



Supporting Information

for

Nanoparticles based on the zwitterionic pillar[5]arene and Ag⁺: synthesis, self-assembly and cytotoxicity in the human lung cancer cell line A549

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Additional experimental parameters and results

1. NMR, MALDI TOF MS, ESI MS, IR spectra of compounds 2-4.....	S2
2. UV spectra.....	S8
3. Dynamic light scattering.....	S8
4. TEM images.....	S10
5. The 2D ^1H - ^1H NOESY, ROESY NMR spectra.....	S13
6. Diffusion experiments.	S15

1. NMR, MALDI TOF MS, ESI MS, IR spectra of compounds 2–4.

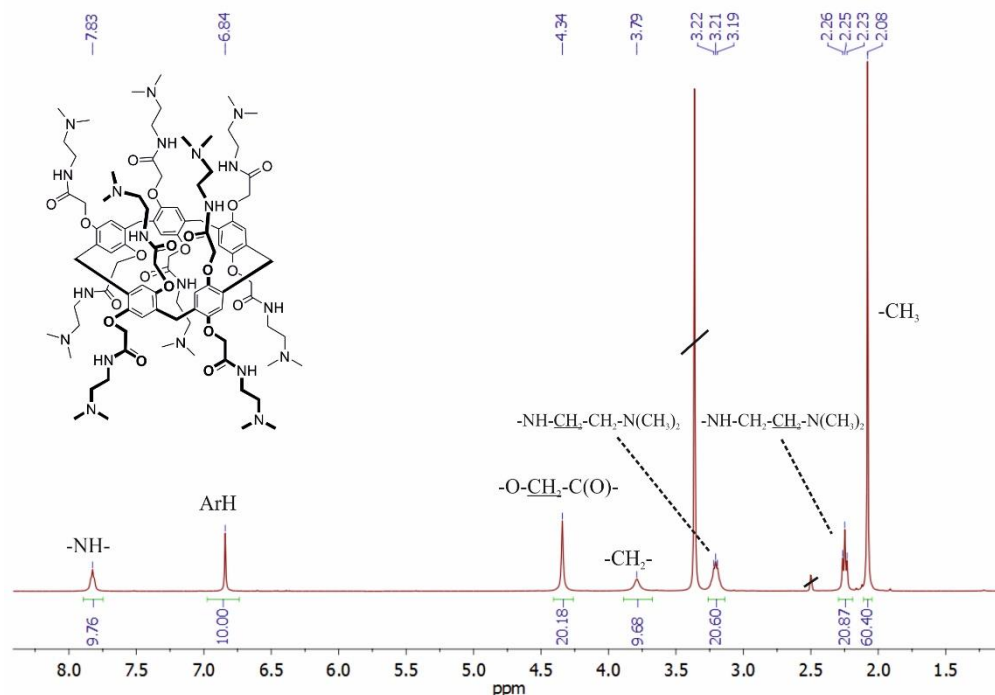


Figure S1: ^1H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethylaminoethyl)carbamoylmethoxy]pillar[5]arene (**2**), $\text{DMSO}-d_6$, 298 K, 400 MHz.

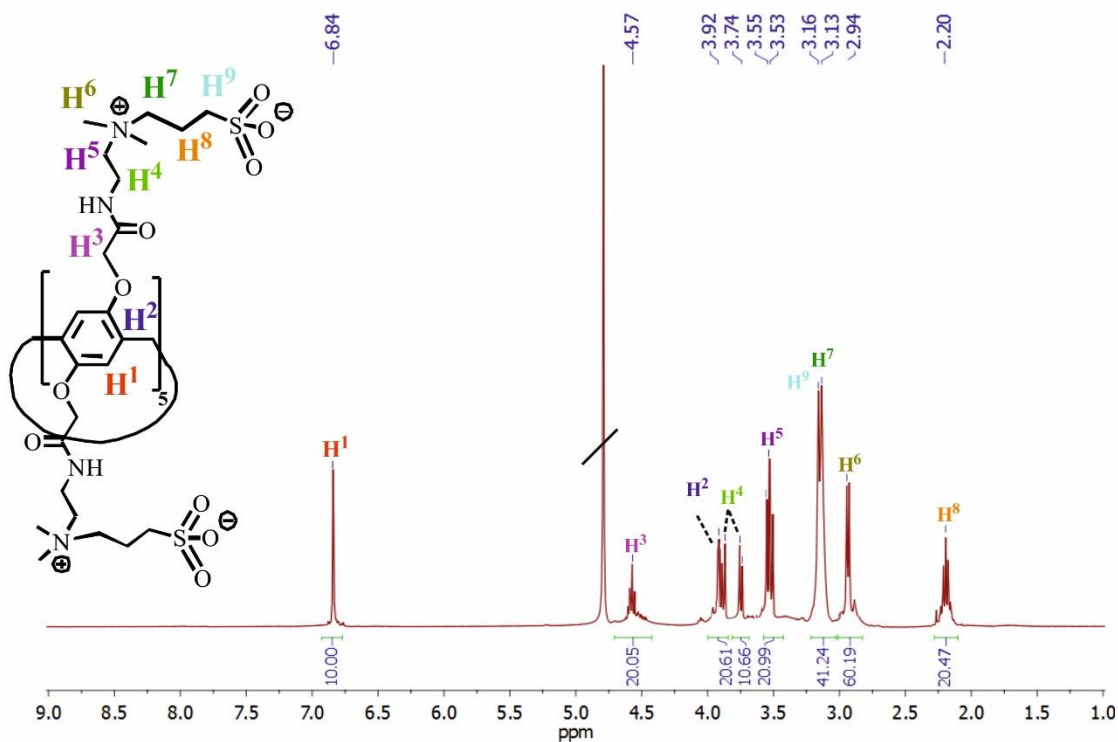


Figure S2: ^1H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca-[*N*-(2',2'-dimethyl-2'-(3''-sulfonatopropyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**3**), D_2O , 298 K, 400 MHz.

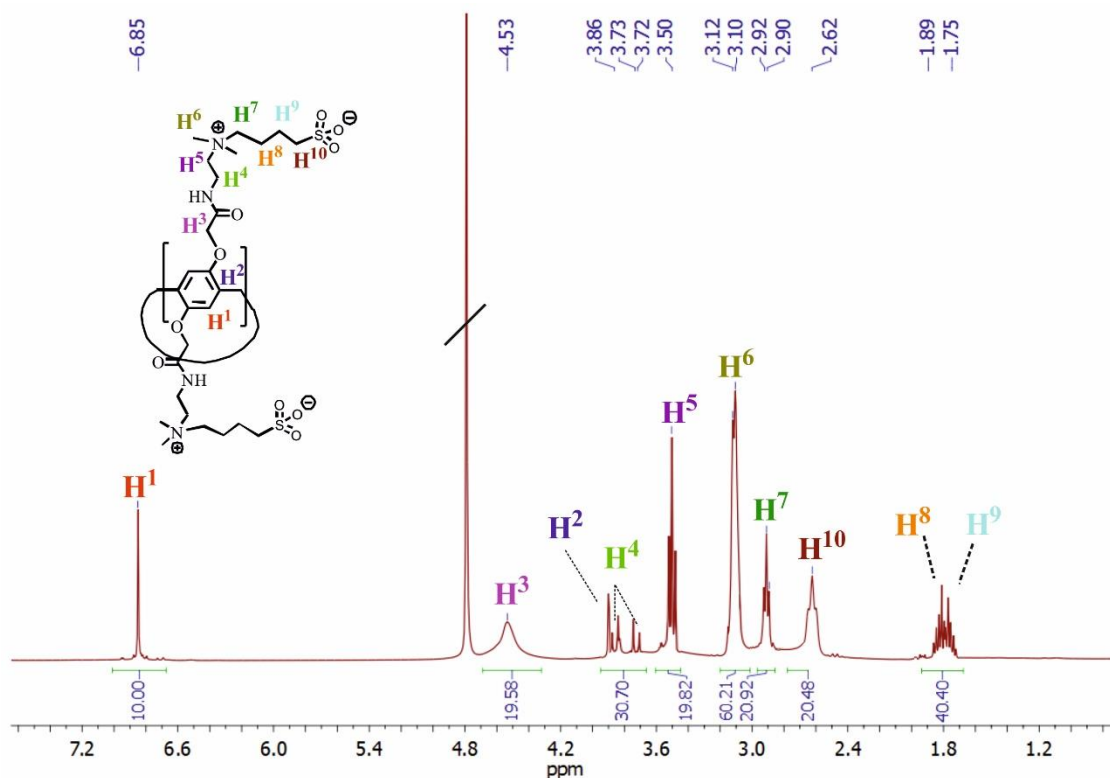


Figure S3: ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(4''-sulfonatobutyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**4**), D₂O, 298 K, 400 MHz.

