

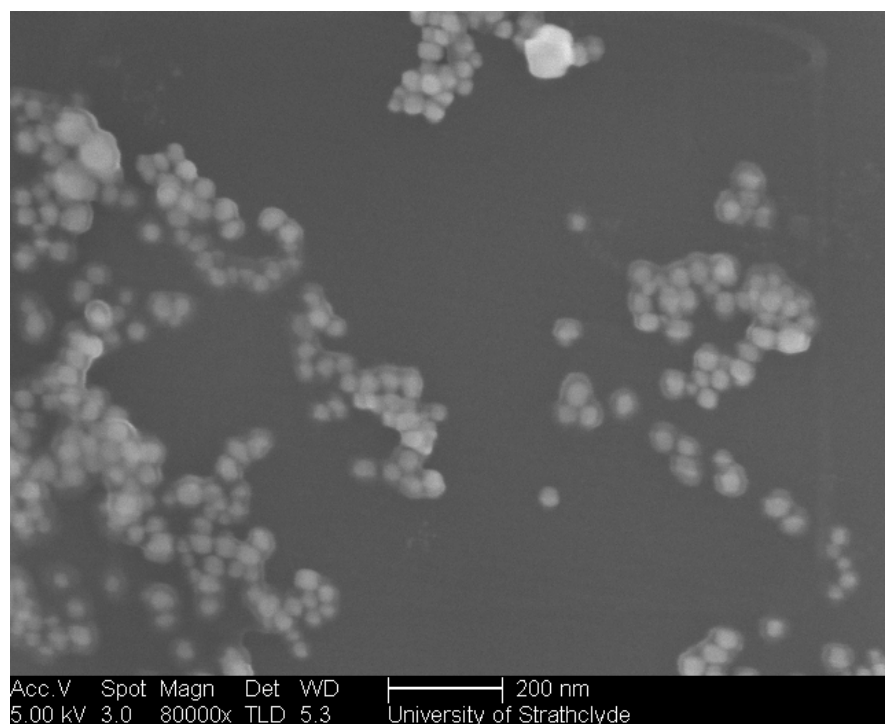


Figure S1: SEM image of silver/ silica core/ shell nanotags synthesised using Dye 1 as a precursor for Stöber condensation of TEOS.

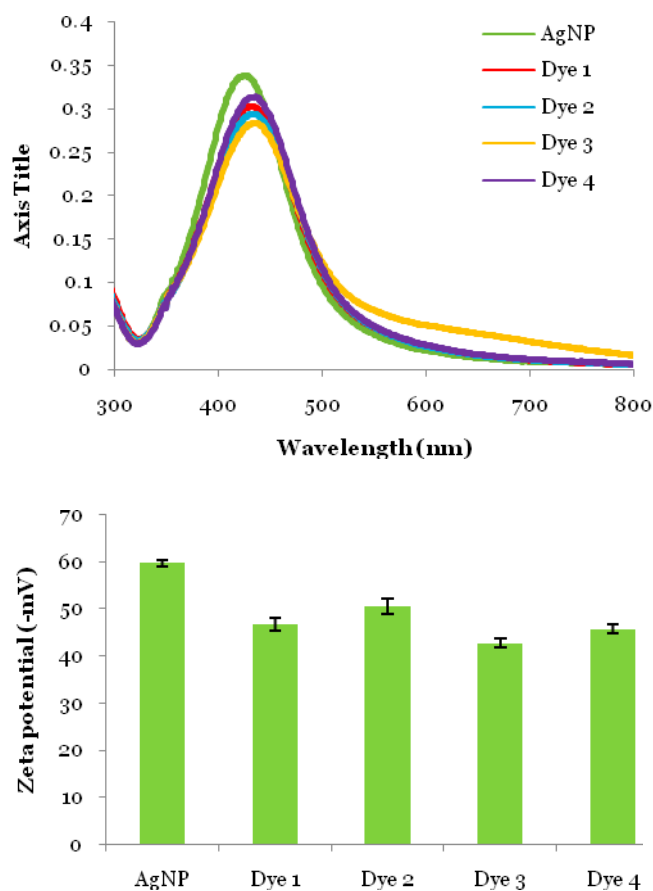


Figure S2: Bare AgNP and the AgNP-dye conjugates a) analysed by UV-vis spectroscopy in an aqueous medium and b) the zeta potential measurements of the nanoparticle dye conjugates, pre silica encapsulation, obtained in an aqueous media 24 hours after synthesis (average $\pm$ 1 standard deviation, n=3).

