Towards new nanoporous biomaterials: self-assembly of sulfopillar[5]arenes with vitamin D3 into supramolecular polymers

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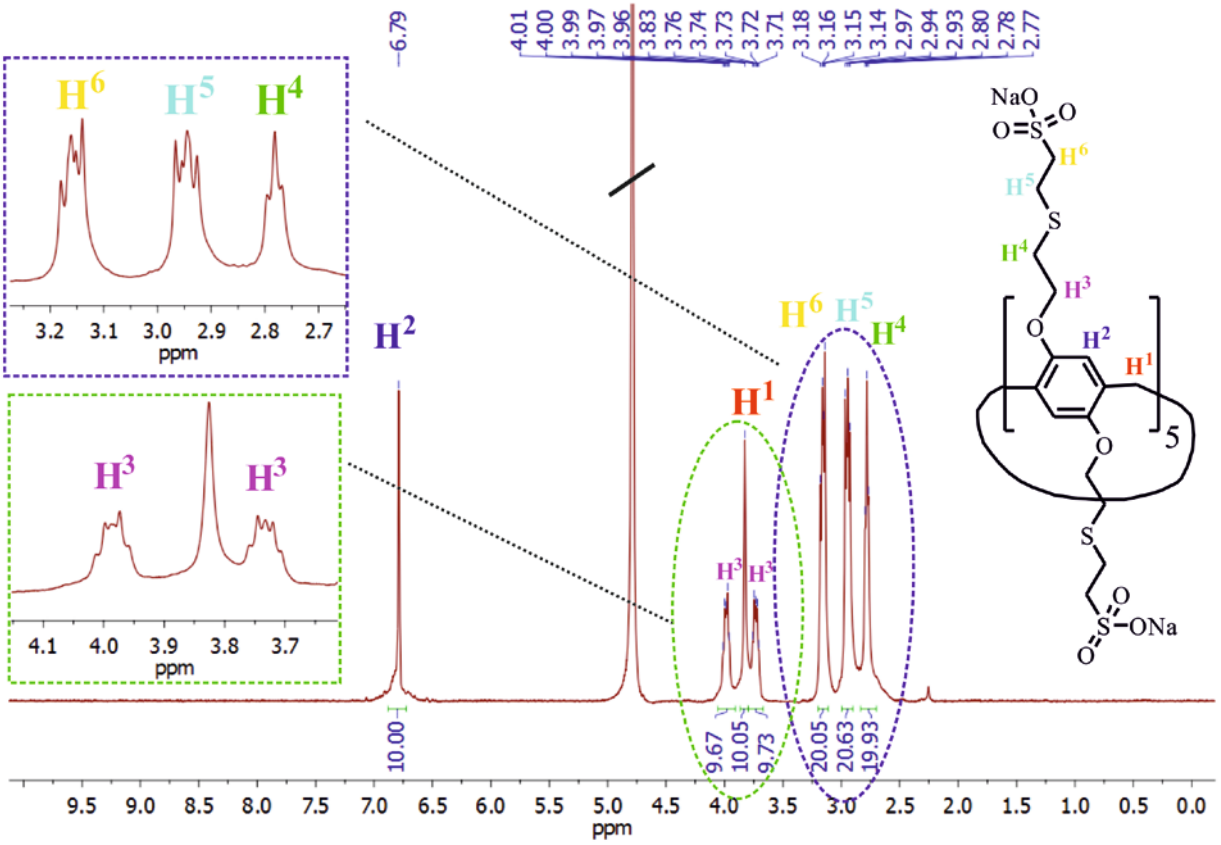
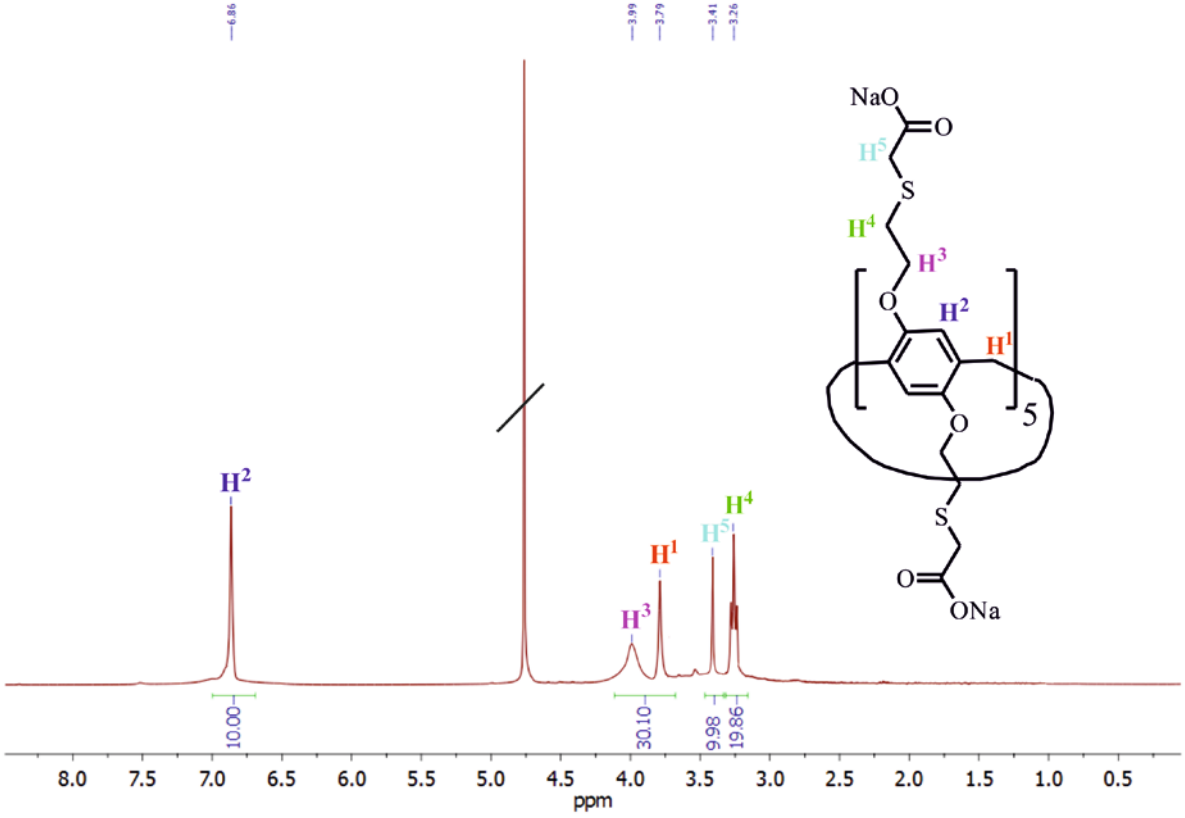
Electronic Supplementary Information (12 pages)