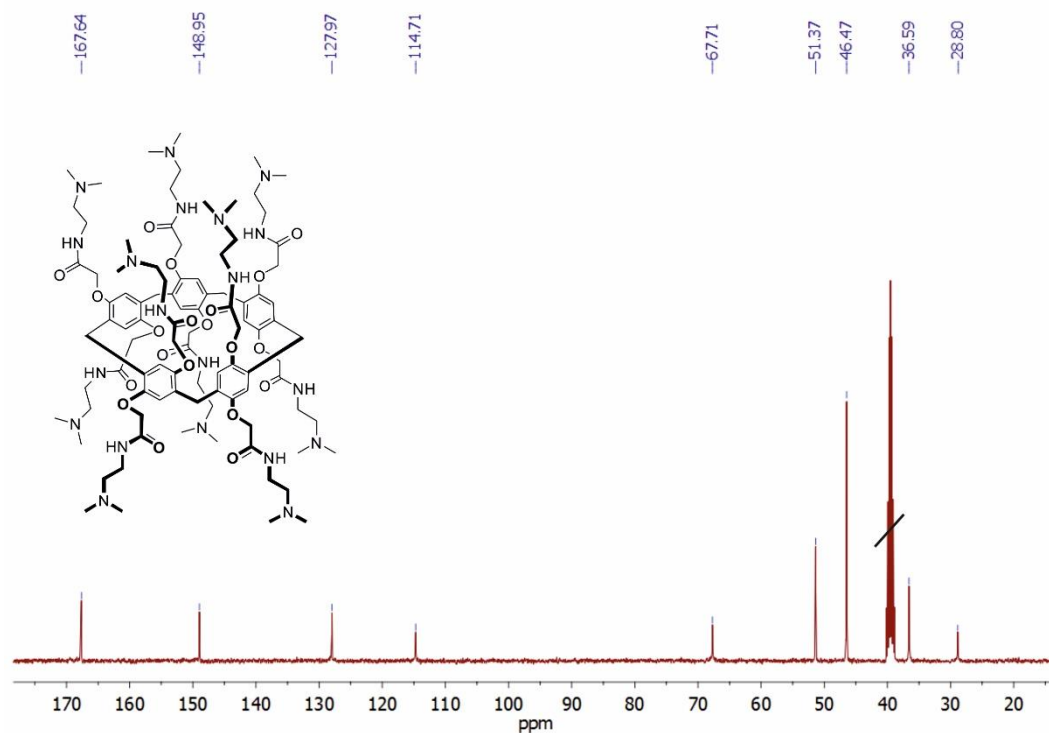


Figure S4: ¹³C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethylaminoethyl)carbamoylmethoxy]pillar[5]arene (**2**), DMSO-*d*₆, 298 K, 100 MHz.

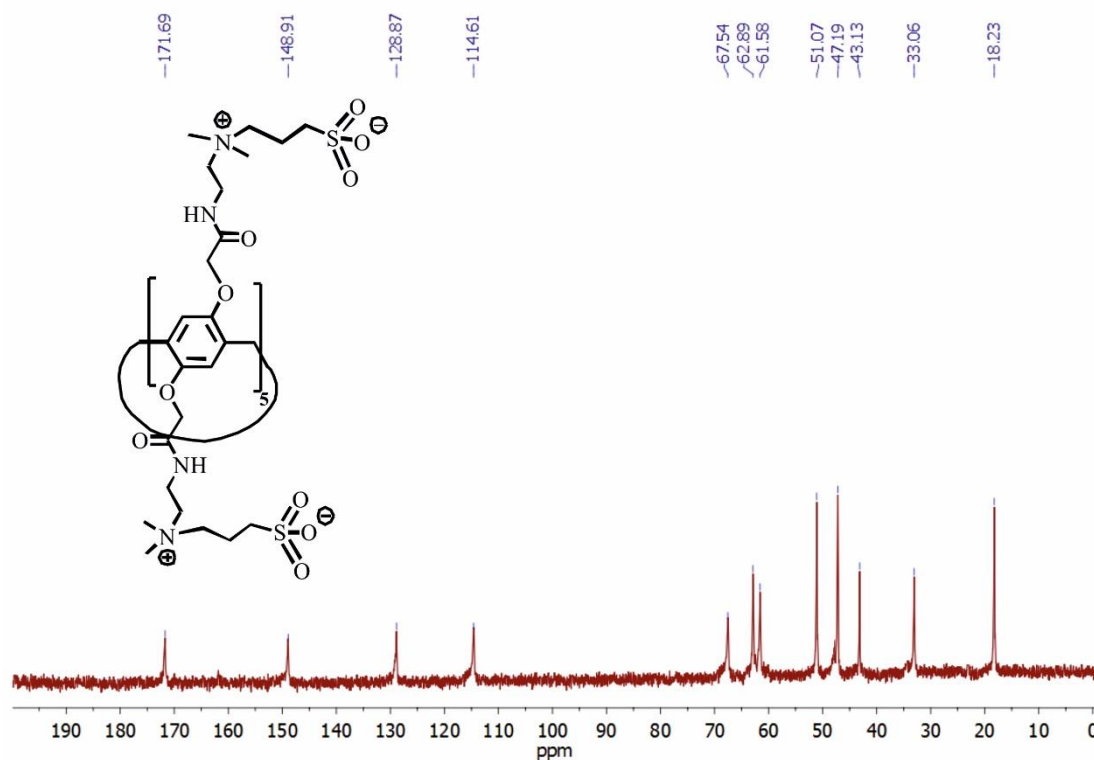


Figure S5: ^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(3''-sulfonatopropyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**3**), D_2O , 298 K, 100 MHz.

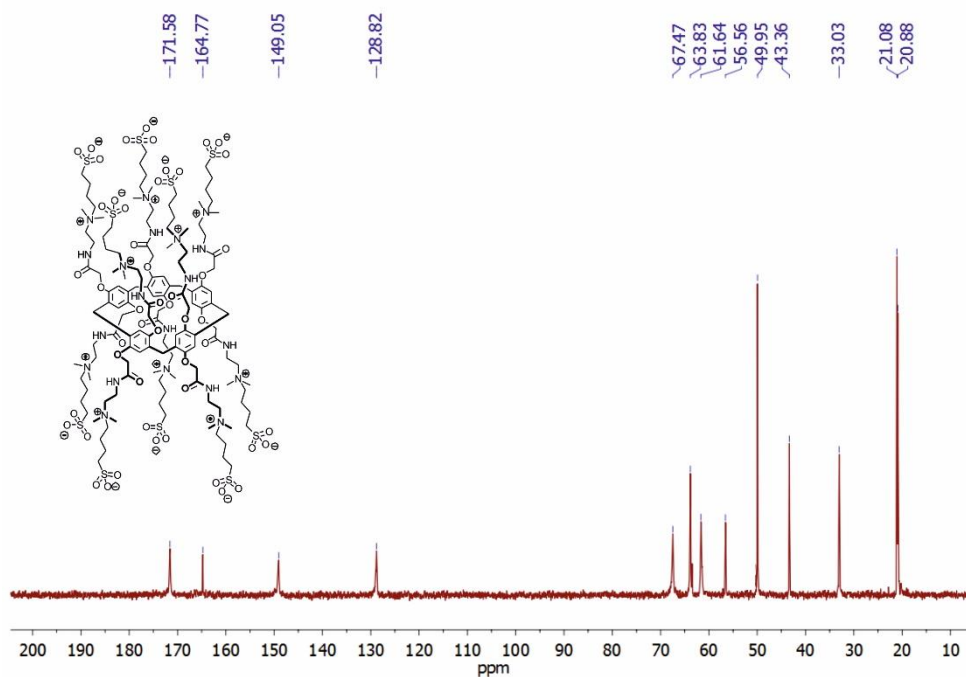


Figure S6: ^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(4''-sulfonatobutyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**4**), D_2O , 298 K, 100 MHz.

