

Supporting information

Adenosine monophosphate-capped gold(I) nanoclusters: synthesis and lanthanide ion-induced enhancement of their luminescence

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Materials and Methods

Adenosine 5'-monophosphate disodium salt (AMP), tetrachloroauric acid (HAuCl_4), lanthanide chlorides, and HEPES were purchased from Sigma-Aldrich. The reagents were of analytical reagent grade and used as received. The reactions were carried out under inert atmosphere (N_2).

UV-vis absorption spectra were recorded on an Agilent 8453E spectrophotometer. All the data were acquired using 1cm×1cm path length quartz cuvettes.

Luminescence spectra were measured in an Aminco Bowman Series 2 Luminescence spectrophotometer, equipped with a lamp power supply and working at room temperature. The AB2 software (v.25 5.5) was used to register the data. The quantum yields were measured with a Hamamatsu C9920-02 absolute PL Quantum Yield Measurement System. Lifetime measurements were performed using a Quantaurus-Tau C11367 Compact fluorescence lifetime spectrometer.

Structural and morphological characterizations of Au@AMP/HEPES were performed using bright field transmission electron microscopy (TEM) JEOL JEM-1011 and high resolution TEM (HRTEM). A field emission gun (FEG) TECNAI G2 F20 microscope, operated at 200 kV, was used. Samples were deposited on carbon films 72 hours prior to measurement in each of the means of dispersion and dried in a vacuum. The diameter of the nanoparticles was determined by ImageJ, in nanometres. Statistical analysis was obtained by measuring the diameter value of 500 nanoparticles.

X-ray photoelectron spectroscopy (XPS, K-ALPHA, Thermo Scientific) was used to analyze the samples surface. All spectra were collected using Al-K_α radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot (elliptical in shape with a major axis length of 400μm) at 3 mA × 12 kV. The alpha hemispherical analyser was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50eV in a narrow scan to selectively measure the particular elements.

The ¹H-NMR spectra were registered at room temperature in a BrukerDPX400 spectrometer, with a 400 MHz Bruker magnet. The chemical shifts (δ) are reported in ppm using deuterium oxide, 99.9% atom (D_2O) as solvent. IR spectrum was recorded in solid on a Nicolet iS10 FT-IR spectrometer.

The thermogravimetry analysis was carried out using a Mettler 50 Toledo TGA 851e system with an operative temperature range of 25-1000 °C and 1 microgram sensitivity.

FTIR spectrometer Nicolet IS10 equipped with a Nicolet Smart Performer SR-ATR attachment, enabling easy measurement of the spectra of solids and liquids. The UV irradiation experiments were conducted by using Luzchem Photoreactor (Intensity ~ 1.75 mW·cm⁻²) and a radiation wavelength 300 nm (UVB).

The method used for the determination of luminescence quantum yield is the Comparative Method, which relies on the use of fluorescence standards, in this case, were estimated by comparison with 9,10-Diphenylanthracene in cyclohexene as a standard of quantum yield 0.95.¹

¹ A. Brouwer, Pure Appl. Chem., 2011, **83**, 2213.

Synthesis of Au⁺ NCs.

A mixture of an aqueous solution of AMP (40 μ L, 50 mM), milli-Q water (760 μ L), and an aqueous solution of tetrachloroauric acid (25 μ L, 50 mM), was stirred for 10 min, forming a pale yellow solution. Next, an aqueous solution of the HEPES salt (500 μ L, 10mM, pH 8) was added and the reaction mixture was stirred at 25 $^{\circ}$ C under room light for 72 h (the color of the reaction mixture gradually changed from yellow to colorless). The reaction was monitored by UV-Vis absorption and fluorescence spectroscopy. The AuNCs were precipitated with acetone and centrifuged at 11000 rpm and re-dispersed in water. The rinse steps were repeated twice.

Optimisation of the procedure

For the optimisation of the above mentioned synthesis, several synthetic parameters were studied.

-The reaction was carried out under the lab light and followed during 72 h (Figure S1).

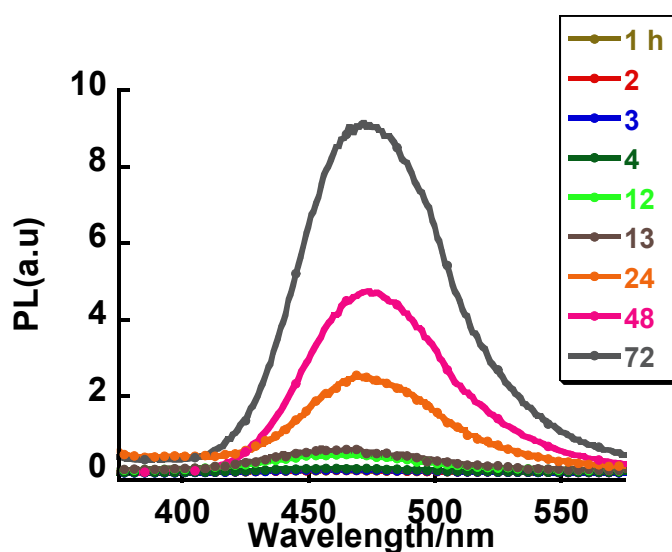


Figure S1. Evolution of the emission spectra of the AMP/HEPES/Au³⁺ samples in water under the laboratory light (λ_{exc} =300 nm, λ_{em} =474 nm).