1. NMR, Mass spectrum (ESI), IR spectra of the compounds 2,3.

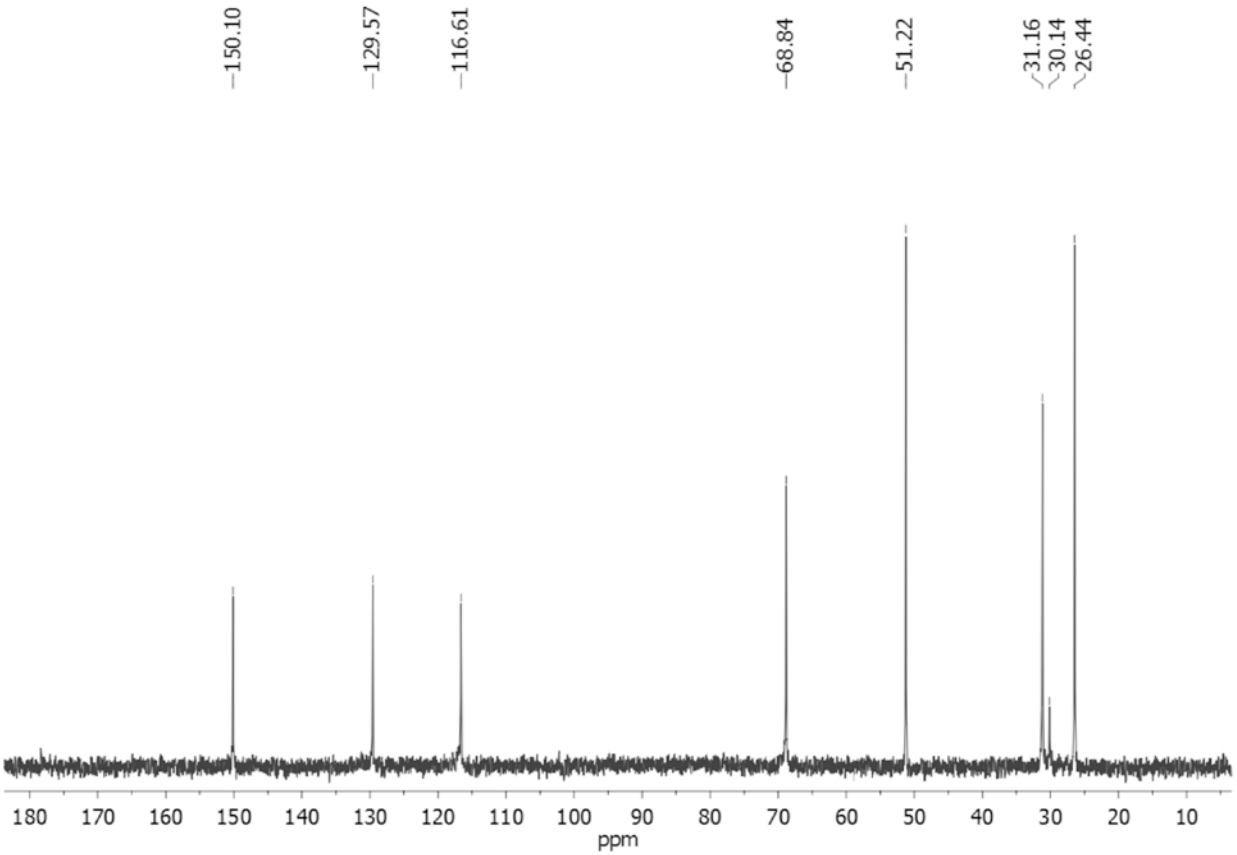
^{1}H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca-[(thiaetansulfonate)ethoxy)]- pillar[5]arene sodium salt (2), D_2O, 298 K, 400 MHz



^{1}H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca-[(thiaacetate)ethoxy]-pillar[5]arene sodium salt (3), D_2O, 298 K, 400 MHz



^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca-[(thiaetansulfonate)ethoxy)]- pillar[5]arene sodium salt (2), D_2O, 298 K, 400 MHz



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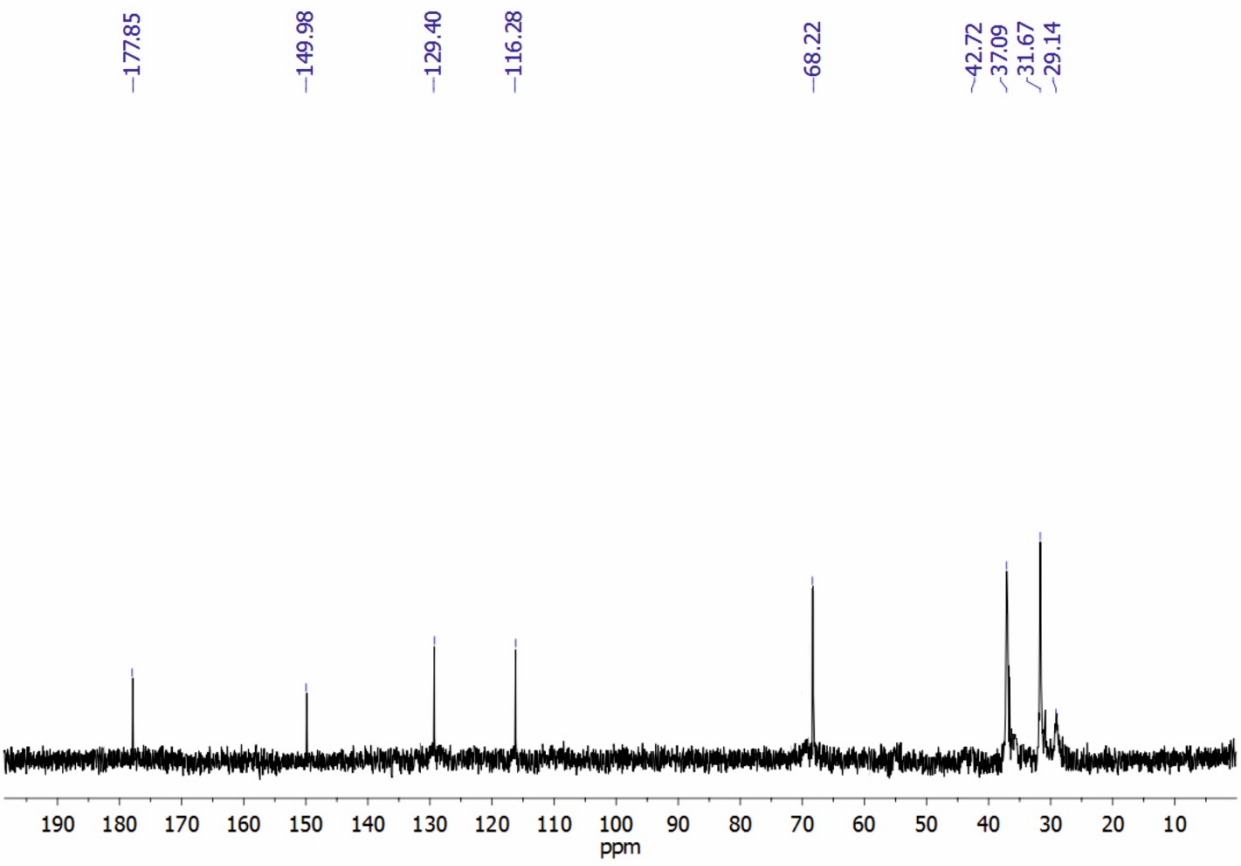

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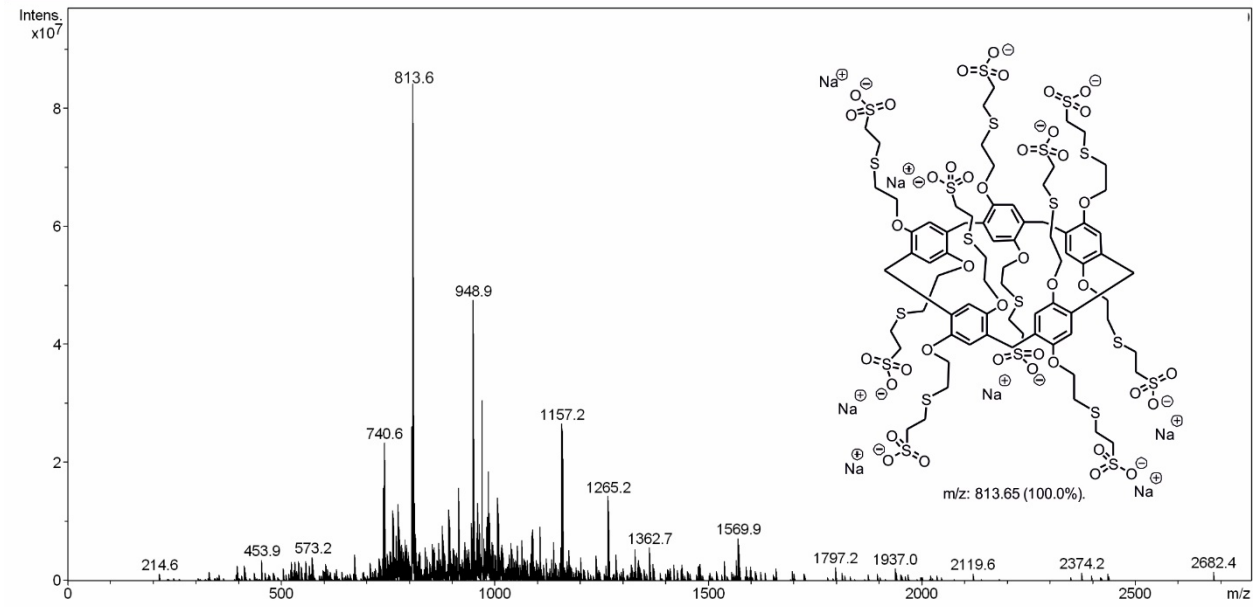