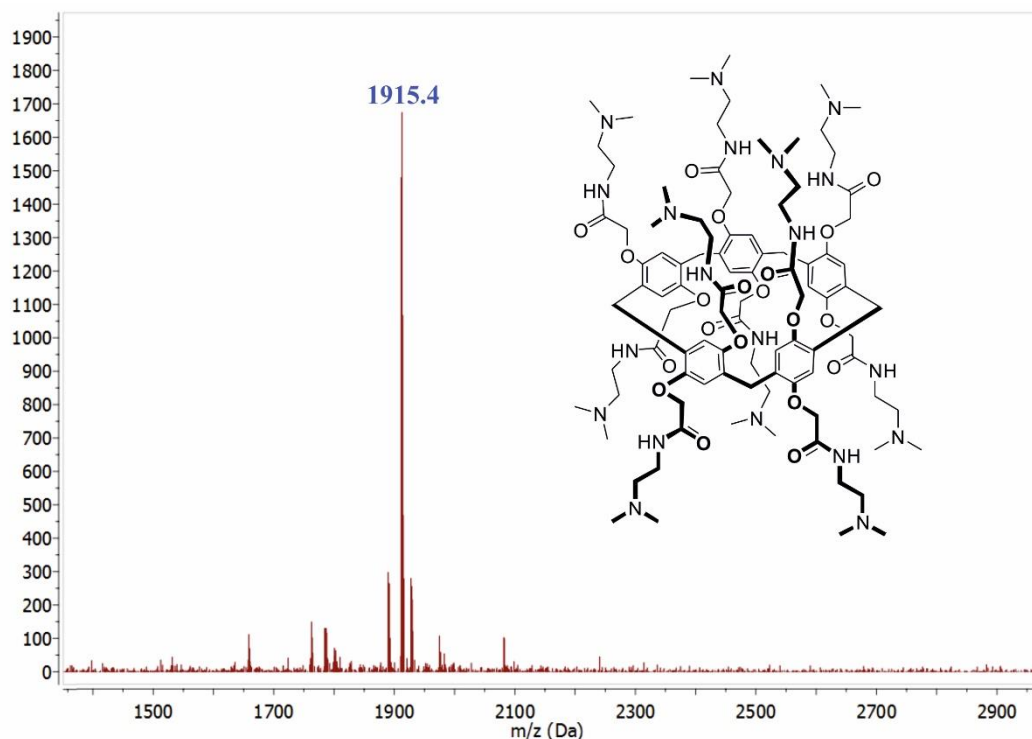


Figure S7: Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethylaminoethyl)carbamoylmethoxy]pillar[5]arene (**2**).

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	UltraScan	Scan Begin	70 m/z	Scan End	2700 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	73.0
Accumulation Time	486 μ s	Averages	5 Spectra	Auto MS/MS	off

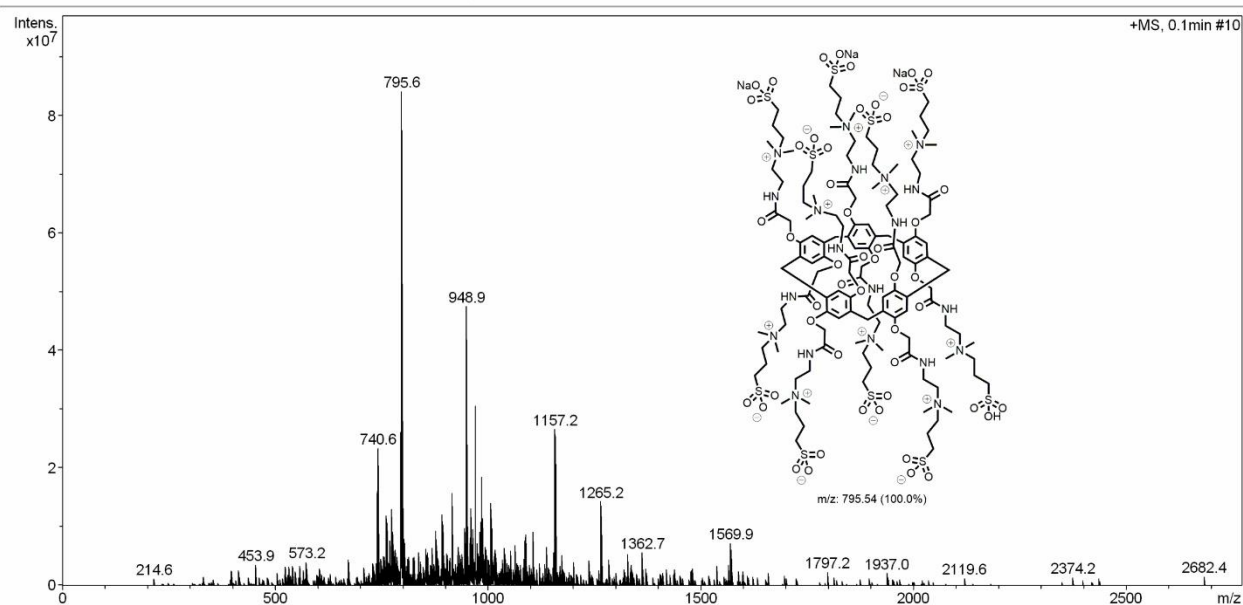


Figure S8: Mass spectrum (ESI) of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(3''-sulfonatopropyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**3**).

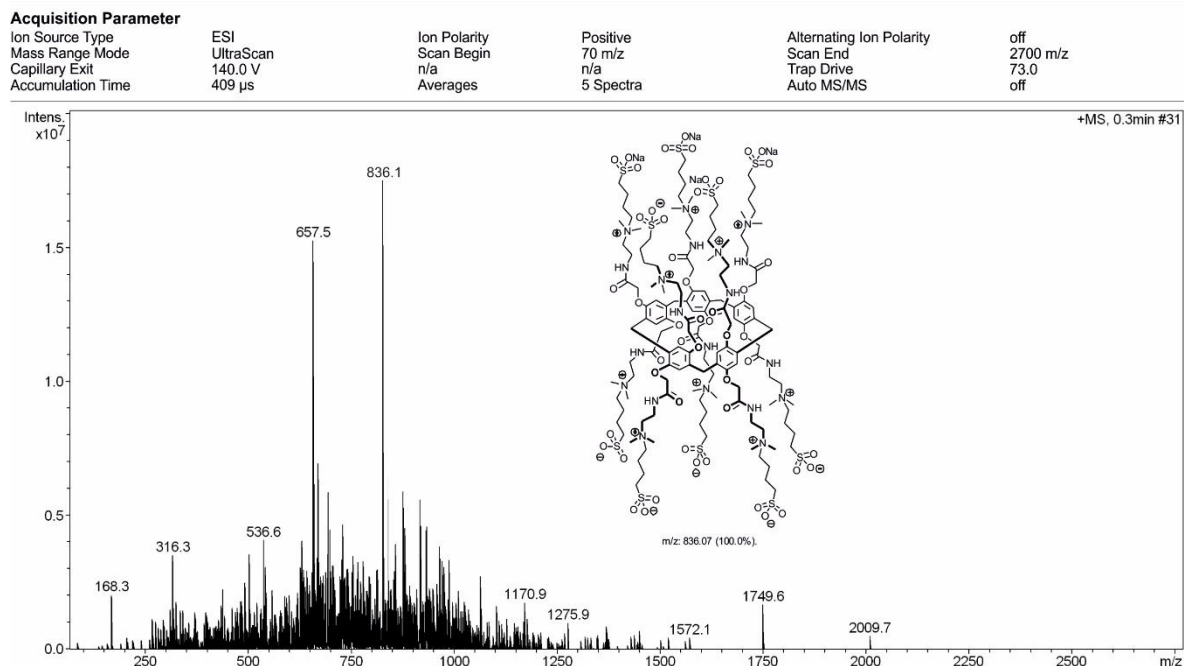


Figure S9: Mass spectrum (ESI) of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(4''-sulfonatobutyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (**4**).

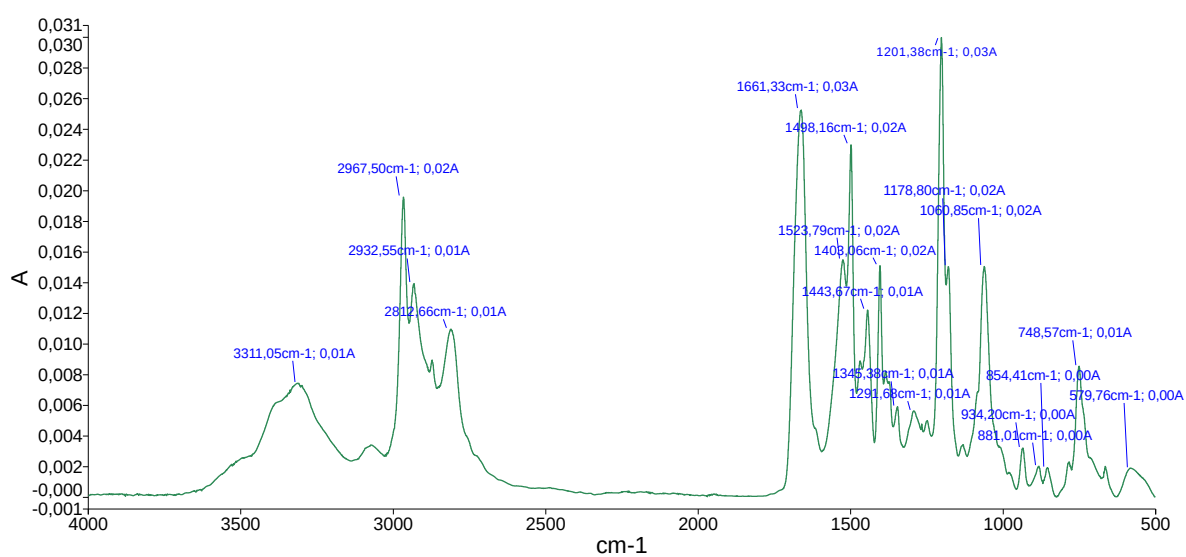


Figure S10: IR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethylaminoethyl)-carbamoylmethoxy]pillar[5]arene (**2**).