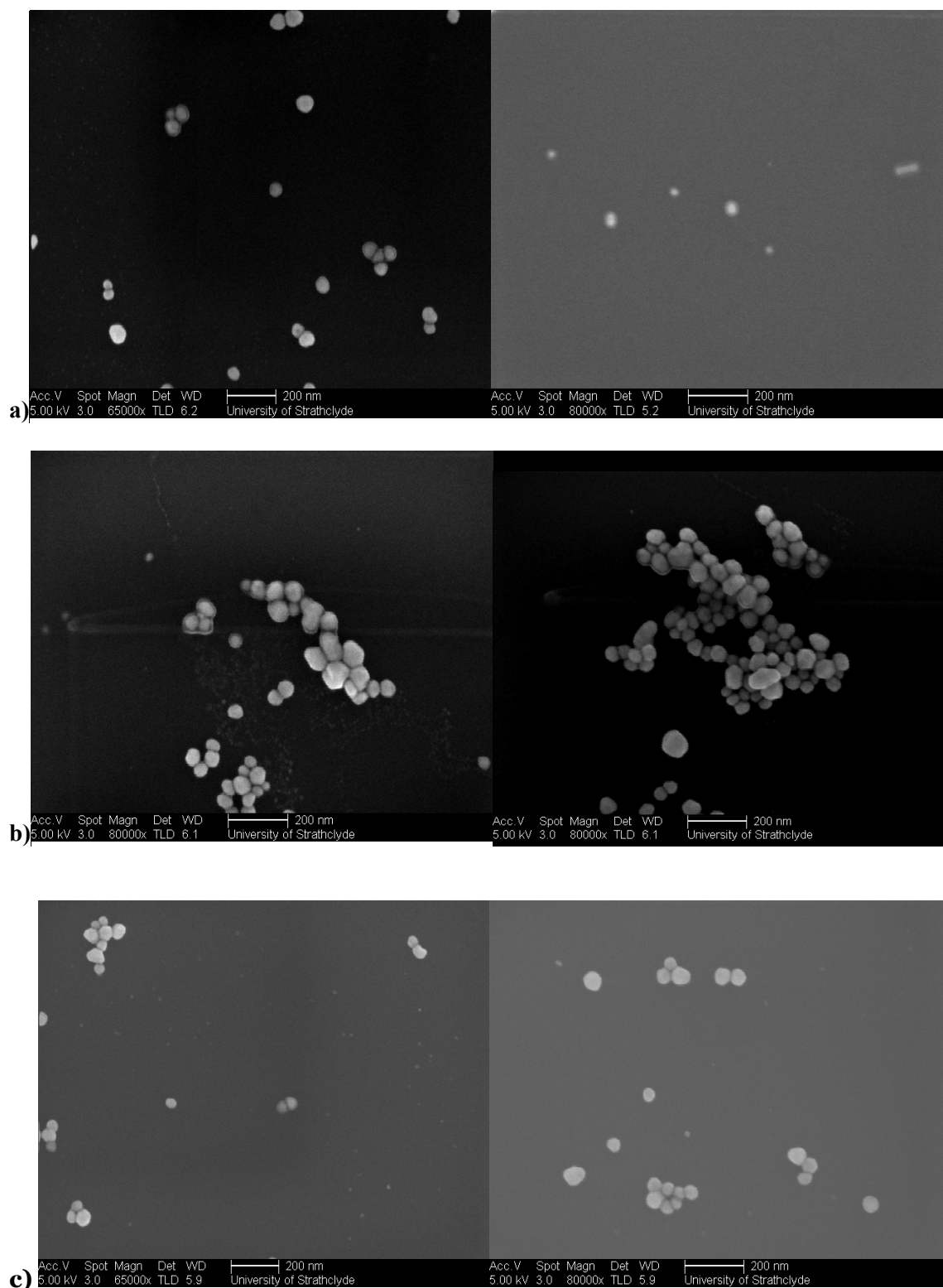


Figure S3: SEM image of silver/ silica core/ shell nanotags synthesised using a) Dye 2 b) Dye 3 and c) Dye 4 as a precursor for Stöber condensation of TEOS.

