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Supporting Information

Colourimetric and Spectroscopic discrimination between nucleotides and nucleosides using para-sulphonato-calix[4]arene capped silver nanoparticles

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Experimental details:

Synthesis of *para*-sulphonatocalix[4]arene

The synthesis of *para*-sulphonatocalix[4]arene was carried out according to the method described in Coleman [1].

para-sulphonatocalix[4]arene analysis

Yield 85%
Purity>95%

^{1}H NMR (500 MHz, [d6]DMSO, tetramethylsilane): δ=3.72–3.94 (-CH2-), 7.14–7.36 (Ar-H);
MALDI-TOF-MS: m/z $[M+H]^+$ calculed for (C28H24O16S4+H): 744,8, found: 745,8;

Synthesis of *para*-sulphonatocalix[4]arene modified silver nanoparticles

The procedure of Xiong [2] was slightly modified as follows. 10 mL of 10^{-2} M $AgNO_3$ solution was added to 80 mL of deionized water. To this solution, 10 mL of 10^{-2} M *para*-sulphonatocalix[4]arene aqueous solution was added as stabilizer with stirring for 30 min. And then, 44 mg of $NaBH_4$ was added to the solution. The silver colloidal suspensions were obtained after 5 minutes. Hence a final concentration of 10^{-3}M in silver.

Calculation of the concentration in solution of silver nanoparticles :

We used 10mL of a solution at 1.10^{-2}M of silver nitrate. This corresponds to $1\text{x}10^{-4}$ moles, and so $6.02\text{x}10^{19}$ atoms.

A nanoparticle with 20nm of diameter (volume= $4.18\text{x}10^{-24}m^3$) can contain 700 000 silver atoms (volume= $6.02\text{x}10^{-30}m^3$).

The solution at 1.10^{-2}M of silver nitrate, once reduced, can produce $8.6\text{x}10^{13}$ nanoparticles.The solution is diluted to 100mL in order to obtain a final concentration of $8.6\text{x}10^{11}$ nanoparticles / mL.

Calculation of the number of *para*-sulphonato-calix[4]arene (SC4) complexed per nanoparticle :

Assuming that the shape of a silver nanoparticle is a sphere, we can calculate the surface of the nanoparticle with a diameter of 20nm to $S = 1.25\text{x}10^{-15}$ m^2.

In the same way, it is possible to calculate the surface of a SC4, who possess a circular surface of a diamater of 1 nm, $S = 3.14\text{x}10^{-18}m^2$. Now, it is possible to correlate these data to

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see that we can deposit 400 SC4 / nanoparticles, if a bilayer this will be around 600 SC4/nanoparticles.

Calculation of the concentration of SC4 complexed with nanoparticles : For a solution concentrated to 8.6×10^{11} nanoparticles / mL, it equals to a solution concentrated to 3.4×10^{14} SC4 / mL or 5.7×10^{-10}moles / mL or 5.7×10^{-7}M.The above numbers must be treated as highly approximate with variance of at 25%.

UV-Visible Absorption assays

The mixture experiments were conducted by monitoring the change in absorbance between 340 nm and 650 nm, using a 96 well titre visible spectrometer, (BioTek Power Wave 340). To 20µL of a solution of *para*-sulphonatocalix[4]arene modified silver nanoparticles at 10^{-3} M was added 20µL of a solution of the nucleotides or nucleosides at 10^{-2}M and the whole diluted to 200µL in the titre plate wells. This gives a molar ration of 1000 nucleotids/nucleosides per complexed *para*-sulphonatocalix[4]arene.

TEM Imaging:

The TEM sample was prepared by dropping 6 µL of the sample solution on carbon coated grid (50 mesh, Ted Pella). After 30 seconds, the sample was wicked from the grid by touching its edge with a piece of filter paper. TEM studies were conducted by using a Topcon EM 002B microscope, operating with an accelerating voltage of 200 kV.