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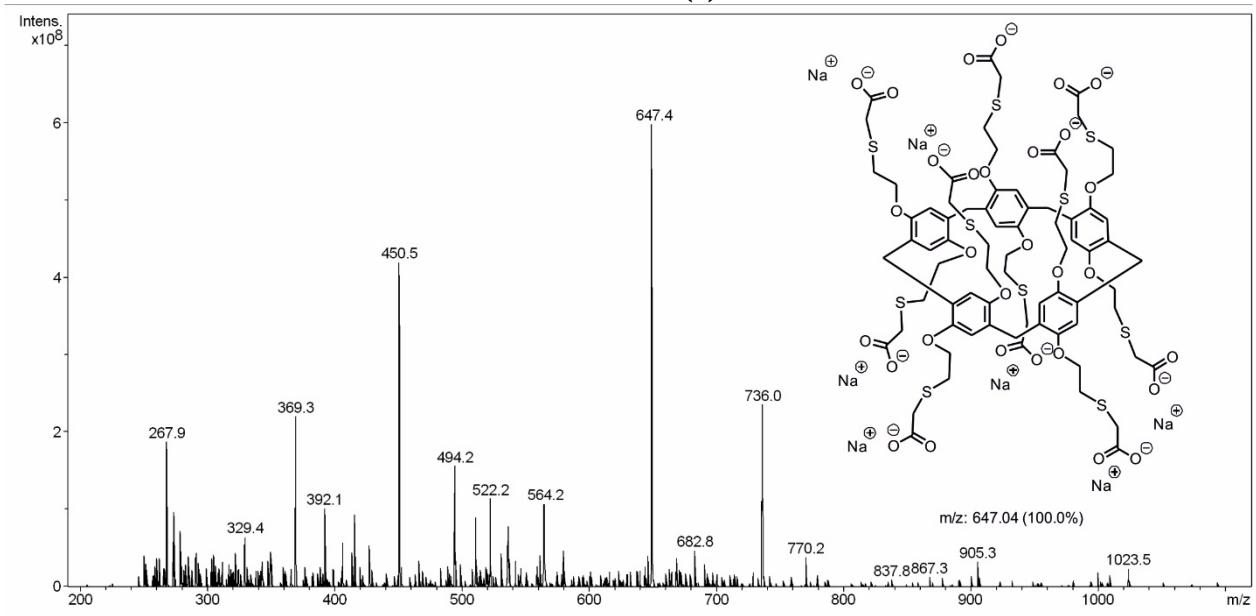

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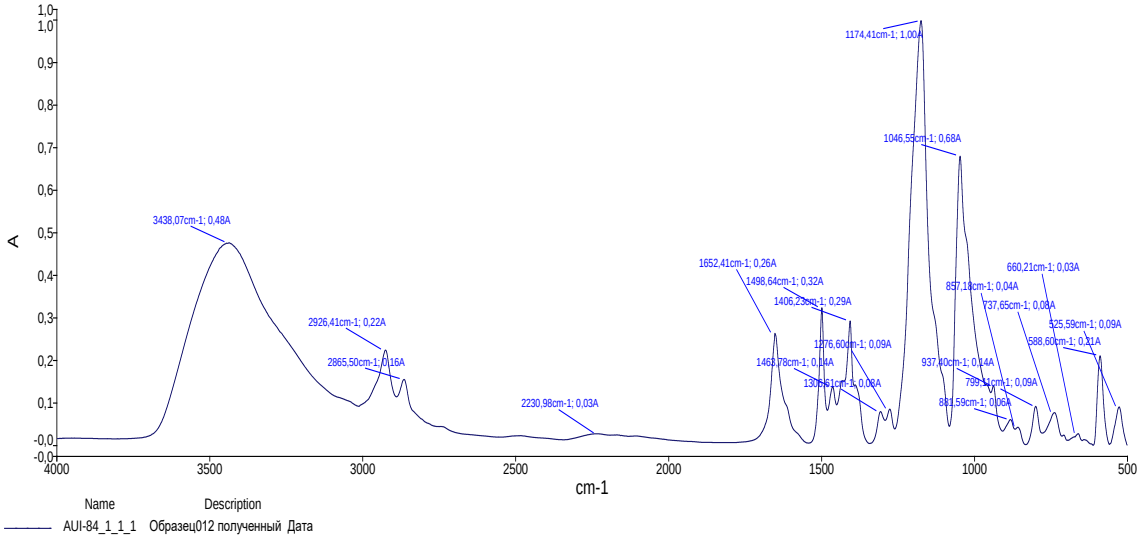
IR spectrum of 4,8,14,18,23,26,28,31,32,35-deca-[(thiaetansulfonate)ethoxy]- pillar[5]arene sodium salt (2).