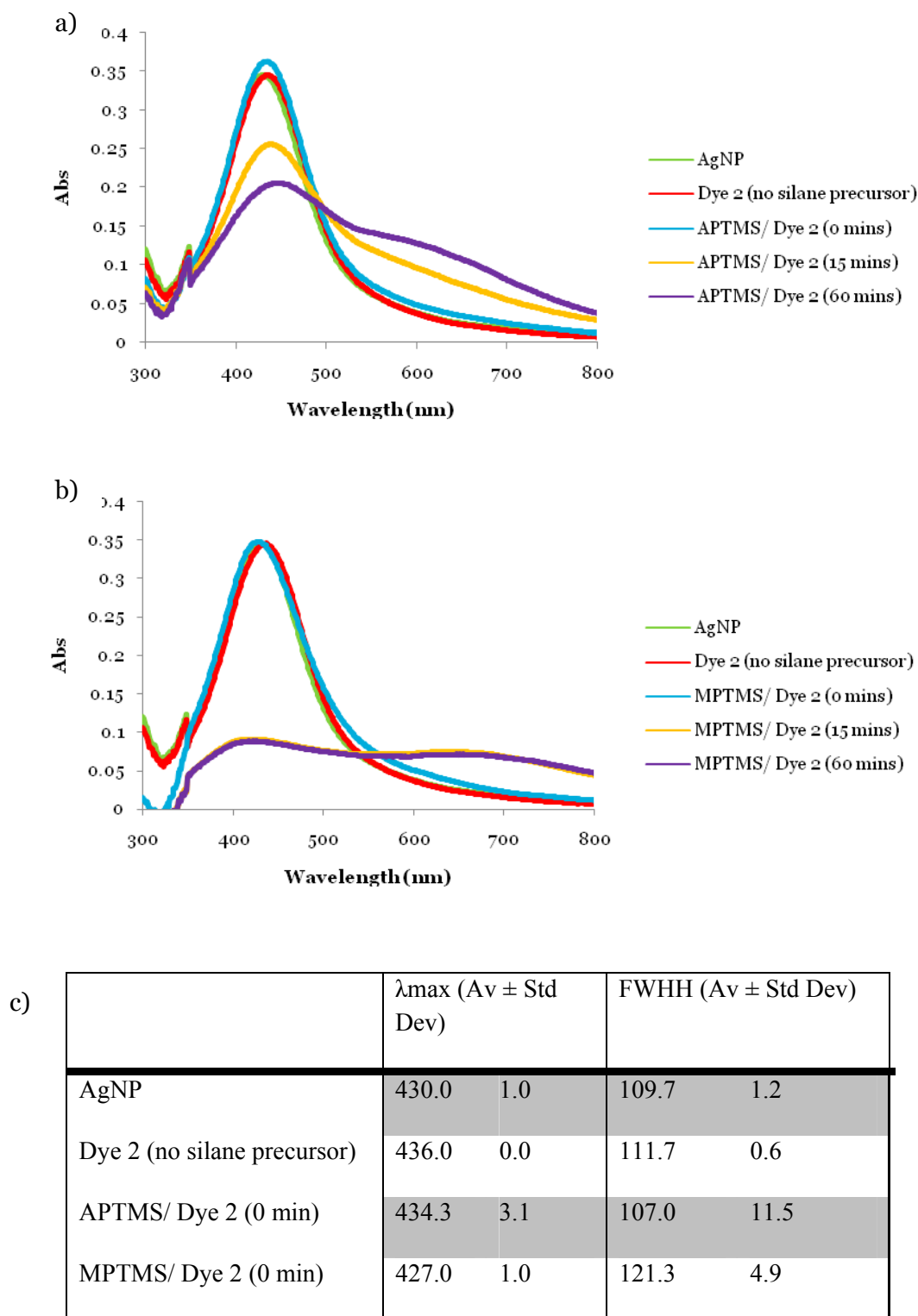


Figure S4: UV visible spectra obtained from AgNP-dye 2 conjugates after incubation with vitreophilising silane precursors a) APTMS and b)MPTMS. Spectra shown are average of three replicates. c) Absorption maximum and full width at half height data obtained from AgNP-dye 2 samples where aggregation is not obvious.