- The reaction was performed at different pHs 7.3, 7.6, 8.0, 8.6, 9.4, 11.0 (at pH 3 y 5.7 a black precipitate was obtained).

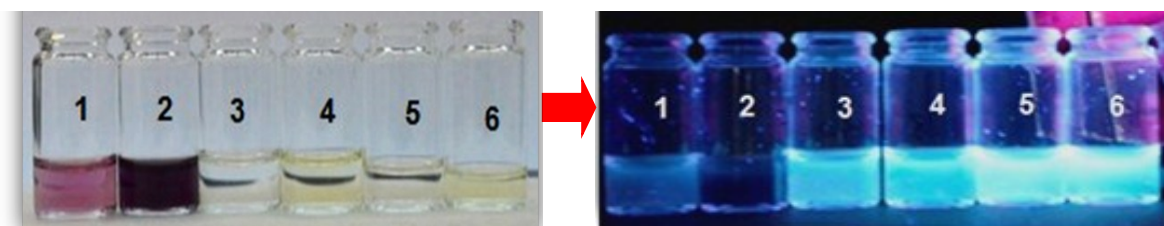
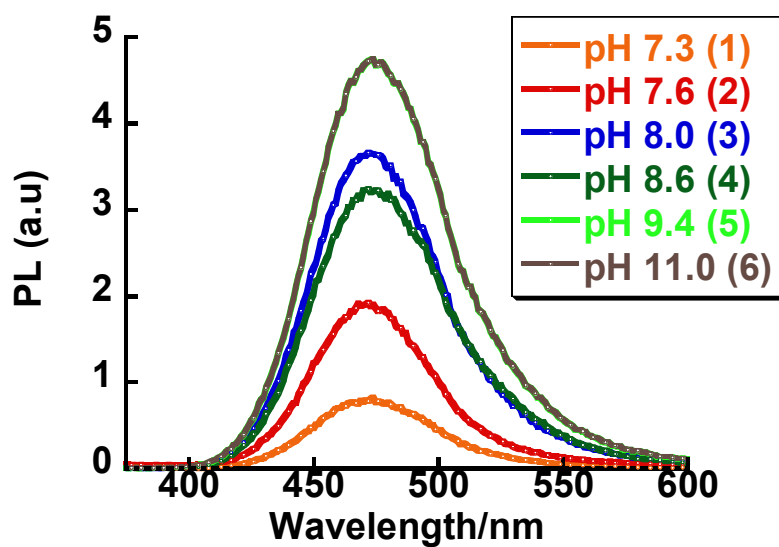


Figure S2. Top: Emission spectra of the AMP/HEPES/Au³⁺ samples in water at different pHs (1:pH7.3, 2:pH7.6, 3:pH8.0, 4:pH8.6, 5:pH9.4, 6: pH11) ($\lambda_{exc}=300$, $\lambda_{em}=474$). Down: Photos showing the effect of the pH variation in the colour and emission of the samples.

- The reaction was also carried out inside a photoreactor equipped with UVB lamps and the evolution of the AMP/HEPES/Au³⁺ sample was followed for 9 h (Figure S3). For comparative purposes, the emission of two identical samples, one kept in the dark and other under lab light, were also followed during 9h (Figure S3).