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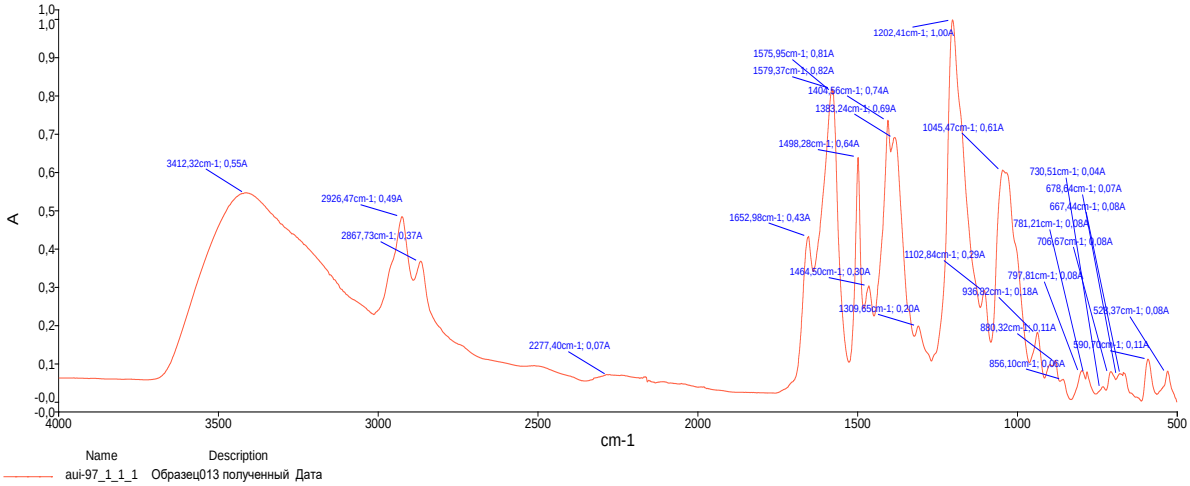
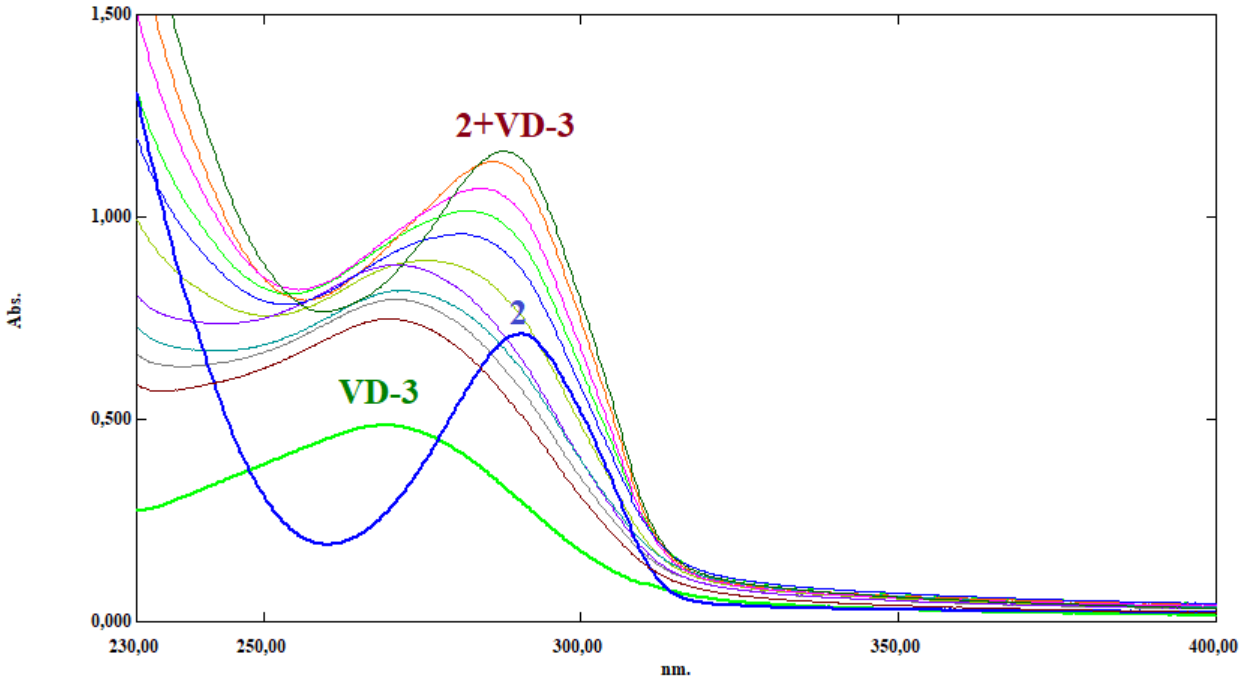
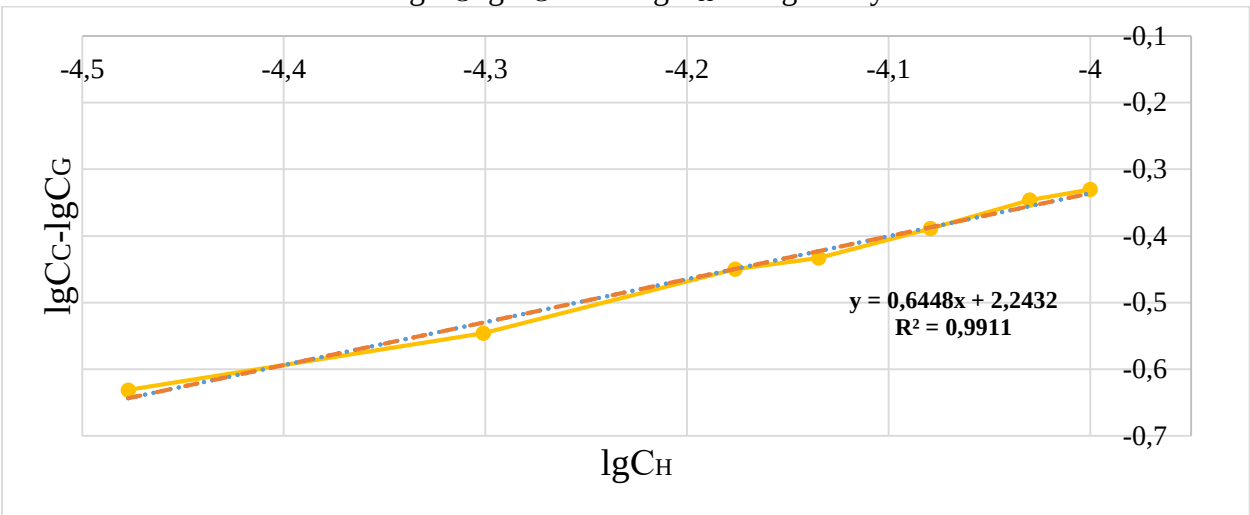


2. UV spectra

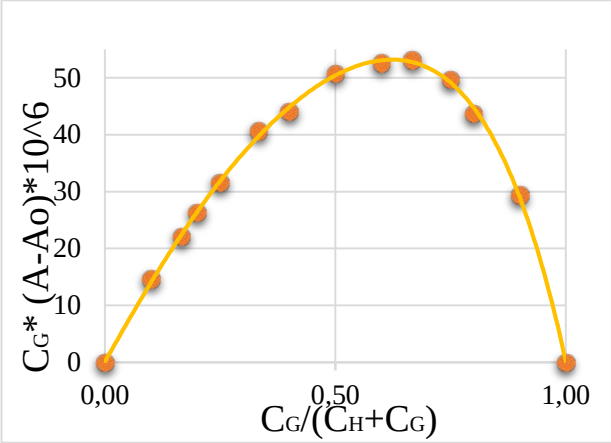
UV-vis spectra of mixtures of vitD$_3$ (4×10^{-5}M) pillar[5]arene **2** with different concentrations of pillar[5]arene **2** (3.33×10^{-6}- 4×10^{-5} M)



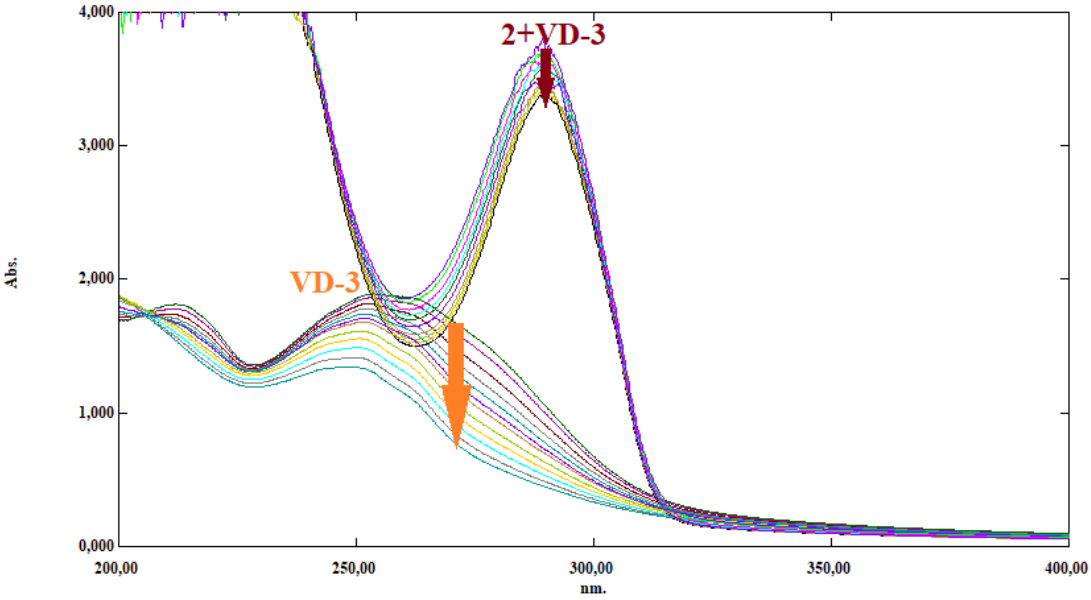
Plot of lg C_C-lg C_G versus lg C_H host/guest system



