutions were performed, resulting in concentration range of 1-100ppm, with the results summarised in a table below, with selected AFM images.

Table S1 – Summary of fibre formation as a function of calixarene concentration.

Concentration (ppm)	Fibre Formation
1	Y
10	Y
20	Y
30	Y
40	Y
50	N
60	N
70	N
80	N
90	N
100	N

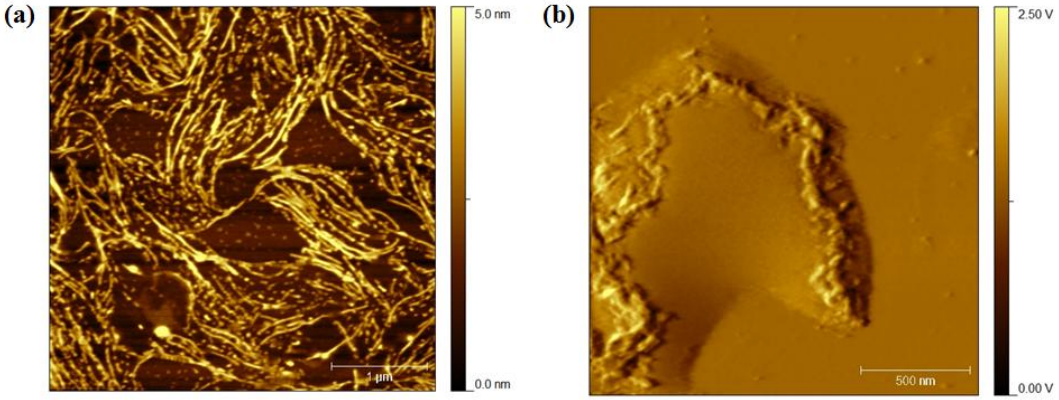

Figure S1 – Height and amplitude image respectively of the self assembly of an amphiphilic calix[4]arene at (a) 40 ppm and (b) 70 ppm.

Different stoichiometric amounts of fluorophore were added to a solution of the amphiphilic calix[4]arene and the size of the nano-fibres formed investigated. In all cases the solutions were mixed for four hours, deposited onto a freshly cleaved mica substrate and then washed with chloroform to remove any excess fluorophore. Fibre sizes were determined through averaging the height of all the measurable fibres present in the AFM image.

Table S2 – Fibre size for various ratios of calixarene:fluorophore

Calix[4]arene	Fluorophore	Fibre size (nm)
1	10	140
1	5	60
2	1	60

The 2:1 calix[4]arene: fluorophore solution was also taken and diluted 10x with toluene. This solution was then mixed for four hours, deposited onto a freshly cleaved mica substrate and washed with chloroform. The nano-fibres observed had a height of 6nm, the same as for the amphiphilic calix[4]arene with no fluorophore incorporation.

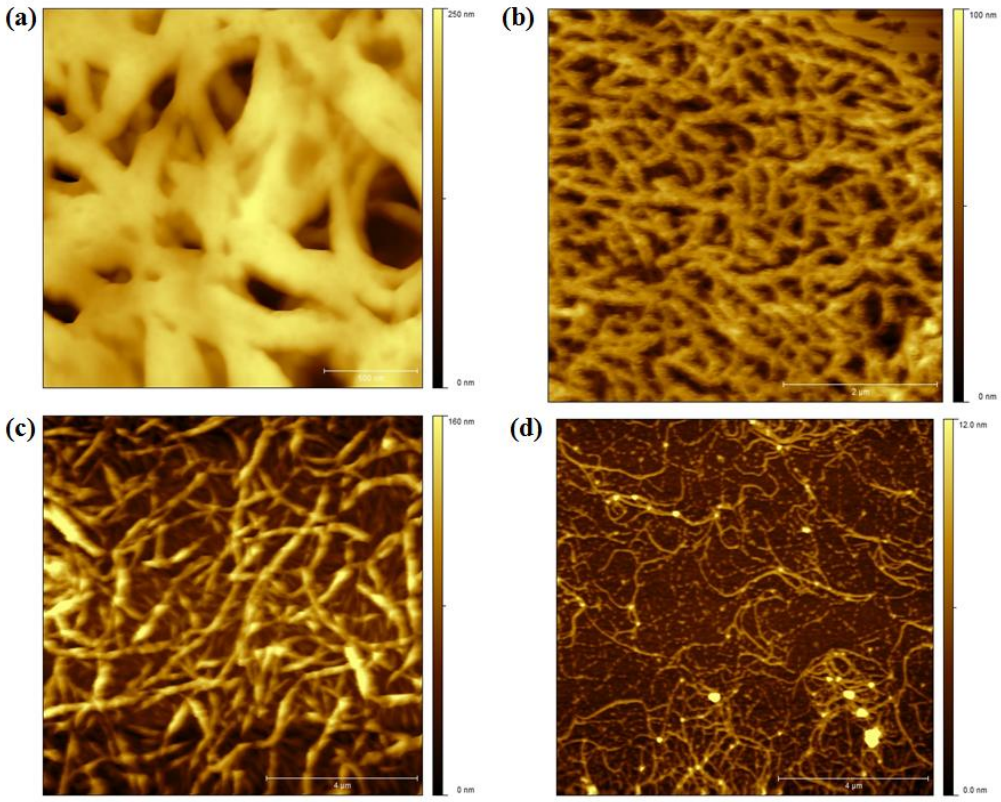

Figure S2 – AFM height micrographs of calix[4]arene: fluorophore ratios of 1:10 (a), 1:5 (b), 2:1 (c) and 2:1 diluted 10x (d).