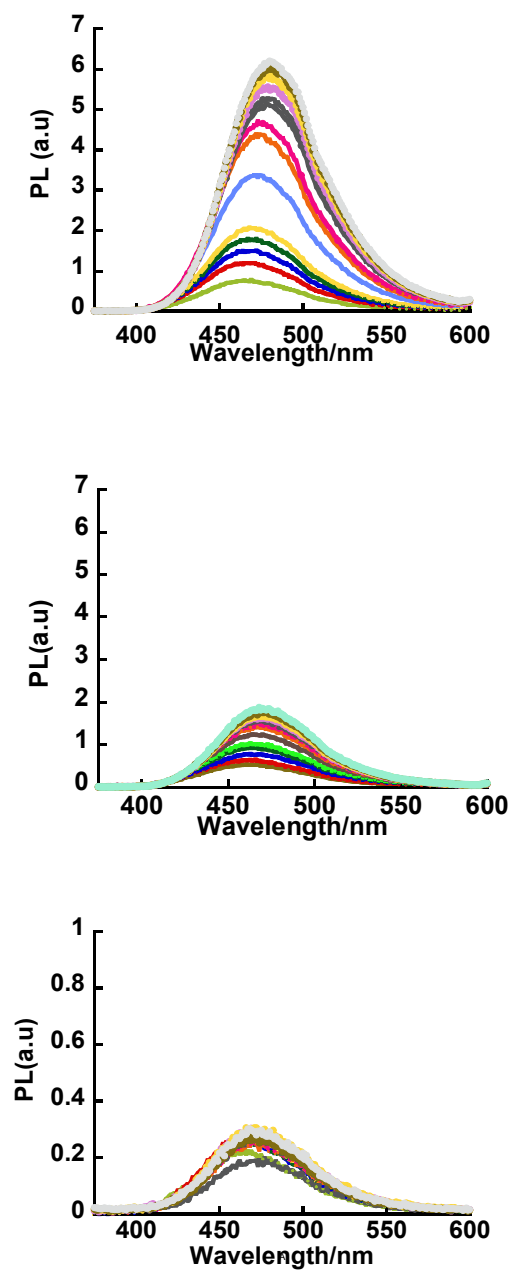


Figure S3. From the top to the bottom: evolution of the emission spectra ($\lambda_{exc}=300$ nm, $\lambda_{em}=474$ nm) of the AMP/HEPES/Au³⁺ samples in water under UVB irradiation in the photoreactor, laboratory light and in the absence of light.

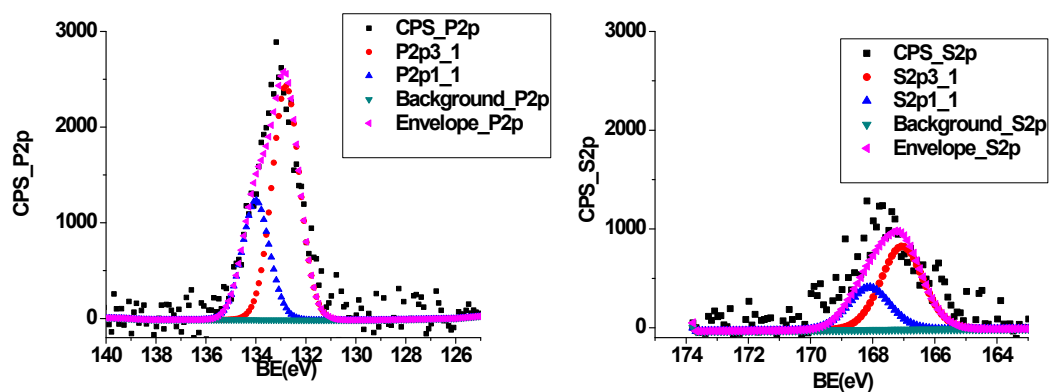


Figure S4. P 2p and S2p XPS spectra of Au⁺ NCs

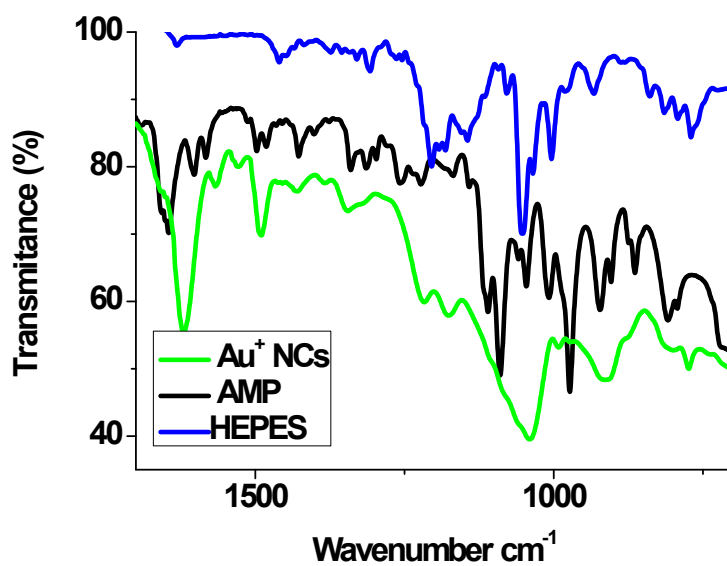
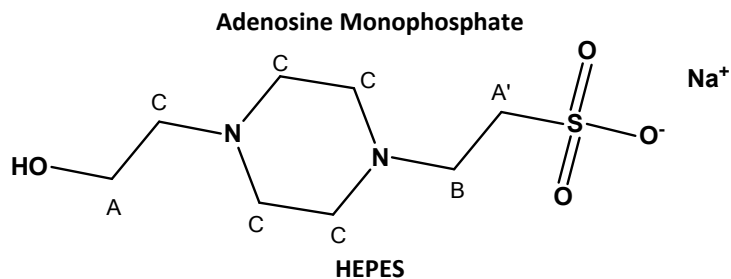
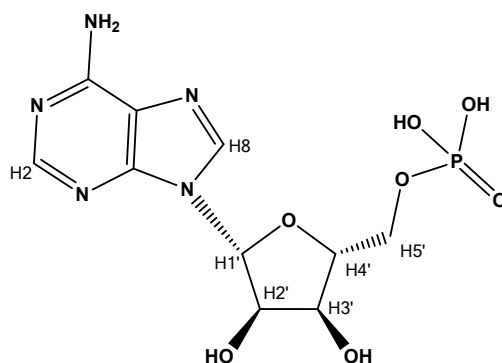


Figure S5. FT-IR spectrum of AMP, HEPES and the Au⁺ NCs

Table S1. ¹HMRN chemical shifts of AMP and AMP/Y³⁺; Au⁺ NCs Au⁺ NCs+Y³⁺; HEPES, and HEPES+ Y³⁺.