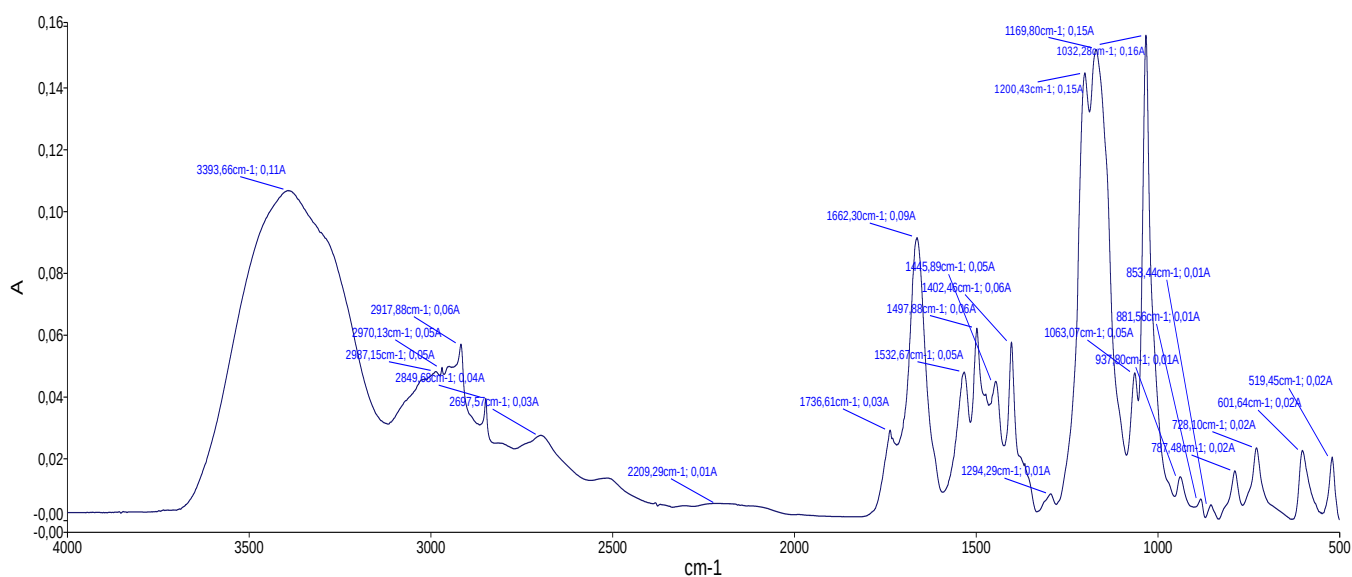


Figure S11: IR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(3"-sulfonatopropyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (3).

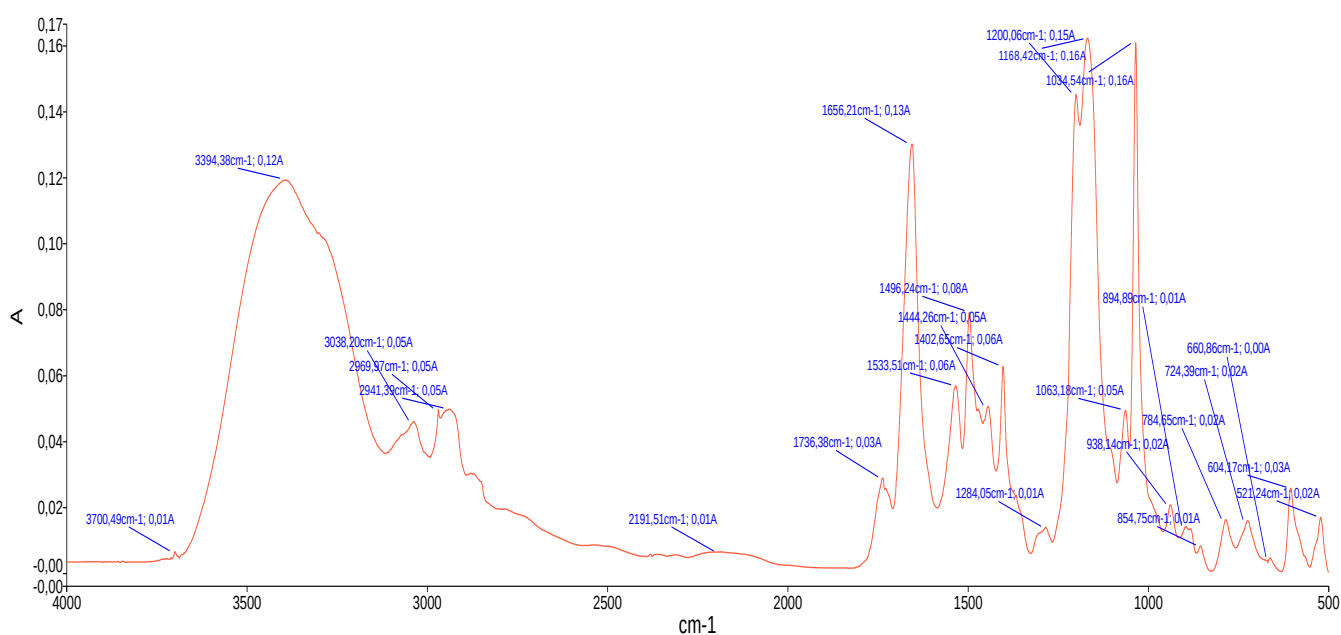


Figure S12: IR spectrum of 4,8,14,18,23,26,28,31,32,35-deca[*N*-(2',2'-dimethyl-2'-(4"-sulfonatobutyl)ammoniummethyl)carbamoylmethoxy]pillar[5]arene (4).

2. UV spectra.

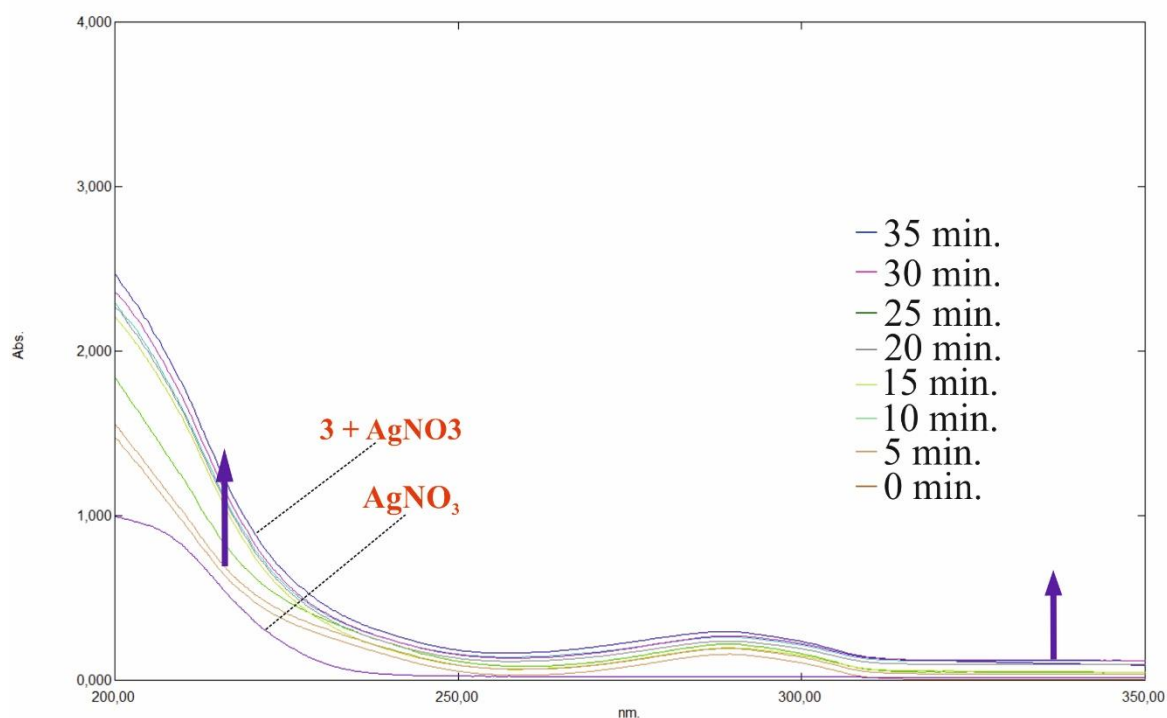


Figure S13: UV-vis spectra of pillar[5]arene **3** (10^{-5} M) with AgNO_3 (10^{-4} M) in water with the time interval 0–35 min.

