Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information:

Light Activated Synthesis of the Atomically Precise Fluorescent Silver Cluster $Ag_{18}(Capt)_{14}$

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1. Instrumentation

Absorbance spectra of nanoclusters were recorded using an Agilent Cary 60 UV-Vis absorbance spectrometer. Fluorescence excitation-emission matrix (EEM) spectra and emission-excitation scans were taken using the Horiba Duetta Fluorescence and Absorbance Spectrometer, and Rayleigh scattering was corrected using EzSpecTM software. Electrospray ionization mass spectrometry was performed using a Thermo Scientific LTQ Orbitrap Velos hybrid FT mass spectrometer, connected via a liquid junction to a syringe pump. The pump delivered the electrospray solution at a given flow rate through a transferring capillary (360 µm outer diameter and 75 µm inner diameter). The voltage was set to 3.0 kV with a capillary temperature of 275ºC, a sweep gas rate of 6 arb and a sheath flow gas rate of 15 arb. All experiments were performed in positive ion mode. SDS PAGE was performed using the Bio Rad Mini-PROTEAN Tetra Vertical Electrophoresis Cell. 1.5 mm gels were synthesized that contained a 6% pH 6.8 stacking gel and a 29% pH 8.8 separation gel, which were then loaded with aqueous sample and run at 120 V for 15 minutes and then increased to 300 V for 1 hour.

2. Supporting Figures

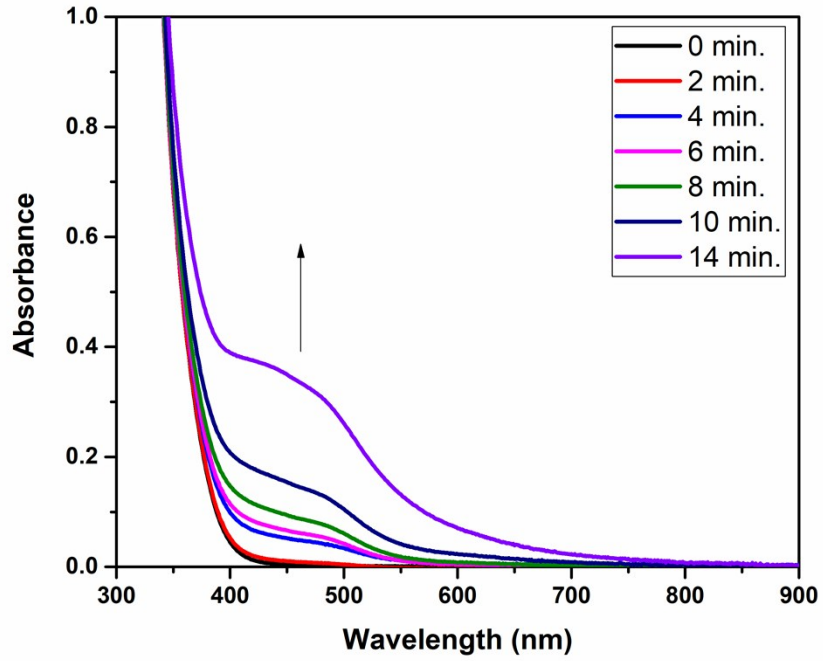

Figure S1. Absorbance spectra of formation of $Ag_{18}(Capt)_{14}$ over 8 minutes, with new absorbance features indicating the formation of new products being formed after 8 minutes.

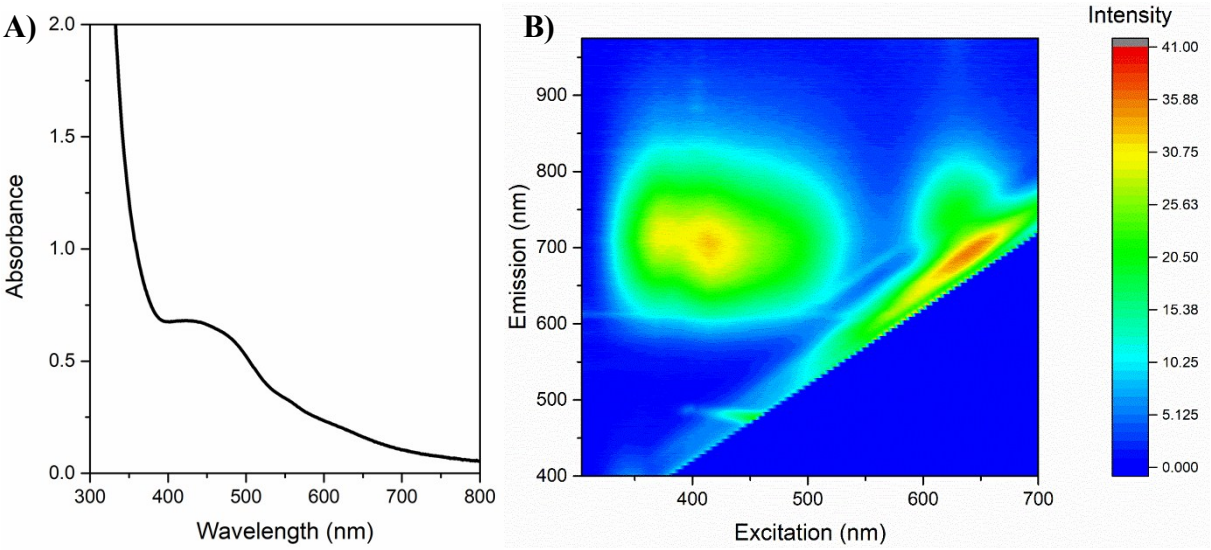

Figure S2. A) Absorbance spectroscopy and B) fluorescence EEM spectroscopy of product that forms when reaction solution is left irradiating under UVA exposure panel for 20 minutes.