Signal	AMP	AMP+Y ^{3+a}	Au ⁺ NCs	Au ⁺ NCs + Y ^{3+a}	HEPES	HEPES + Y ^{3+a}
Signal						
AMP						
H2	8,57	8,55	8,48	8,50		
H8	8,27	8,36	8,24	8,28		
H1'	6,16-6,14	6,19-6,18	6,13-6,11	6,16-6,14		
H2'	-	-	-	-		
H3'	4,54-4,52	4,52-4,50	4,49-4,47	-		
H4'	4,40-4,39	4,41-4,39	4,38-4,35	-		
H5'	4,09-4,07	4,18-4,10	4,10-4,09	4,13-4,12		
Signal						
HEPES						
A			(m) 3,44-3,42 (m)3,36-3,34	m) 3,50 (m)3,37	3,76-3,72	3,93-3,90 3,51
A'			(m) 3,27-3,23	(m) 3,29-3,26	3,16-3,10	3,36-3,26
B			(m)3,20-3,16	(m)3,21-3,18	2,85-2,80	3,21-3,18
C+D			(m)3,03-2,97	(m)3,05-3,00	2,61-2,57	3,05-3,00

^aYCl₃*6H₂O (9.5 μL, 4.26 Mm)



Addition of the lanthanide ions to Au⁺ NCs

Aqueous solution of corresponding lanthanide salt (LnCl₃ · 6H₂O,) (9.5 μL, 4.26 mM) was added to an aqueous solution of the Au⁺NCs (2 mL, A<0.5). The mixture was kept at room temperature for 4 days.

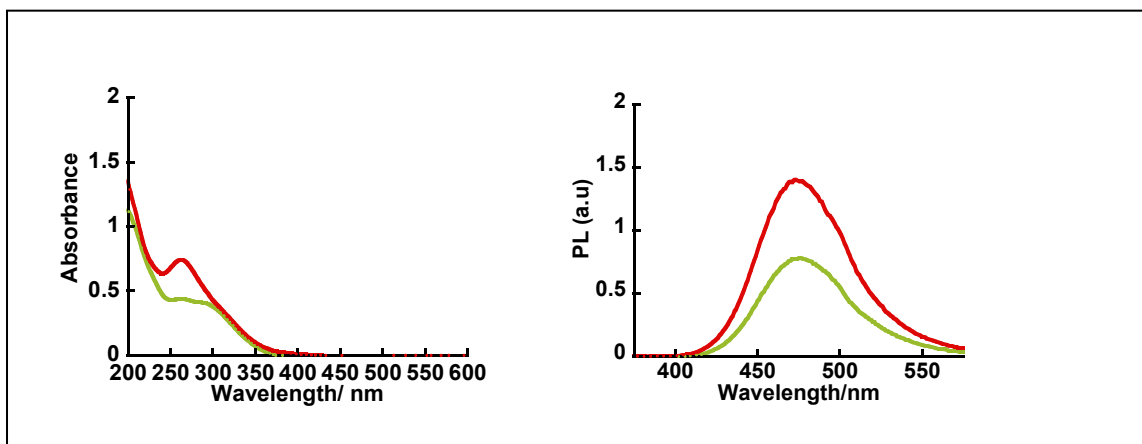


Figure S6. UV-Visible absorption (left) spectra and fluorescence spectra (right) of Au⁺ NCs in water in the absence (green) and in the presence of YbCl₃·6H₂O ($\lambda_{\text{exc}}=300$, $\lambda_{\text{em}}=474$).

Table S2- Au4f and Yd XPS spectra of Au⁺NCs and the precipitate and supernatant of Au⁺NCs /Y³⁺