3. Dynamic light scattering.

Table S1. The average hydrodynamic diameter and polydispersity index (PDI) of associates **3**/ Ag^+ in various ratios.

Ratio of reagents Concentration	Size of associate 3 / Ag^+ , nm (PDI)				
	2:1	1:1	1:5	1:10	1:15
10^{-3}	294.0±32.2 (0.51)	105.9±4.7 (0.34)	116.7±5.3 (0.41)	75.4±0.9 (0.13)	142.2±7.9 (0.22)
10^{-4}	111.5±3.2 (0.23)	151.5±3.2 (0.22)	160.7±3.1 (0.17)	122.12±0.001 (0.041)	675.5±195.3 (0.79)
10^{-5}	115.9±5.1 (0.36)	155.6±2.7 (0.24)	101.9±0.7 (0.12)	142.7±3.4 (0.22)	630.2±152.2 (1)

Table S2. The average hydrodynamic diameter and polydispersity index (PDI) of associates **4**/ Ag^+ in various ratios.

Ratio of reagents Concentration	Size of associate 4 / Ag^+ , nm (PDI)				
	2:1	1:1	1:5	1:10	1:15
10^{-3}	60.4±2.1 (0.40)	82.7±4.3 (0.45)	108.3±4.2 (0.34)	78.7±2.4 (0.31)	75.0±5.3 (0.48)
10^{-4}	83.9±25.3 (0.50)	287.5±30.8 (0.52)	203.8±38.8 (0.38)	246.6±45.32 (0.65)	244.2±89.3 (0.57)
10^{-5}	>800 (1)	>800 (1)	321.1±93.4 (0.49)	>800 (1)	773.2±112.2 (0.88)

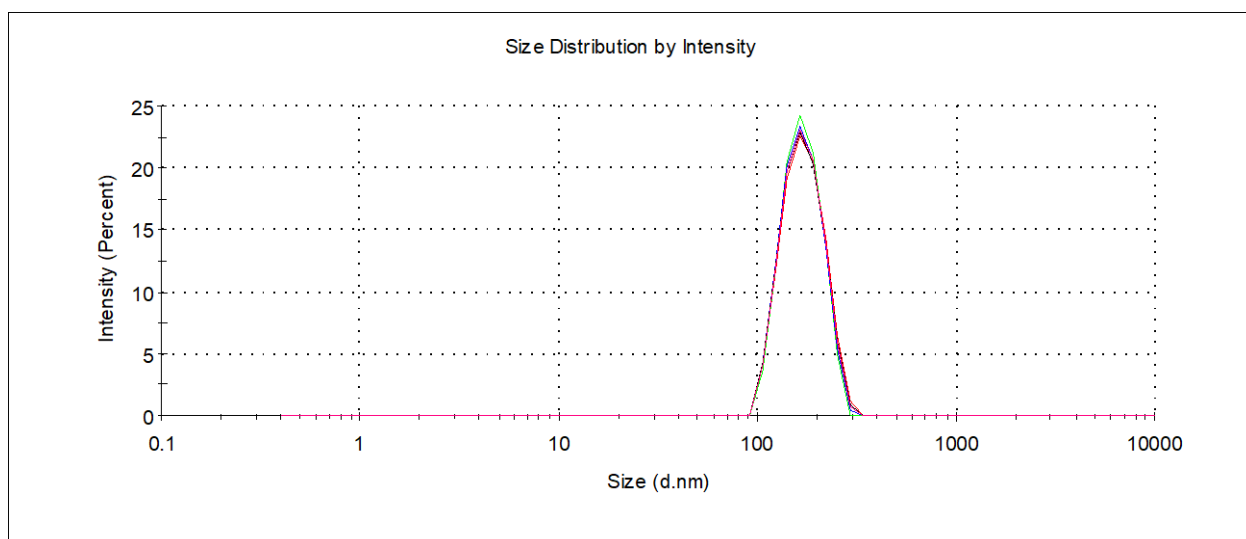


Figure S14: Size distribution of the particles by intensity for **3**/ Ag^+ ($c(\mathbf{3}) = 10^{-4}$ M, $c(\text{AgNO}_3) = 10^{-3}$ M, 1:10) in water.

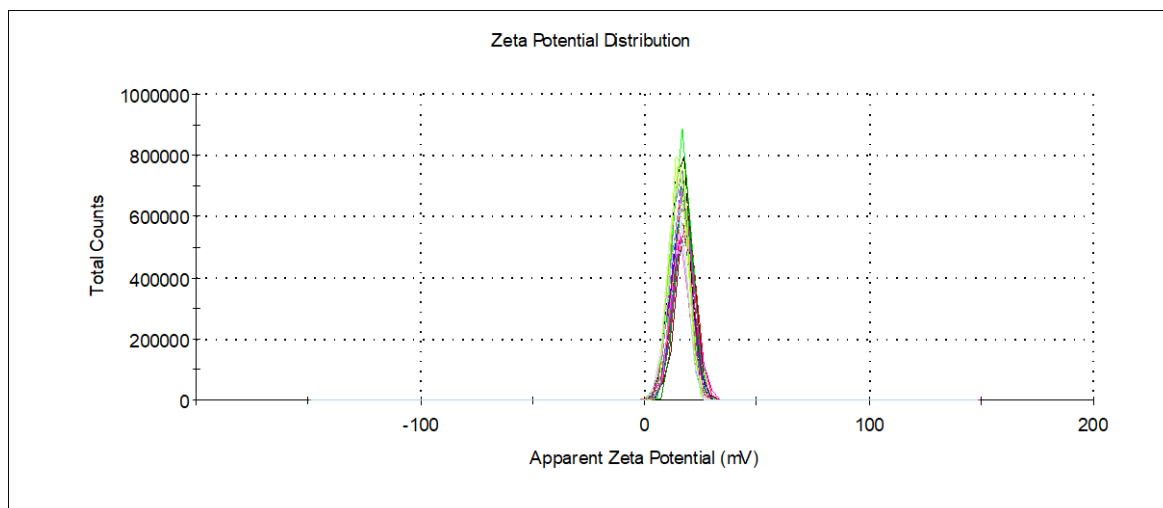


Figure S15: ζ -potential of the system $3/\text{Ag}^+ = 1:10$ ($c(3) = 10^{-4}$ M, $c(\text{AgNO}_3) = 10^{-3}$ M) in water.