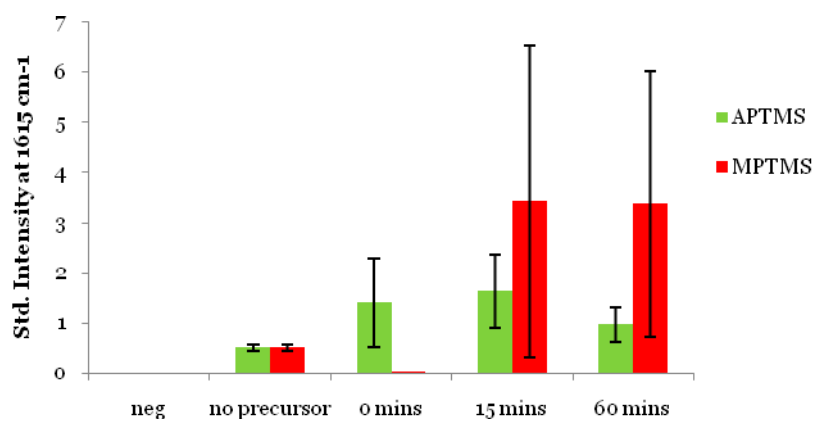


Figure S5: Standardised SERRS intensity recorded at 1615 cm⁻¹ using 514 nm excitation wavelength.

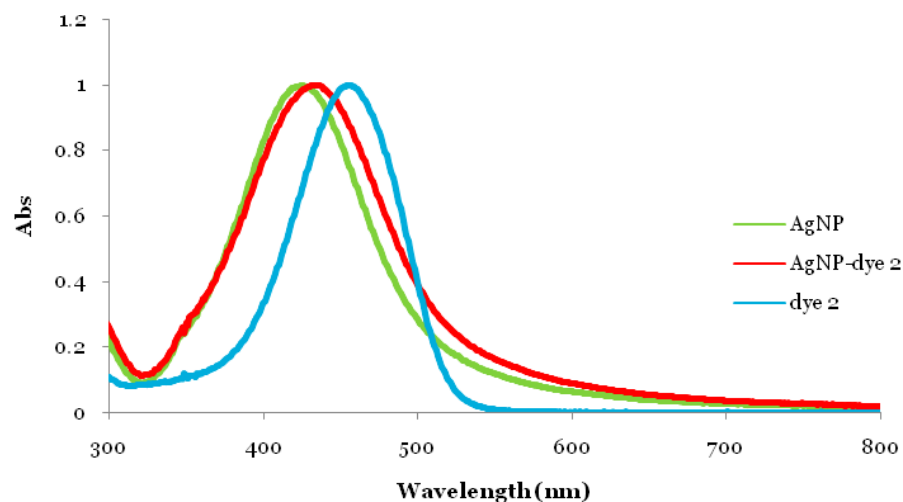


Figure S6: UV-vis spectra of silver nanoparticles (AgNP, green line), silver nanoparticles coated with a monolayer of dye 2 (AgNP-dye2, red line) and an aqueous solution of dye 2 (dye 2, blue line).

Experimental section

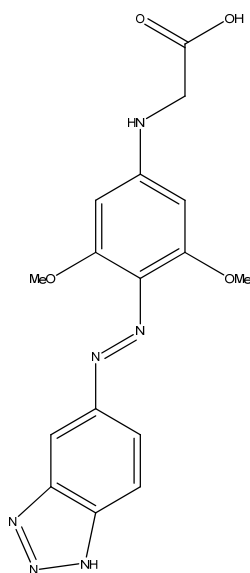
All chemical, unless otherwise stated, were purchased from Sigma/ Aldrich/ Fluka.

Synthesis of Dye 2 (Figure 1): 3,5-dimethoxyaniline (2 g, 1 equiv, 13.06 mmol) and acrylic acid (0.9409 g, 1 equiv, 13.06 mmol) were dissolved in toluene (60 mL). The reaction mixture was refluxed at 110 °C for 48 hours under an inert atmosphere. Compound A was purified by column chromatography.

5-aminobenzotriazole (0.0327 g, 1.1 equiv, 1.9 mmol) was dissolved in HCl (5 mL, 50% (v/v)) and diazotized by the dropwise addition of sodium nitrite (0.184 g, 1.2 equiv, in 1 mL H₂O) at 0 °C with stirring over 30 minutes. Compound A (0.5 g, 1 equiv, 1.7 mmol) was dissolved in sodium acetate buffer (1.0 M, 5 mL, pH 6.0). This was added to the diazotized solution dropwise and stirred overnight. Solid Dye 2 was purified by gravimetric filtration and washed with water.