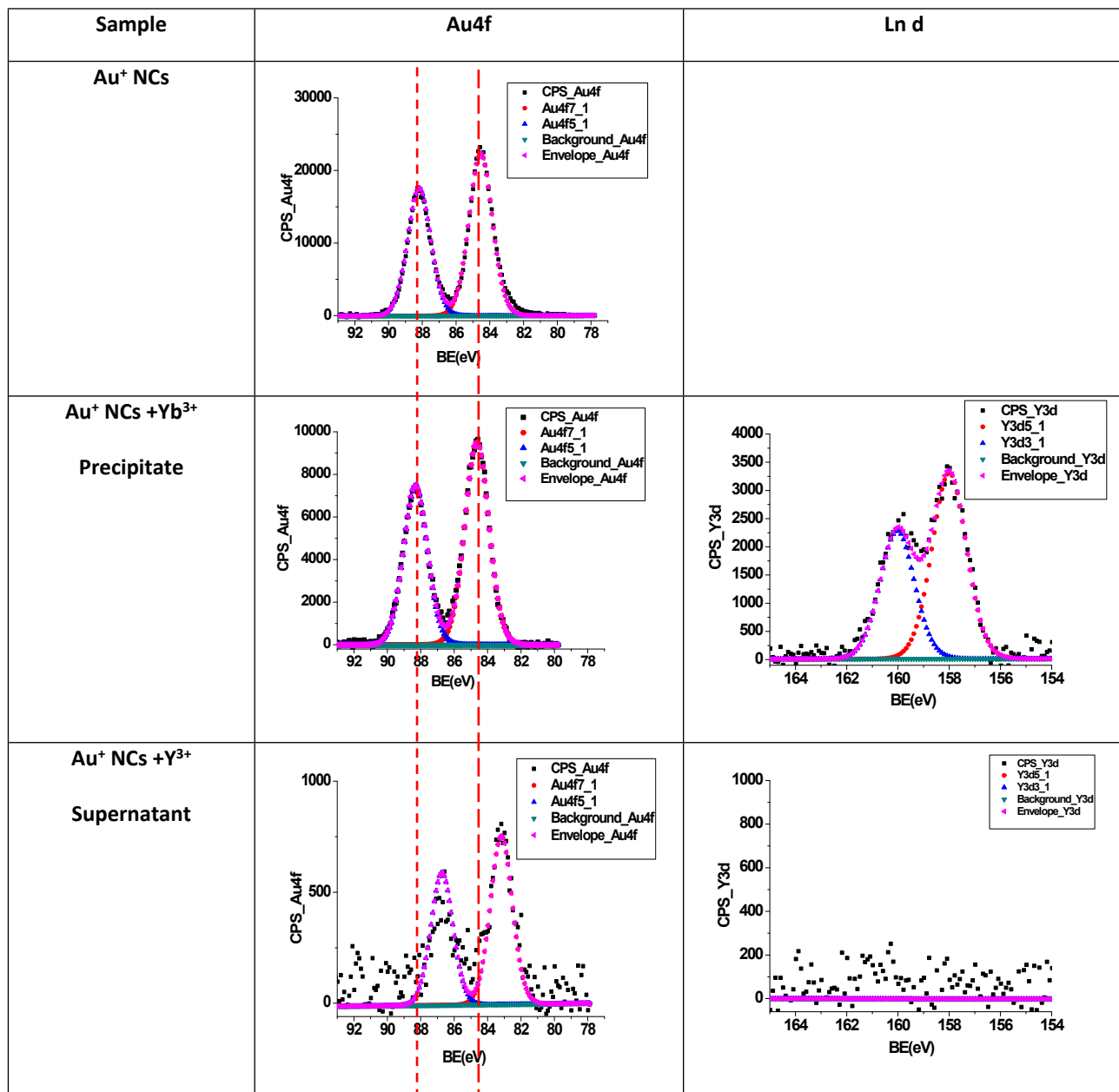


Table S3- Au4f and Yb d XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Yb³⁺ samples

Sample	Au4f	Ln d
Au ⁺ NCs		
Au ⁺ NCs +Yb ³⁺ Precipitate		
Au ⁺ NCs +Yb ³⁺ Supernatant		

Table S4- O 1s and N 1s XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Y³⁺ samples