References and Note

[1] Anthony W. Coleman, Said Jebors, Sebastien Cecillon, Pascale Perret, Dominique Garin, Danièle Marti-Battle and Marcelle Moulin, Toxicity and Bio-distribution of *para*-Sulphonato-calix[4]arene in Mice, New J Chem, (2008), **32**, 780-2

[2] D. Xiong, M. Chen and H. Li, *Chem. Commun.*, 2008, **7**, 880-882;

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Supporting Figures:

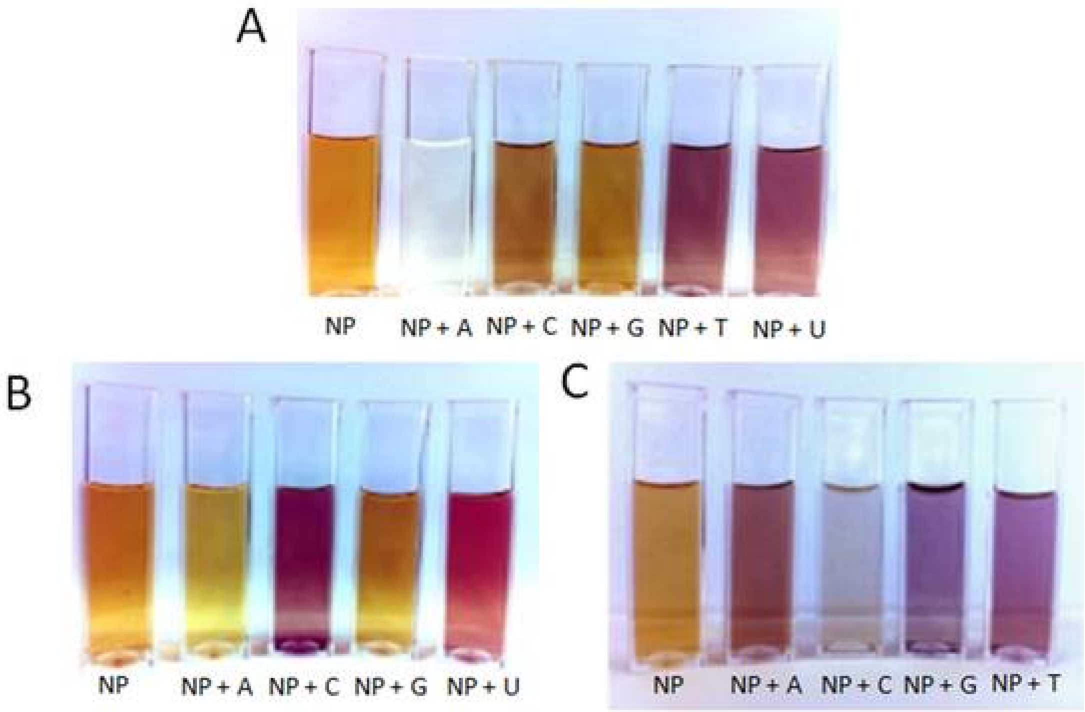

Fig. S1 Photographs of the complexation of A) nucleotides B) nucleosides and C) deoxy-nucleosides bases with SC4:Ag NPs after 24 hours at a final concentration of 10-3M.