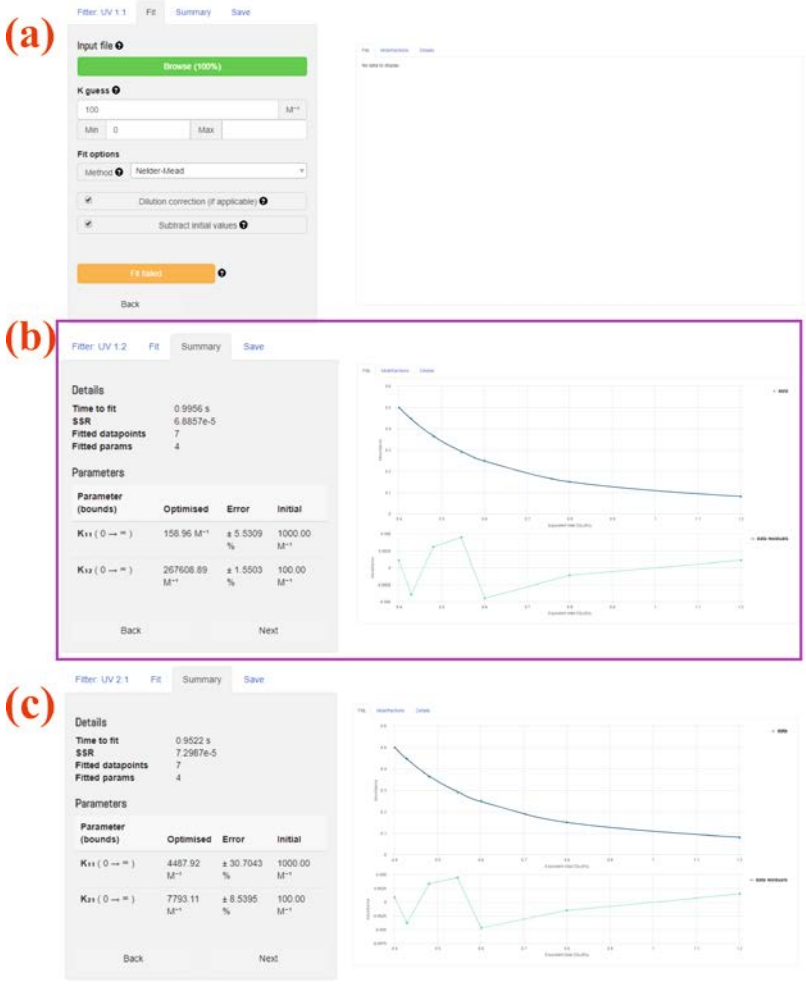
Job's plot for the complex of **2** with vitD$_3$.



UV-vis spectra UV-destruction complex vitD$_3$+**2** in water (C_2 =5×10^{-5} M, C_{VD-3}=1×10^{-4}M) and vitD$_3$ alone in water (C_{vitD3}=1×10^{-4}M) for a time.

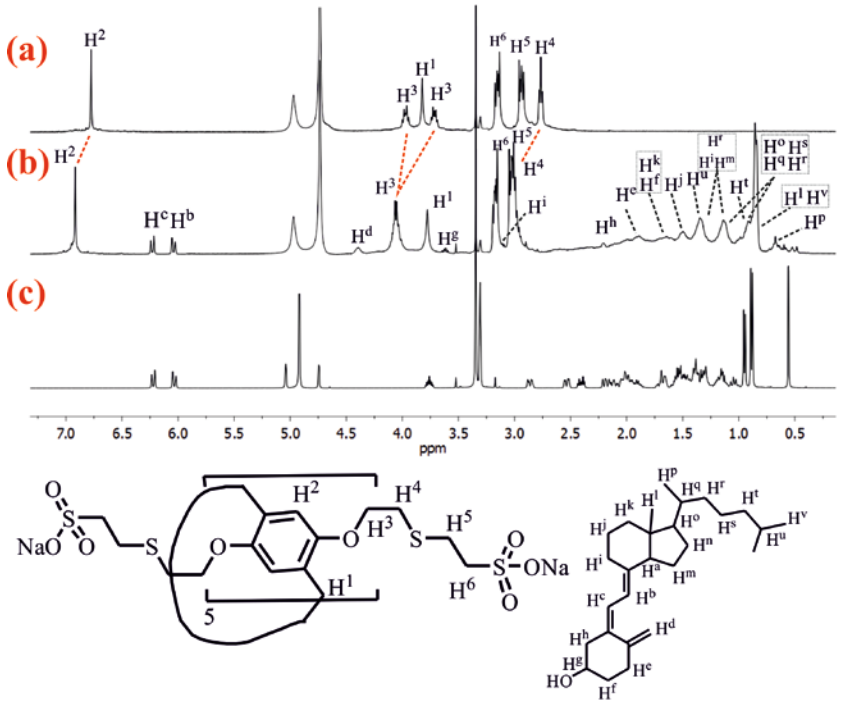


Bindfit (Fit data to 1:1, 1:2 and 2:1 Host-Guest equilibria)
Screenshots taken from the summary window of the website supramolecular.org. This screenshots shows the raw data for UV-vis titration of 2 with VitD$_3$, the data fitted to 1:1 binding model (A), 1:2 binding model (B) and 2:1 binding model (C).

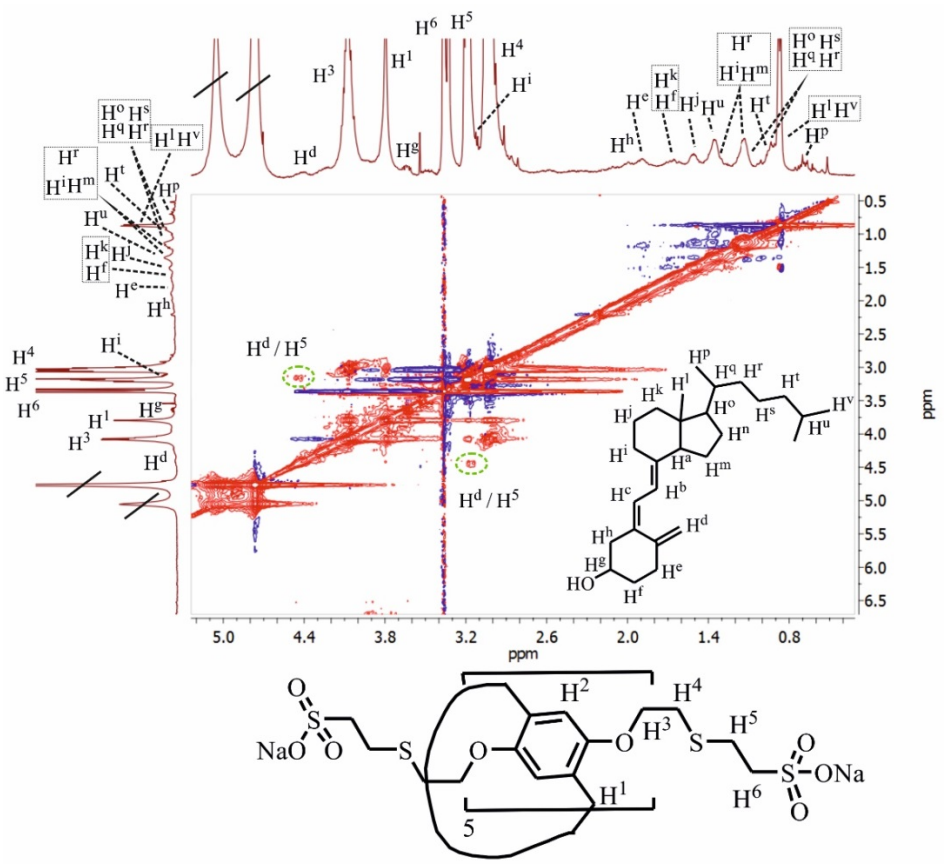


3. NMR study

The ^{1}H NMR spectra of the macrocycle **2 (a)**, **2** / vitD$_3$ (1:2) complexes **(b)**, vitD$_3$ **(c)** in D$_2$O / CD$_3$OD (5×10^{-3} M) and vitD$_3$ **(d)** in CD$_3$OD (5×10^{-3} M) at 25 °C.