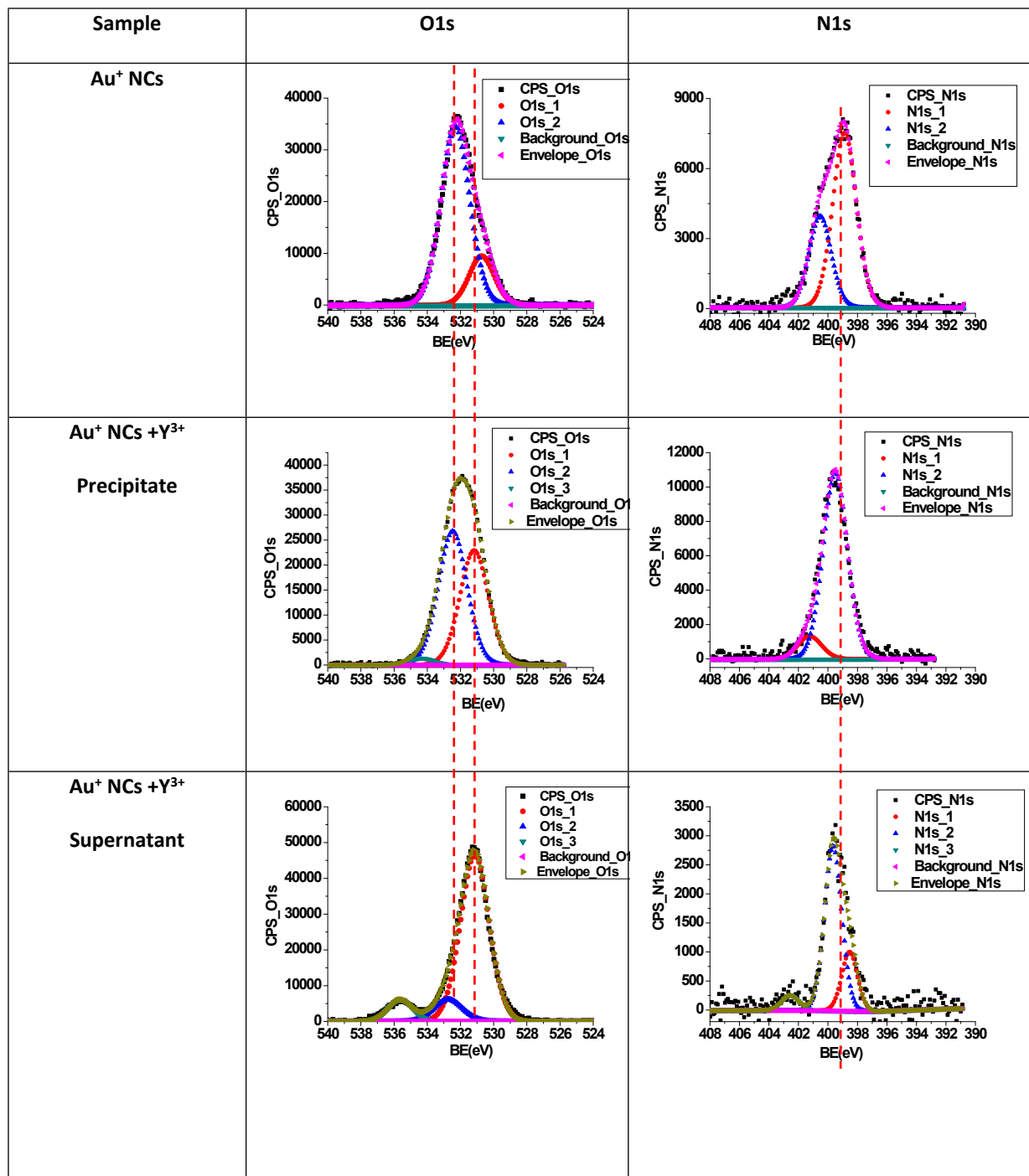


Table S5- O 1s and N 1s XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Yb³⁺ samples