Yield = 0.534 g, 65.53 %,

δ_{H} [400 MHz, (CD₃)₂SO] 2.73 (2 H, t, *J* 6.0, -NHCH₂CH₂), 3.50 (2 H, t, *J* 6.0, -NHCH₂), 3.81 (6 H, s, -OCH₃), 5.45 (2H, s, H-2,6), 7.25 (1 H, d, *J* 8.0, H-5'), 7.33 (1 H, s, H-2'), 7.54 (1 H, d, *J* 8.0 H-6');
FAB MS : *m/z* 371.33 [(M⁺ + H. C₁₇H₁₈N₆O₄ requires 371.14)]



Dye 2

Synthesis of Dye 1: Dye 2 (0.05 g, 1 equiv, 0.135 mmol) and 1,1-carbonyldiimidazole (0.0341 g, 1.558 equiv, 0.210 mmol) were dissolved in anhydrous DMF (2 mL) and heated for 5 minutes at 40 °C under an inert atmosphere. When the solution reached room temperature, APTMS (0.0236 mL, 1 equiv, 0.135 mmol) was added and stirred for 2 hours.

Attempts to purify Dye 1 by column chromatography were unsuccessful and so the crude product was used as a precursor for silica encapsulation via Stöber condensation.

FAB MS: m/z 490.27 [$(M^+ + H)$. $C_{20}H_{27}N_7O_6Si$ requires 490.56]

Synthesis of EDTA-reduced silver colloid (AgEDTA): Nanoparticles of approximately 40 nm diameter were synthesised according to the previously published method by Fabrinko *et al.*¹³ Briefly, sodium hydroxide (0.4 M, 10 mL) was injected to a boiling solution of EDTA (1.62×10^{-4} M, 1 L). Silver nitrate (0.026M, 10 mL) was added to the boiling solution in 2.5 mL aliquots. After 15 minutes continued heating the solution was allowed to reach room temperature. Stirring was maintained throughout.

Conjugation of precursors to silver nanoparticles: Three separate batches of nanoparticle-dye conjugates were synthesised for analysis. The precursors identified in **Figure 1** were added to AgEDTA (1 mL, 7.75×10^{-11} M, pH 12.2) to a final concentration of 10^{-7} M. APTMS and MPTMS were added to a final concentration of 10^{-5} M. The samples were agitated overnight, centrifuged (6000 rpm, 20 min) and resuspended in H₂O (0.5 mL).

Silica encapsulation of silver – precursor conjugates: Three batches of nanotags were synthesised from each dye. The nanoparticle – precursor conjugates were made up to 1mL with the slow addition of ethanol. Silica Growth was initiated by the addition of triethylamine (10 μ L, 1 % v/v in ethanol) and the sequential addition of TEOS (10 μ L, 4 % v/v in ethanol) and over a three hour period until the final concentration of TEOS was 5.4 mM. The silica encapsulated nanoparticles were centrifuged (6000 rpm, 20 min) and resuspended in 1 mL H₂O.

Instrumentation:

514.5 nm: SERRS was recorded using a *Renishaw Probe* spectrometer with an Argon ion laser (514.5 nm) equipped with a 20x / 0.4 long working objective. The inelastically scattered light was collected for an accumulation time of 1 sec and analysed using a grating of 1800 line/ mm centered at 1600 cm^{-1} . Unfocused laser power at sample was approximately 5 mW.

632.8 nm: A Leica DM/ LM microscope equipped with an Olympus 20x / 0.4 long-working-distance objective was used to collect 180° backscattered light from a cuvette using the 632.8 nm line of a helium-neon laser coupled to a *Renishaw Ramascope System 2000*. The inelastically scattered light was collected for an accumulation time of 1 sec and analysed using a 1200 lines/ mm grating centred at 1600 cm⁻¹. Unfocused laser power at sample was approximately 6 mW.

785 nm: SERRS was recorded using a *Renishaw InVia* Raman inverted microscope system equipped with a 20x /0.4 long working distance objective using a 785 nm diode laser and 1 sec accumulation. A grating of 1200 line/ mm was used with a *RenCam* CCD optimized for near infrared wavelengths. Unfocused laser power at sample was approximately 150 mW.

Three separate batches of samples of each type of nanotags were prepared and analysed in triplicate using each system. Signal intensities were normalized to cyclohexane standards throughout all experiments to ensure the Raman intensity was weighted equally between instruments. The spectra shown and the relative standard deviation (RSD) values quoted are based on the mean intensities of three scans of each of the three batches.