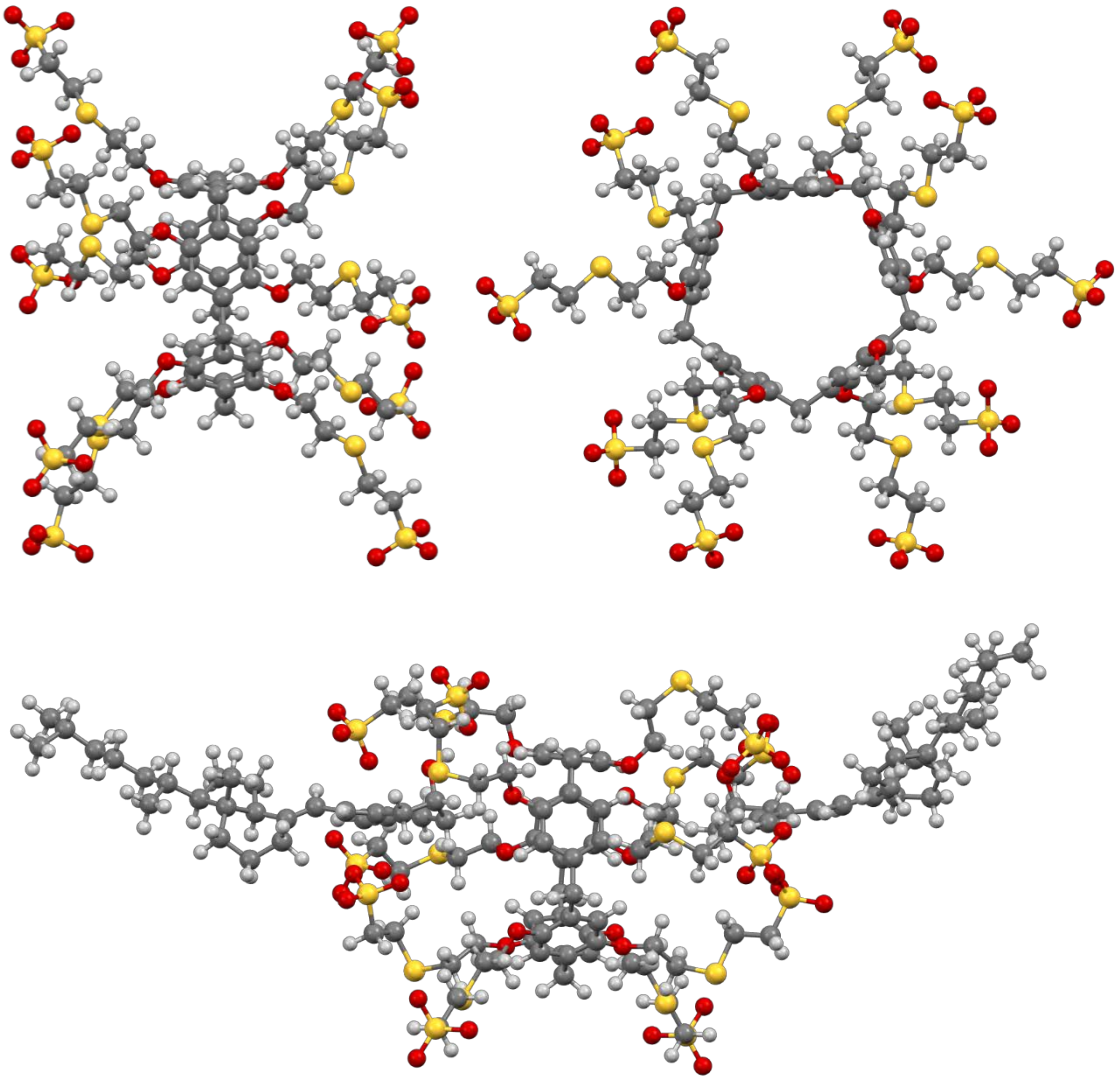


The 2D ^{1}H-^{1}H NOESY NMR spectrum of the **2** / vitD$_3$complexes in D$_2$O / CD$_3$OD (1:2, 5×10^{-3} M) at 25 °C.



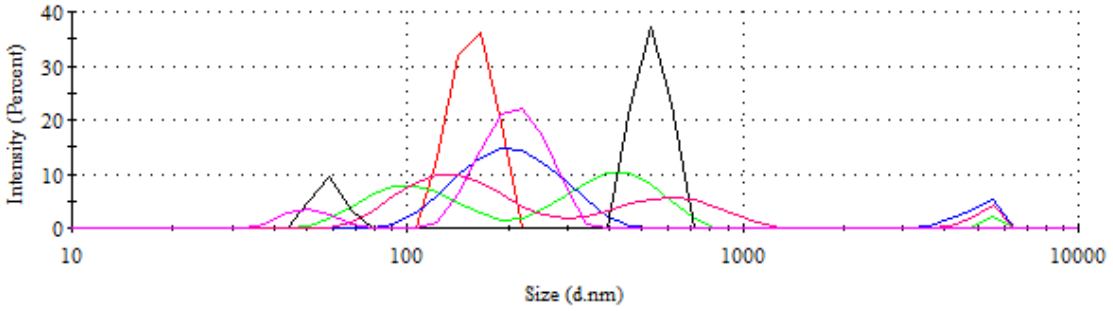
4. Computational determination of the orientation of vitD3 inside pillar[5]arene 2.

Geometry optimized structures of 2 (top, side and end views) and the 2/2 vitD3 complex (bottom).

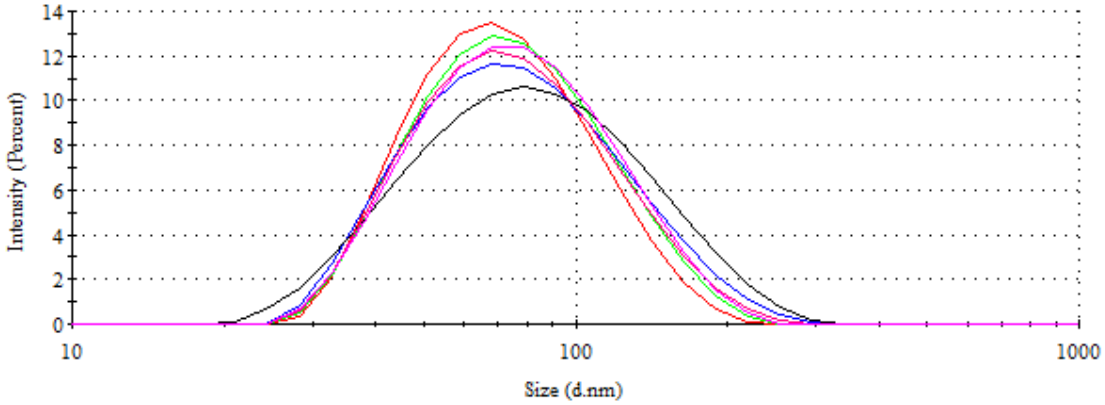


5. Dynamic light scattering.

Size distribution of the particles by intensity for **2** (1×10^{-4}M) in water



Size distribution of the particles by intensity for vitD_3 (5 mkl 10^{-3} C_2H_5OH) 5×10^{-6} M in water (d=69.90 ± 1.01 nm, PDI= 0.19 ± 0.01)