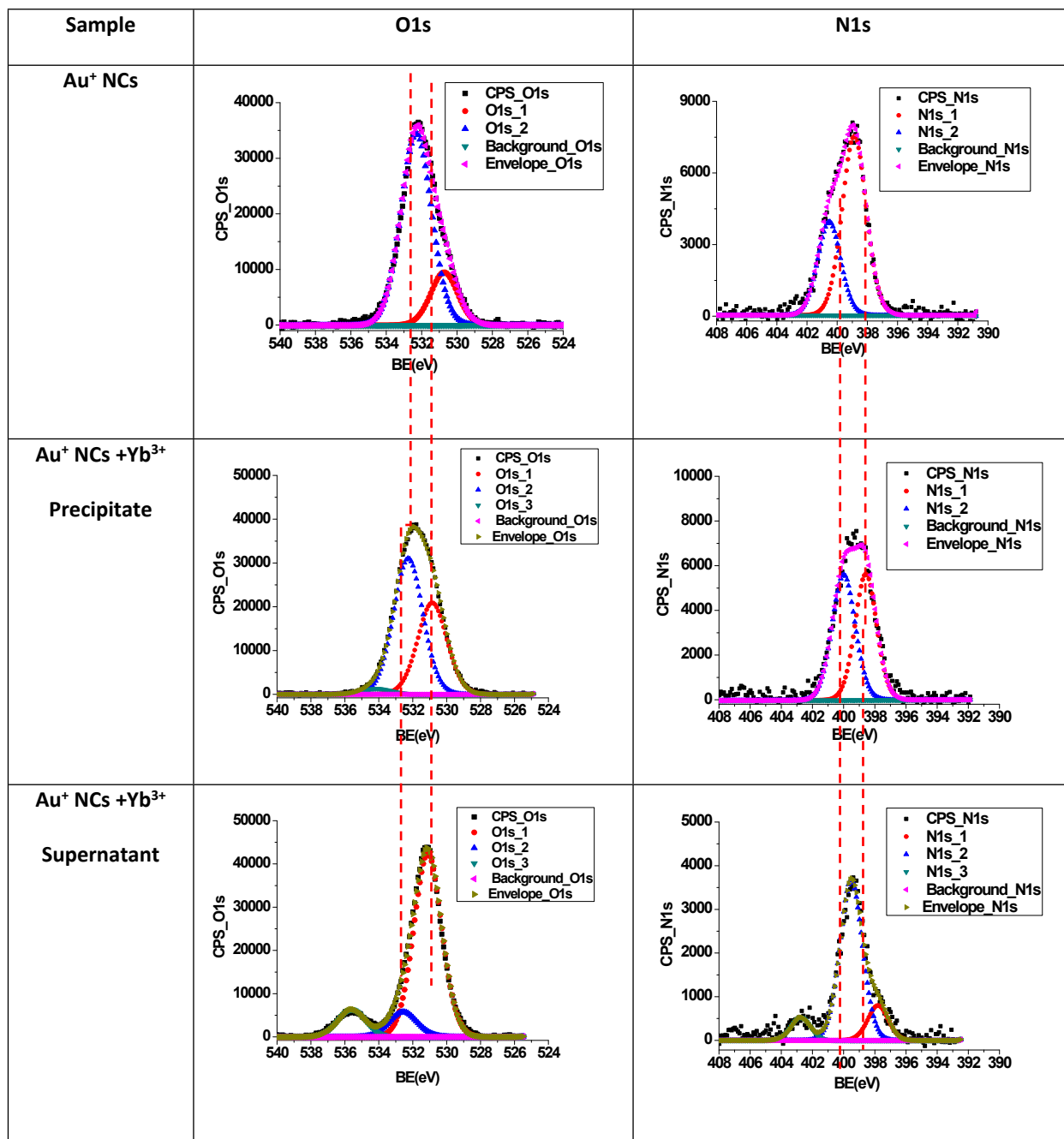


Table S6- C 1s and S 2p XPS spectra of Au@AMP/HEPES and Au@AMP/HEPES/Y³⁺ after precipitated

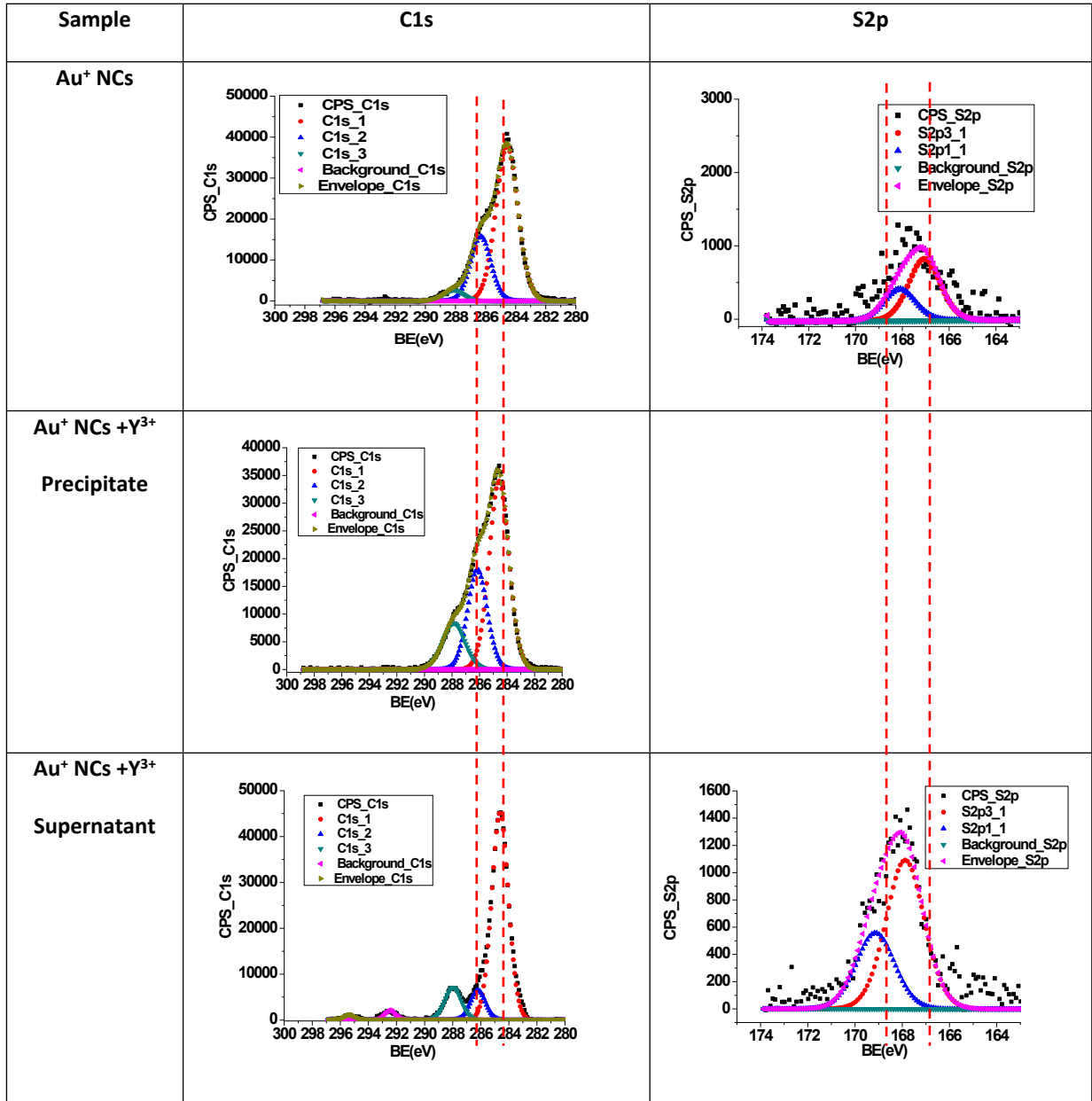


Table S7- C 1s and S 2p XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Yb³⁺ samples