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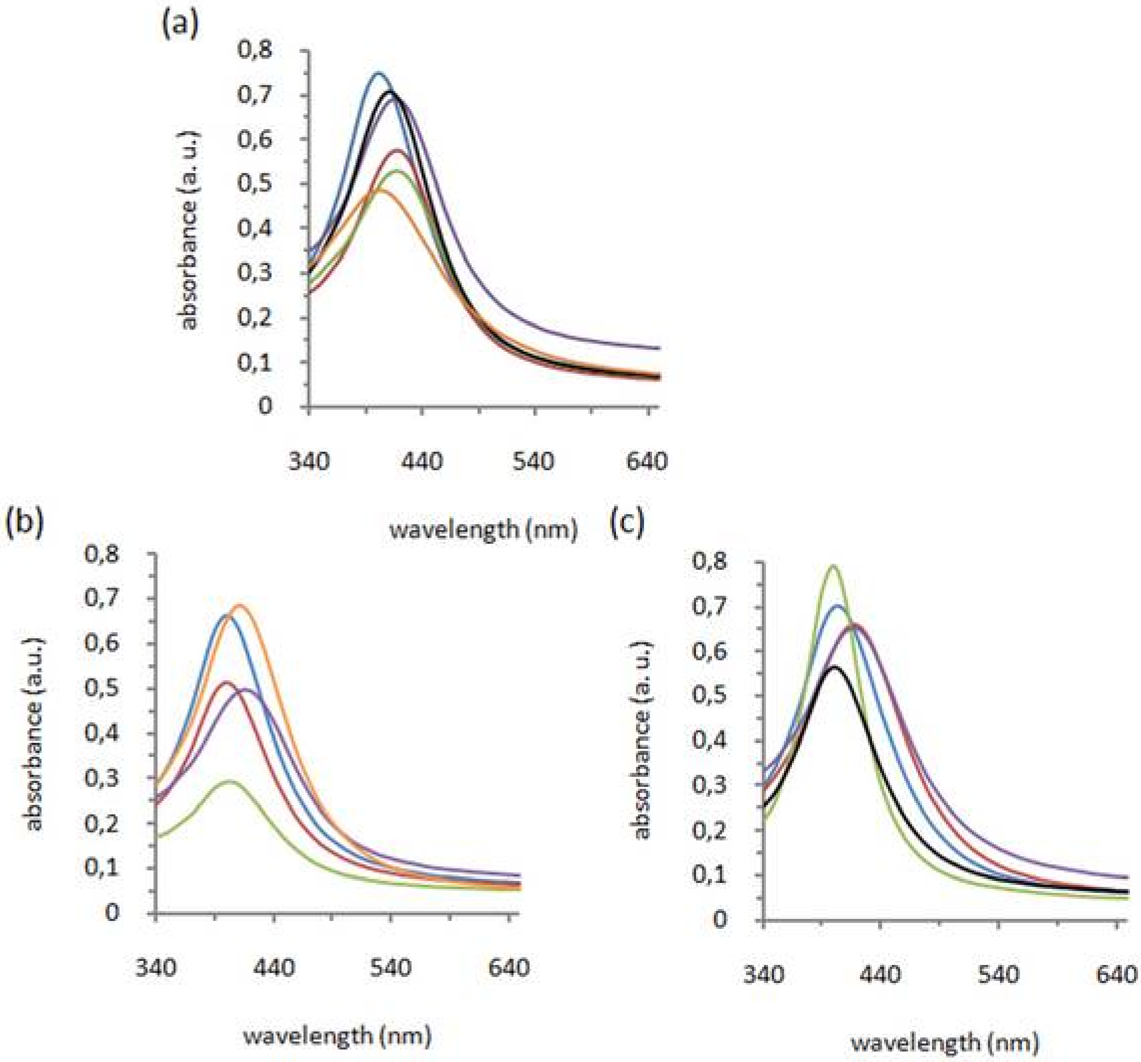

Fig. S2 Visible spectra of the complexation of a) nucleotides, b) nucleosides and c) deoxy-nucleosides bases with SC6:Ag NPs after one hour at a final concentration of 10-3M. Blue line: pSC6:Ag NP; Red line: pSC6-Ag NP + A; Purple line: pSC6-Ag NP + G; Green line: pSC6-Ag NP + C; Orange line: pSC6-Ag NP + U; Black line: pSC6- Ag NP + T.