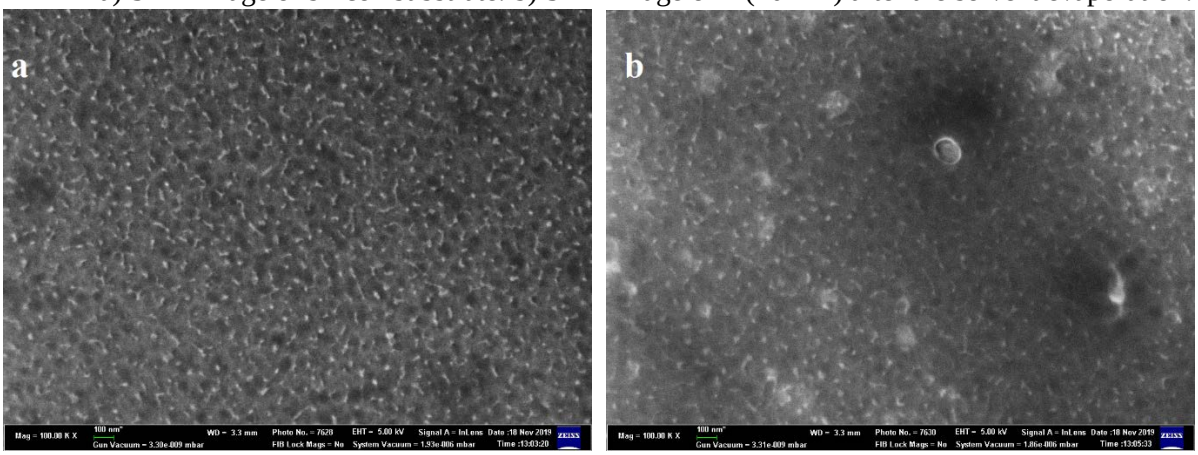


Aggregation of the particles for **2** / vitD_3

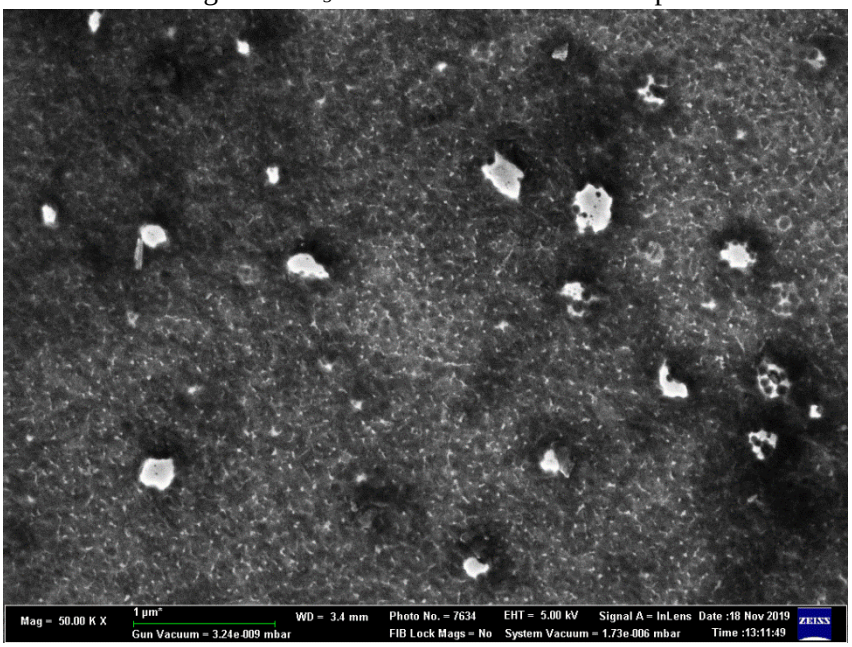
Ratio 2 / vitD_3	**V $_H$, µl**	**C $_H$, M**	**V $_{VD-3}$,µl**	**C $_{VD-3}$, M**	**Z $_{average}$ (d) , nm**	**PDI**	**ζ- potential, mV**
1:0	1000	10^{-3}	0	0	290.40±88.16	0.56±0.16	-
1:0	1000	10^{-4}	0	0	461.70±256.80	0.62±0. 20	-
1:0	1000	10^{-5}	0	0	431.20±178.50	0.38±0.19	-
1:1	1000	10^{-3}	10	10^{-1}	201.90±2.14	0.16±0.01	-21.20±5.10
1:2	1000	10-3	20	10-1	201.80±1.41	0.16 ± 0.01	-25.60±2.04
1:5	1000	10^{-3}	50	10^{-1}	236.00±1.94	0.23±0.01	-19.20±7.50
1:1	1000	10^{-4}	10	10^{-2}	94.38±0.55	0.17±0.01	-39.40±2.71
1:2	1000	10^{-4}	20	10^{-2}	123.70±0.75	0.16±0.01	-50.50±2.29
1:5	1000	10^{-4}	5	10^{-1}	176.60±1.41	0.11±0.01	-57.50±1.26
1:10	1000	10^{-4}	10	10^{-1}	193.5±0.92	0.11±0.02	-42.80±0.77
1:1	1000	10^{-5}	10	10^{-3}	134.20±0.62	0.09±0.02	-35.90±4.54
1:2	1000	10^{-5}	20	10^{-3}	53.13±1.14	0.18±0.01	-33.50±2.78
1:5	1000	10^{-5}	5	10^{-2}	109.70±0.64	0.15±0.01	-55.70±2.24
1:10	1000	10^{-5}	10	10^{-2}	98.35±0.81	0.13±0.01	-51.60±2.04
	H_2O						
0:1	1000	0	5	10^{-3}	69.90±1.01	0.19 ± 0.01	-31.10±5.15

6. Scanning electron microscopy.

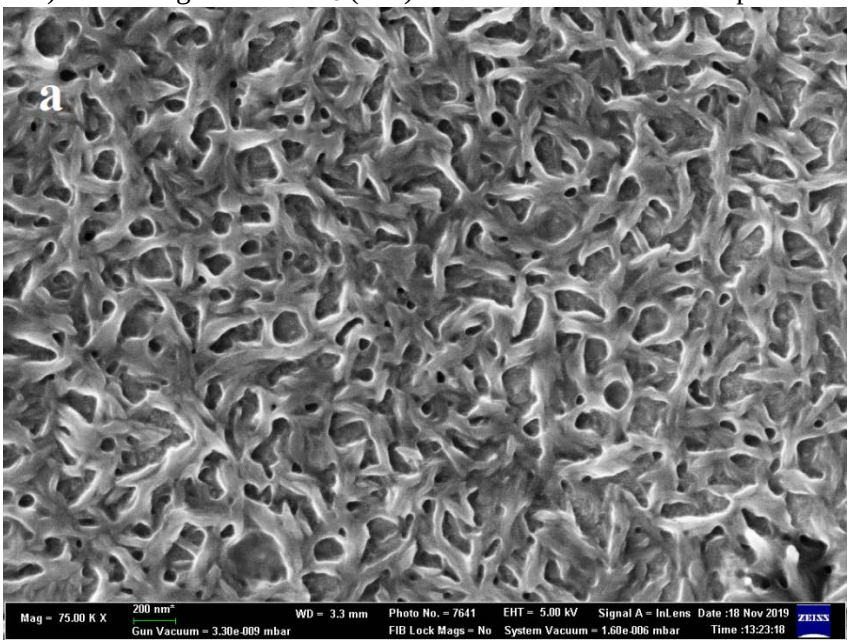
a) SEM image of silicon substrate. b) SEM image of **2** (10^{-4} M) after the solvent evaporation.