4. TEM images.

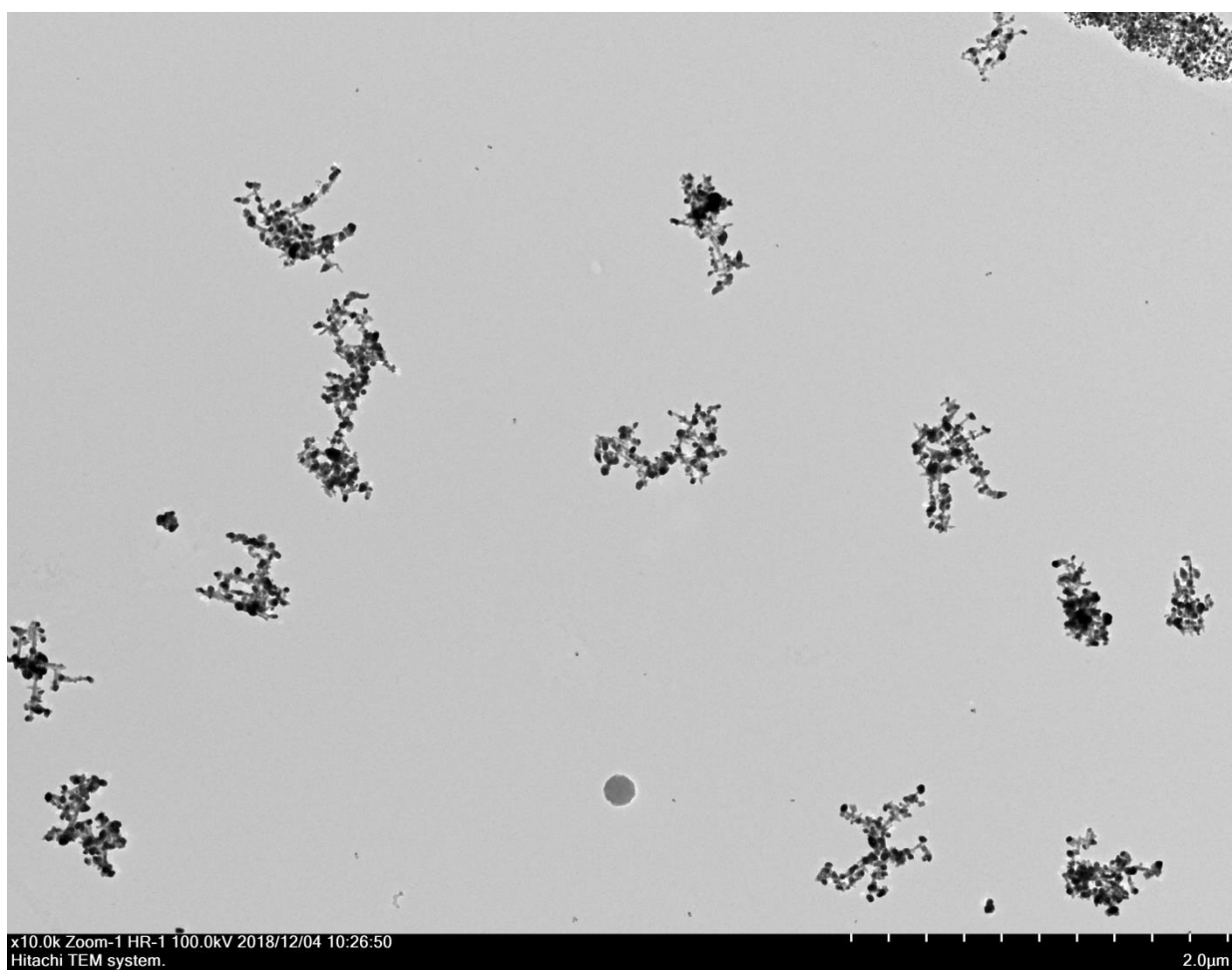


Figure S16: TEM images of pillar[5]arene $3/\text{Ag}^+ = 1:1$ associates in water (1×10^{-4} M).

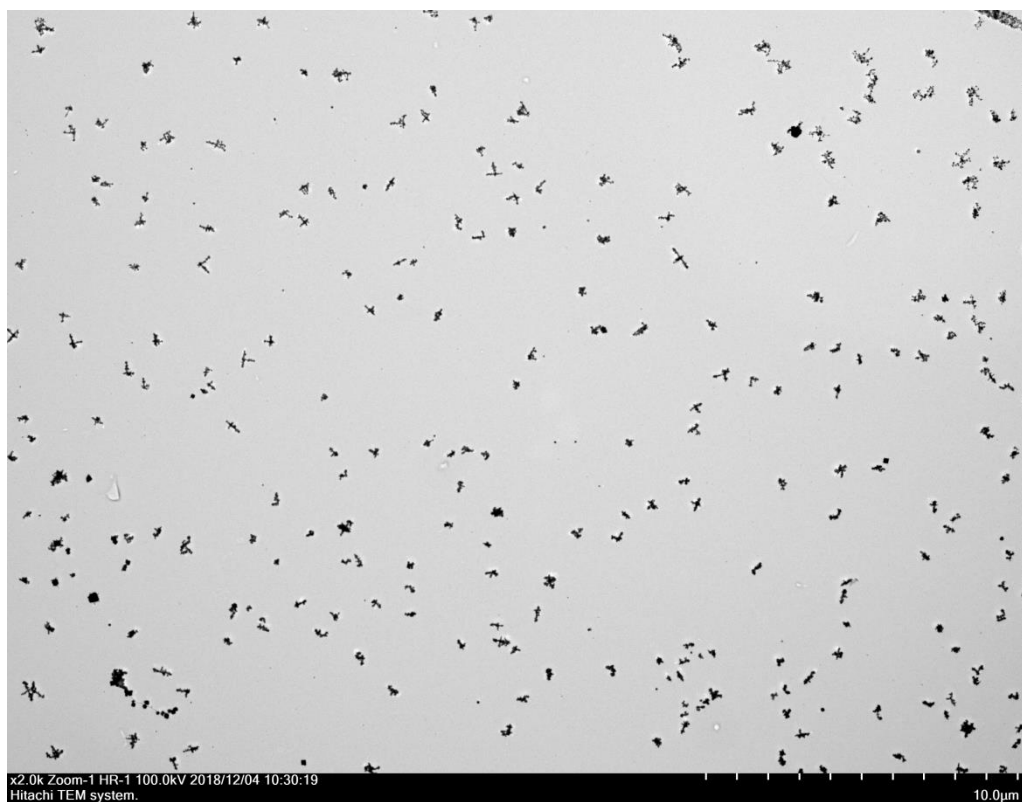


Figure S17: TEM images of pillar[5]arene 3/Ag⁺ = 1:1 associates in water (1×10^{-4} M).

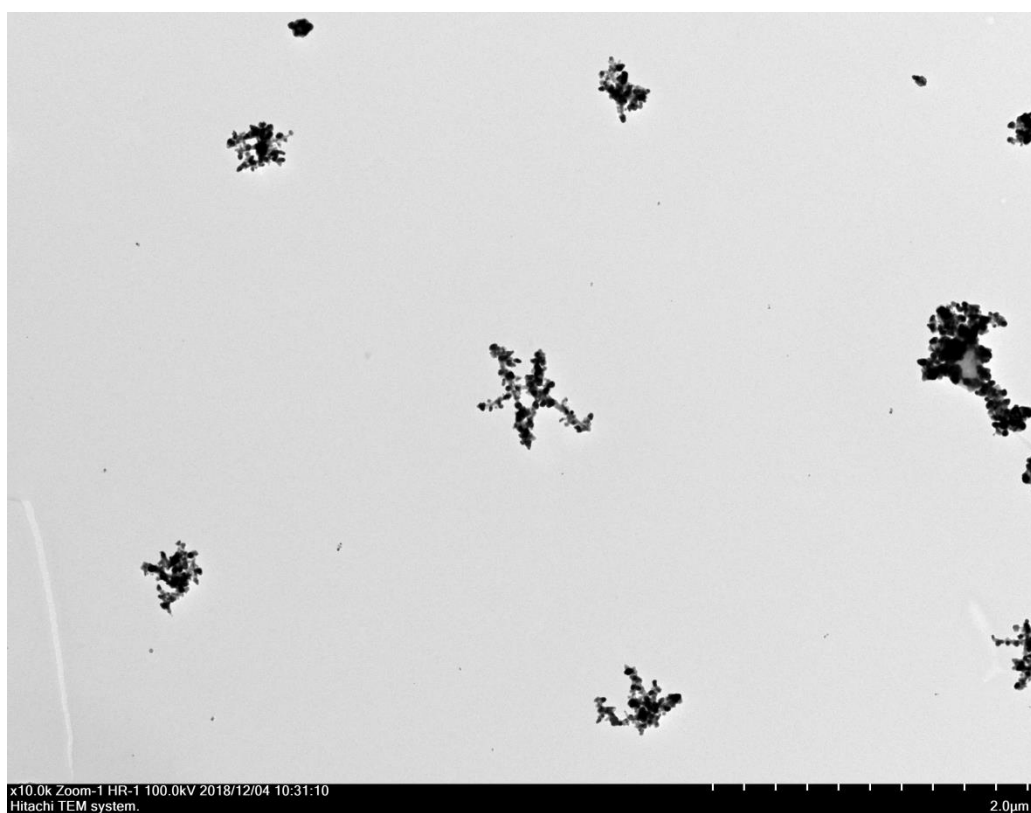


Figure S18: TEM images of pillar[5]arene 3/Ag⁺ = 1:1 associates in water (1×10^{-4} M).