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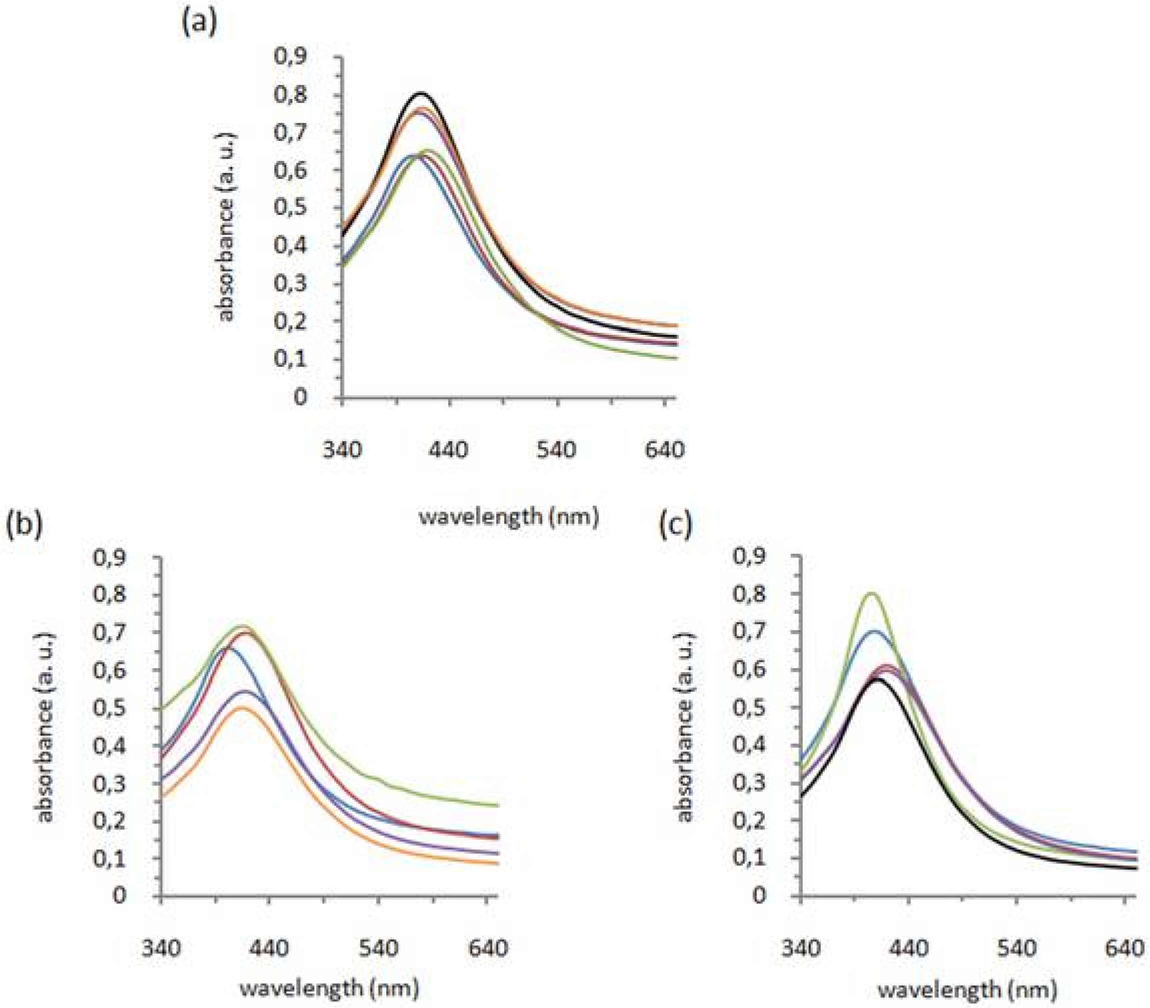

Fig. S3 Visible spectra of the complexation of a) nucleotides, b) nucleosides and c) deoxy-nucleosides bases with SC8:Ag NPs after one hour at a final concentration of 10-3M. Blue line: pSC8:Ag NP; Red line: pSC8-Ag NP + A; Purple line: pSC8-Ag NP + G; Green line: pSC8-Ag NP + C; Orange line: pSC8-Ag NP + U; Black line: pSC8- Ag NP + T.

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Table S1 Summary of the wavelength absorption of SC4:Ag NPs solution mixed one hour with each type of base

Entry	λ 1[a] (nm)	λ 2[b] (nm)	λ 3[c] (nm)	Base class
NP alone	---	390	440	
NP + adenosine	360	400	450	Nucleosides
NP + cytidine	360	400	490	
NP + guanosine	360	400	450	
NP + uridine	---	400	450	
NP + adenosine	360	400	460	Deoxy Nucleosides
NP + cytidine	360	400	---	
NP + guanosine	360	400	460	
NP + thymidine	360	400	490	
NP + adenine	360	400	520	Nucleotides
NP + cytosine	360	400	540	
NP + guanine	360	400	---	
NP + thymine	360	400	580	
NP + uracil	360	400	580	

[a] First wavelength absorption. [b] Second plasmon wavelenght absorption. [c] Thirst plasmon wavelenght absorption.

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Table S2 Summary of the wavelength absorption of SC4:Ag NPs solution mixed 24 hours with each type of base

Entry	λ 1[a] (nm)	λ 2[b] (nm)	λ 3[c] (nm)	Base class
NP	---	390	440	
NP + adenosine	360	400	520	Nucleosides
NP + cytidine	360	400	520	
NP + guanosine	360	400	520	
NP + uridine	360	400	470	
NP + adenosine	360	400	470	Deoxy Nucleosides
NP + cytidine	360	400	---	
NP + guanosine	360	400	500	
NP + thymidine	360	400	520	
NP + adenine	---	---	---	Nucleotides
NP + cytosine	360	400	540	
NP + guanine	360	400	540	
NP + thymine	360	400	580	
NP + uracil	360	400	590	

[a] First wavelength absorption. [b] Second Plasmon wavelenght absorption. [c] Thirst plasmon wavelenght absorption.