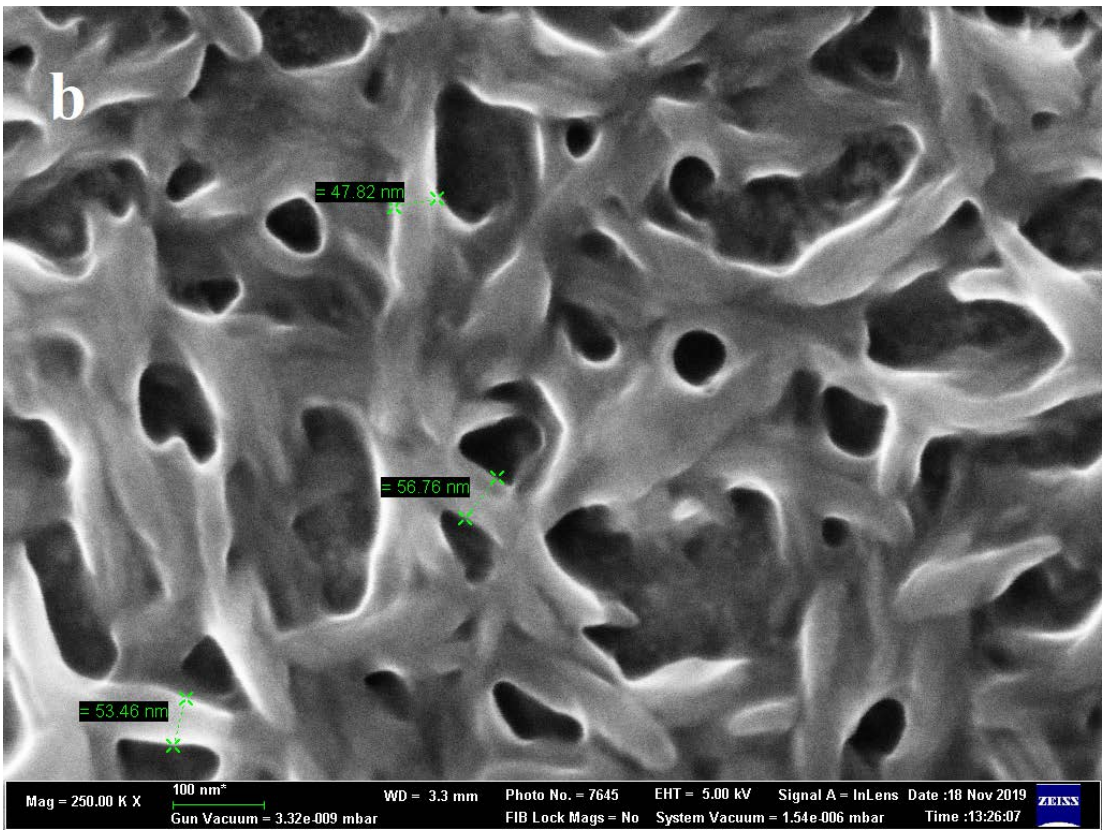


SEM image of vitD_3 10^{-4} M after the solvent evaporation.



a-b) SEM image of **2** / vitD_3 (10^{-4}) M 1:2 after the solvent evaporation.

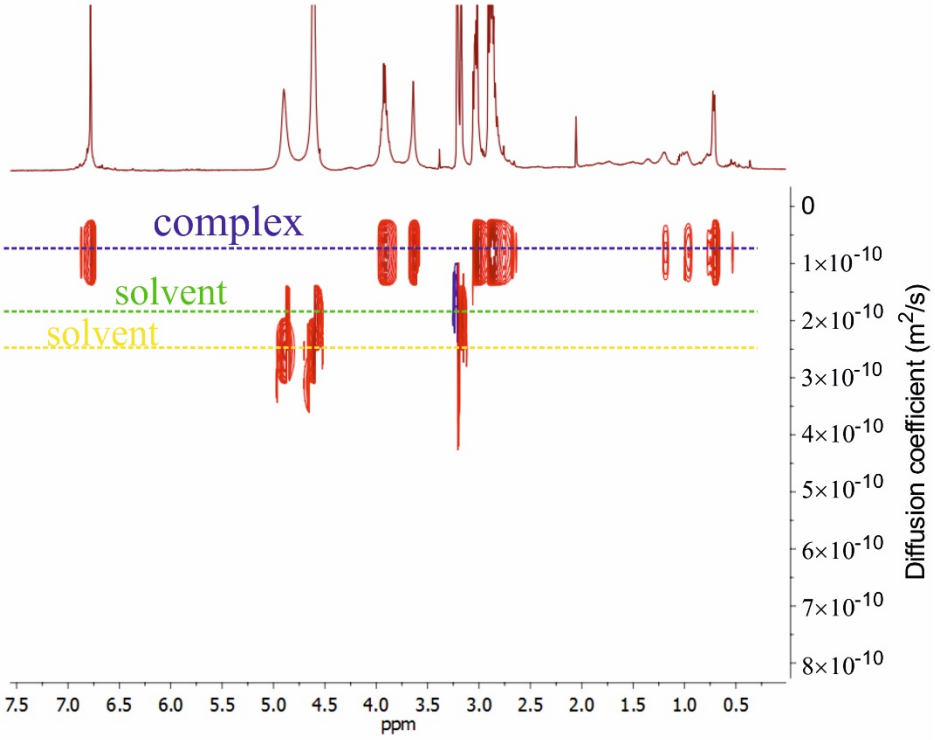




7. Diffusion experiments.

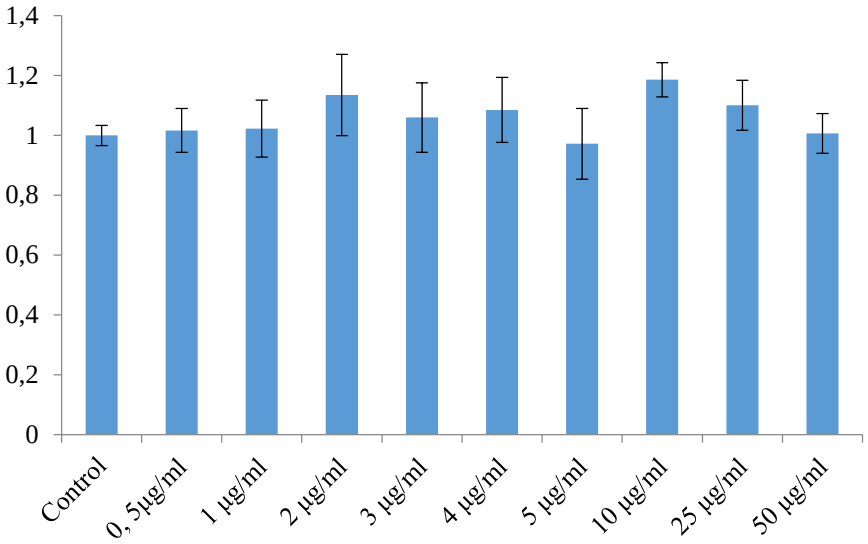
Diffusion coefficients of pure **2**, vitD_3 and **2/** vitD_3 complexes in D_2O / CD_3OD (400 MHz, 298K).

Compounds	**D (10^{-10} m^2 s^{-1})**
2	4.83
vitD_3 / 2	0.76



8. Evaluation of cell viability change under the action of pillar[5]arenes 2 and 3.

Survival of cells after incubation with pillar[5]arene **2** during 24 hours.



Survival of cells after incubation with pillar[5]arene **3** during 24 hours.