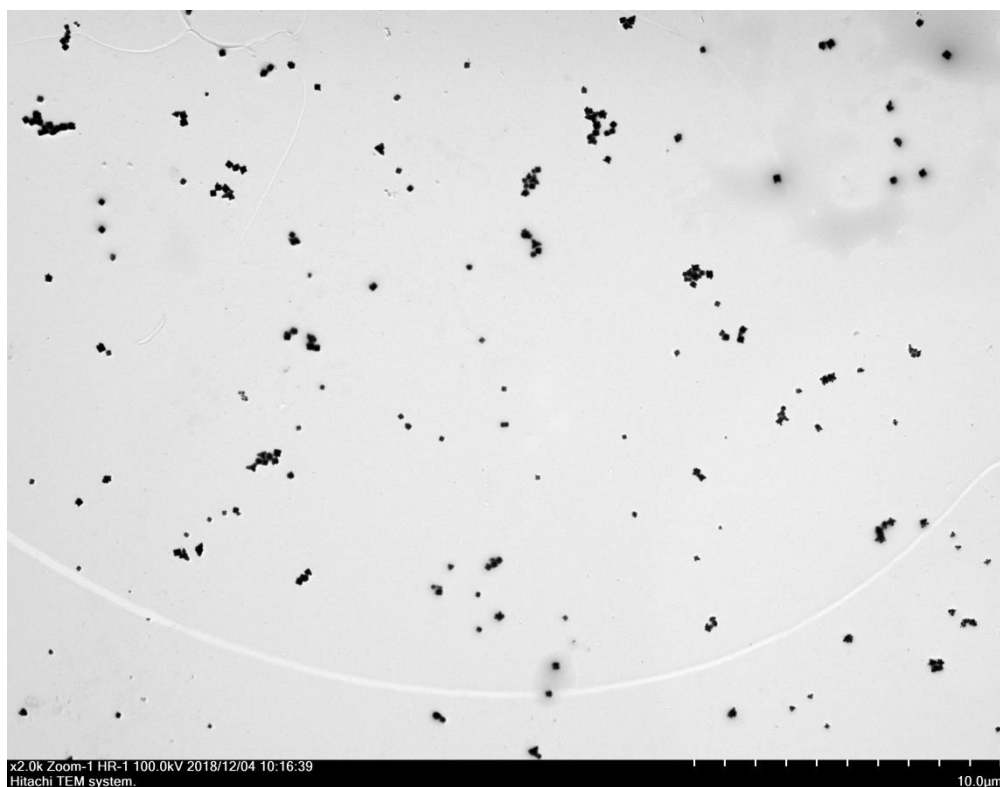


Figure S19: TEM images of pillar[5]arene **3**/Ag⁺ = 1:10 associates in water ($c(\mathbf{3}) = 10^{-4}$ M, $c(\text{AgNO}_3) = 10^{-3}$ M).

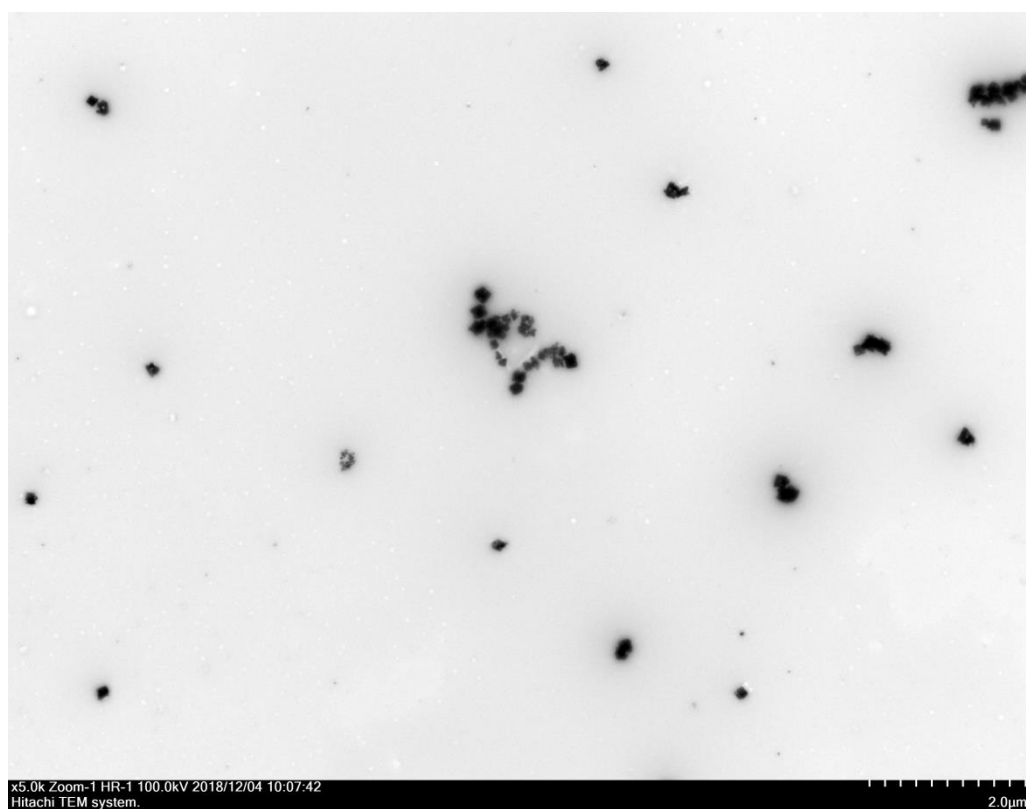


Figure S20: TEM images of pillar[5]arene **3**/Ag⁺ = 1:10 associates in water ($c(\mathbf{3}) = 10^{-4}$ M, $c(\text{AgNO}_3) = 10^{-3}$ M).

5. The 2D ^1H - ^1H NOESY, ROESY NMR spectra.

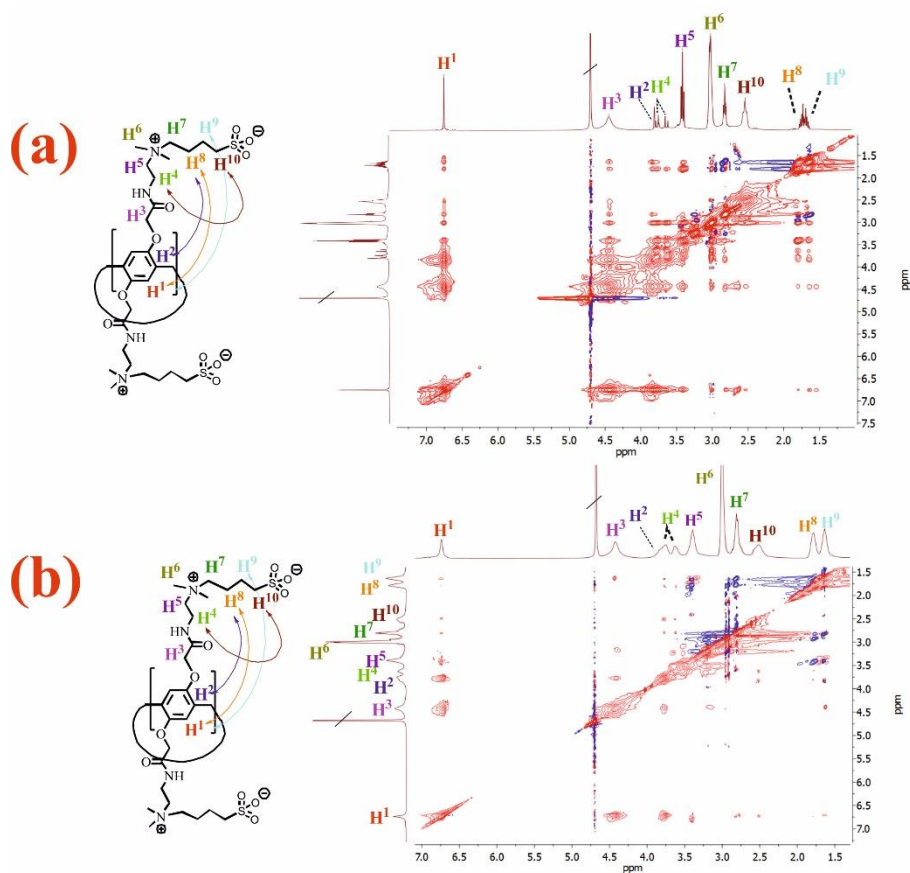


Figure S21: (a) macrocycle 4 (10^{-3} M), (b) associate 4/ Ag^+ (1:10) in D_2O at 25 °C.