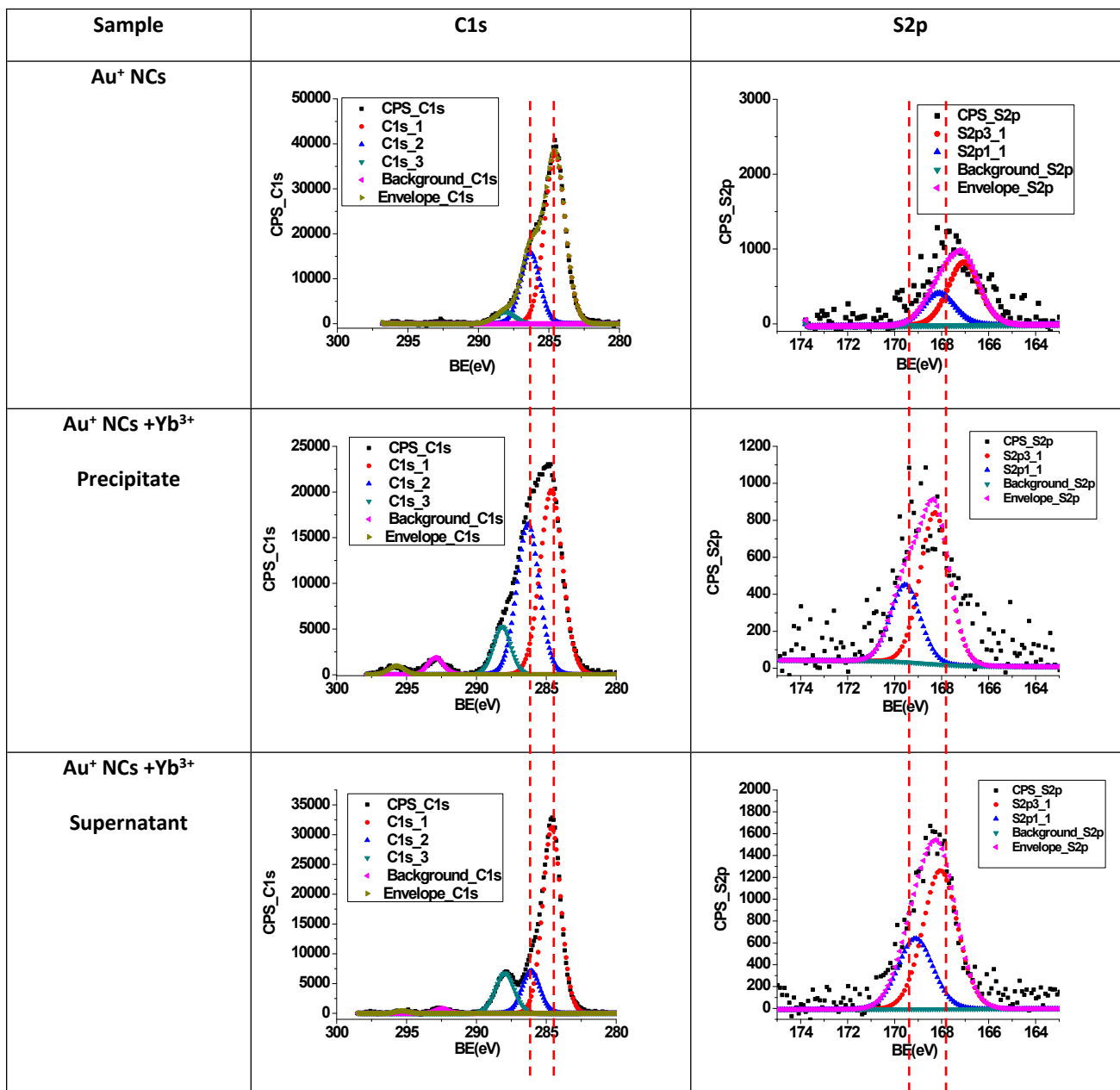


Table S8- P 2p XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Y³⁺ samples

Sample	P2p
Au ⁺ NCs	
Au ⁺ NCs +Y ³⁺ Precipitate	
Au ⁺ NCs +Y ³⁺ Supernatant	

Table S9- P 2p XPS spectra of Au⁺ NCs and of the precipitate and supernatant of Au⁺ NCs/ Yb³⁺ samples

Sample	P2p
<p style="text-align: center;">Au⁺ NCs</p>	
<p style="text-align: center;">Au⁺ NCs +Yb³⁺ Precipitate</p>	
<p style="text-align: center;">Au⁺ NCs +Yb³⁺ Supernatant</p>	