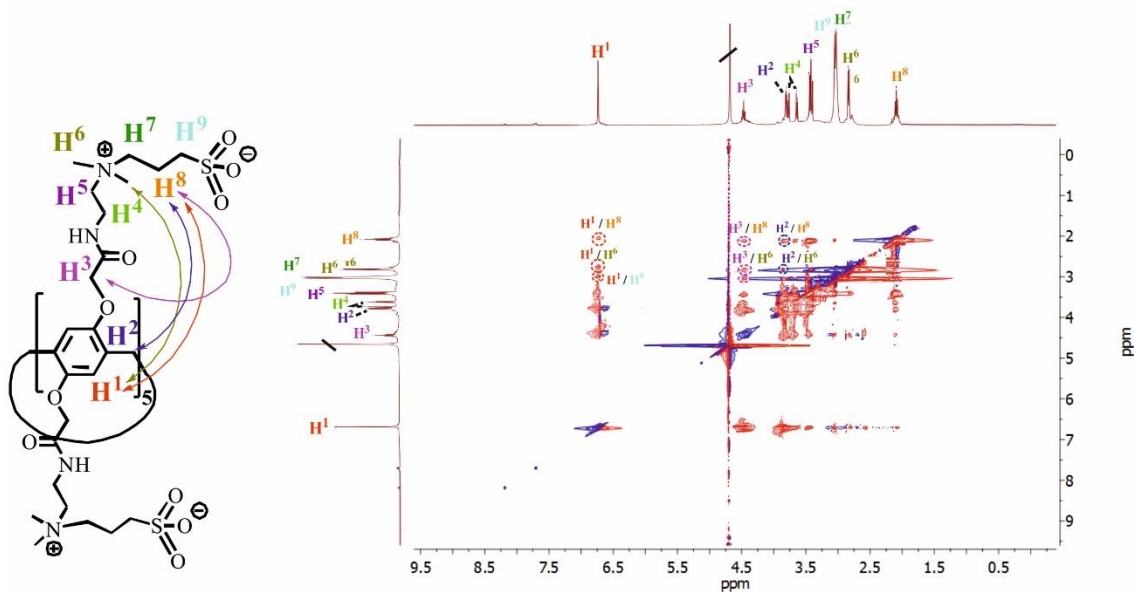


Figure S22: The 2D ^1H - ^1H ROESY NMR spectra of macrocycle 3 in D_2O at 25 °C.

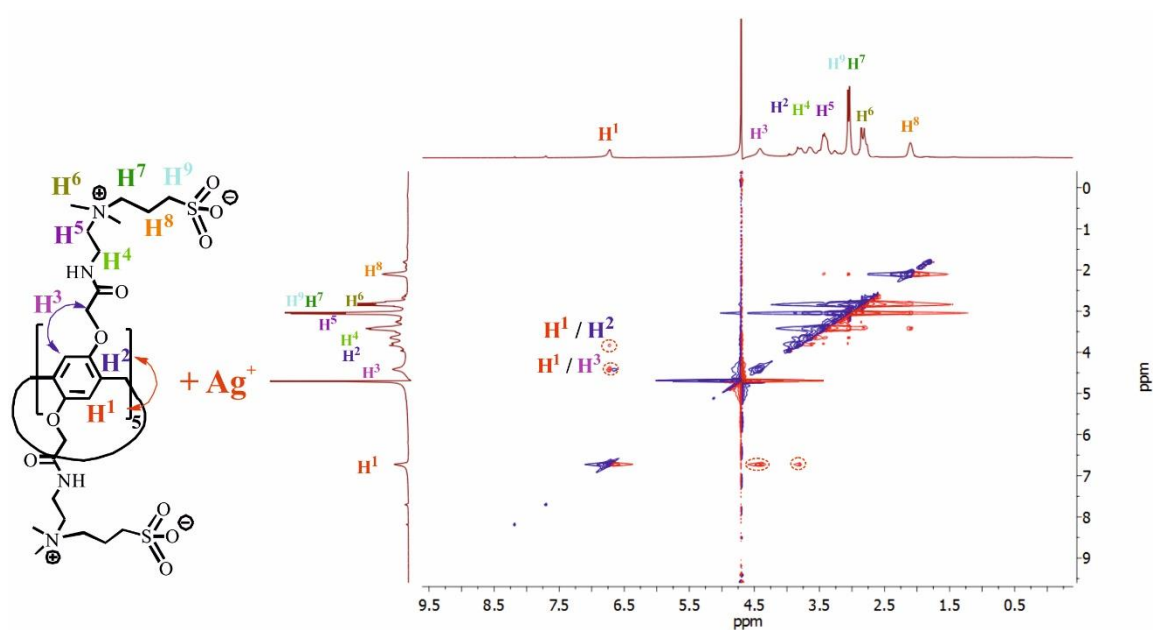


Figure S23: The 2D ^1H - ^1H ROESY NMR spectra of associate **3**/ Ag^+ (1:10) in D_2O at 25 $^\circ\text{C}$.

6. Diffusion experiments.

Table S3. Diffusion coefficients of pure **3** and **3**/Ag⁺ complex in D₂O (400 MHz, 298 K).

C(Ag ⁺)/ C(3)	0	0.5	1	2	3	5	7	10
D, 10 ⁻¹⁰ m ² s ⁻¹	4.22	3.75	3.19	3.21	3.23	3.25	3.31	3.40
r, nm	0.45	0.6	0.91	0.82	0.80	0.79	0.75	0.70

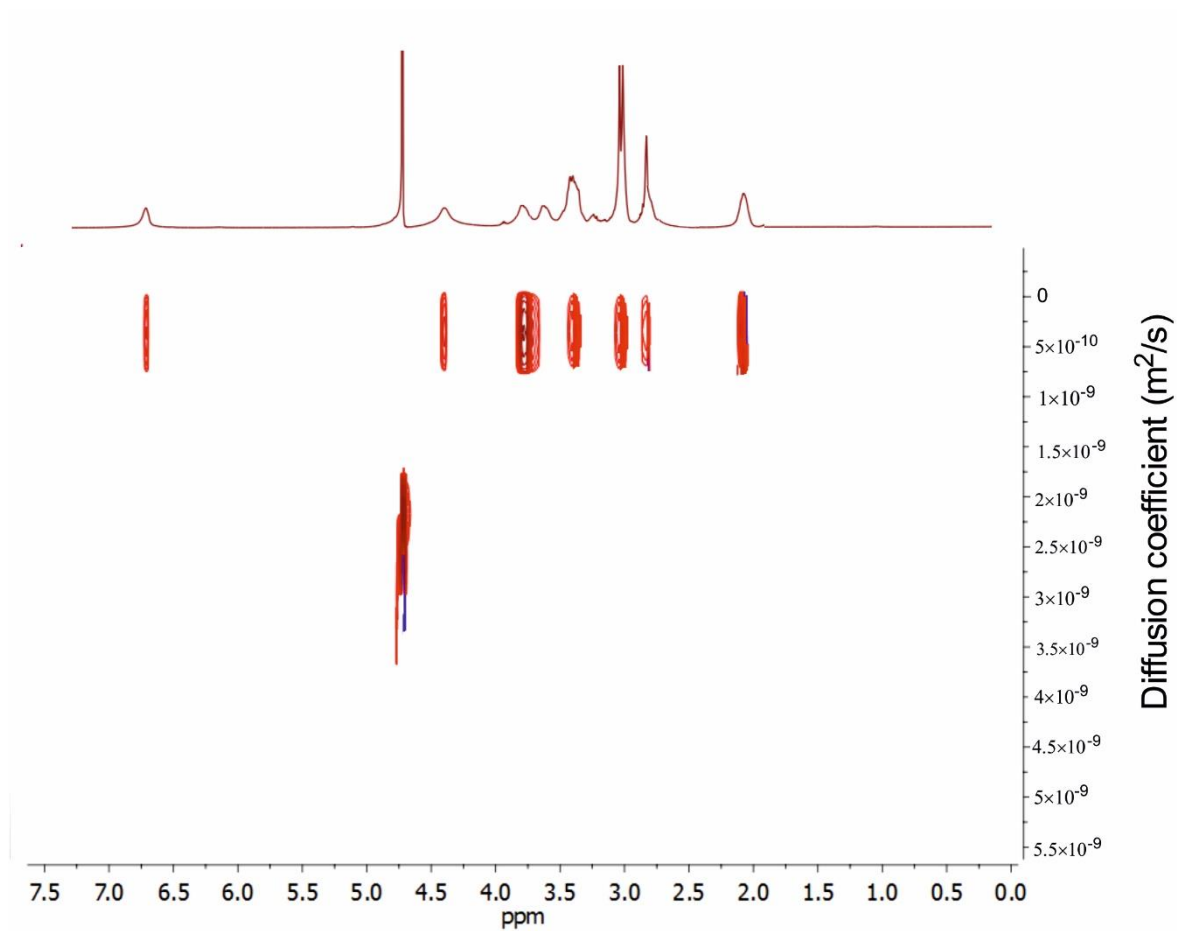


Figure S24: The DOSY spectrum **3**/Ag⁺ complex in D₂O (400 MHz, 298 K).