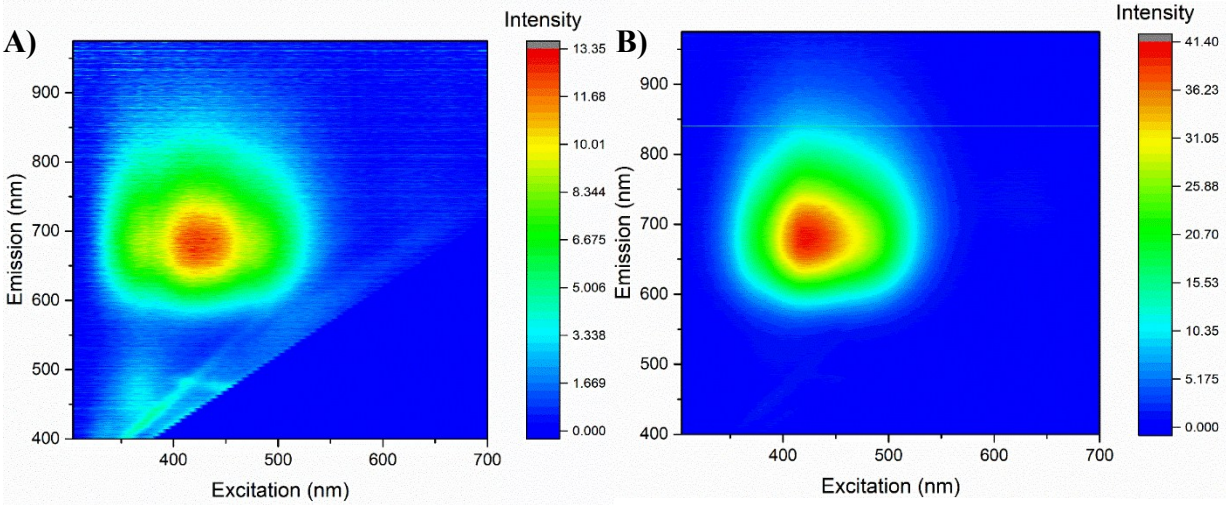

Figure S3. Fluorescence EEM spectroscopy scans of product (A) directly after synthesis and (B) after washing with ultrapure water in centrifugal filters with a 3 kDa cutoff 10 times.

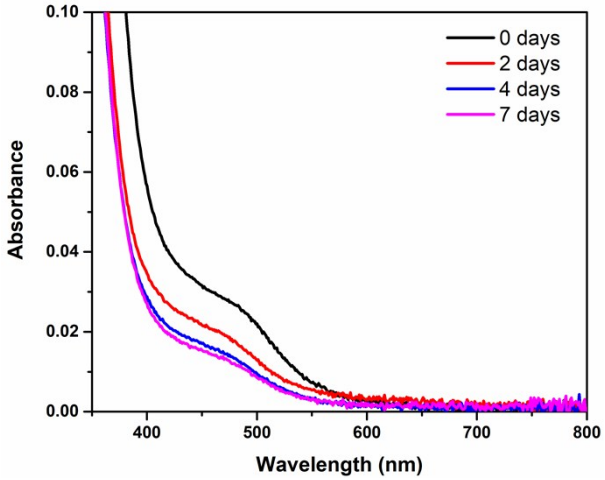

Figure S4. Absorbance decay of $Ag_{18}(Capt)_{14}$ over the course of 7 days when stored at 37°C.

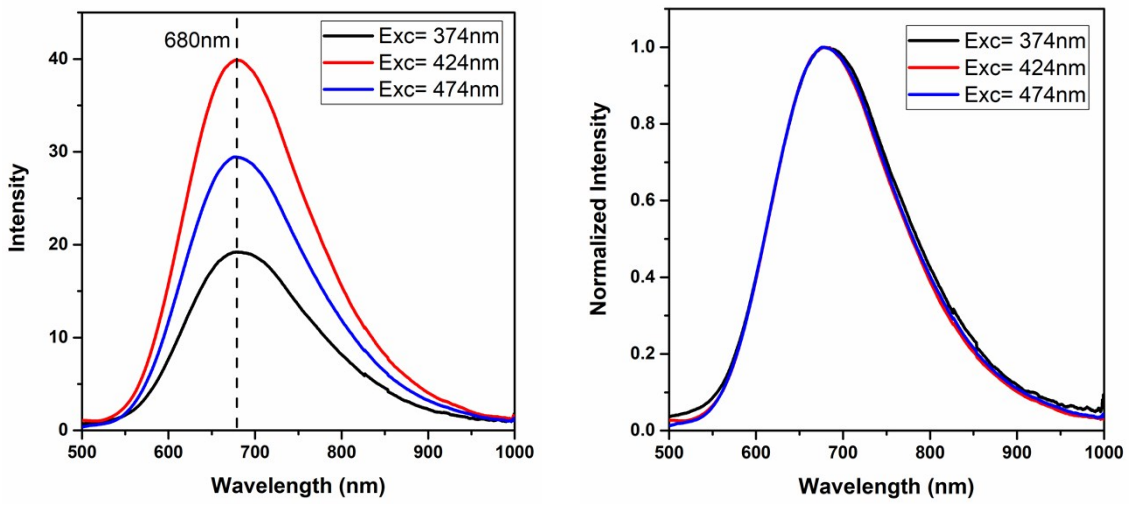

Figure S5. Emission spectra of $Ag_{18}(Capt)_{14}$ recorded at wavelengths of 374 nm, 424 nm and 474 nm (left) and normalized (right).

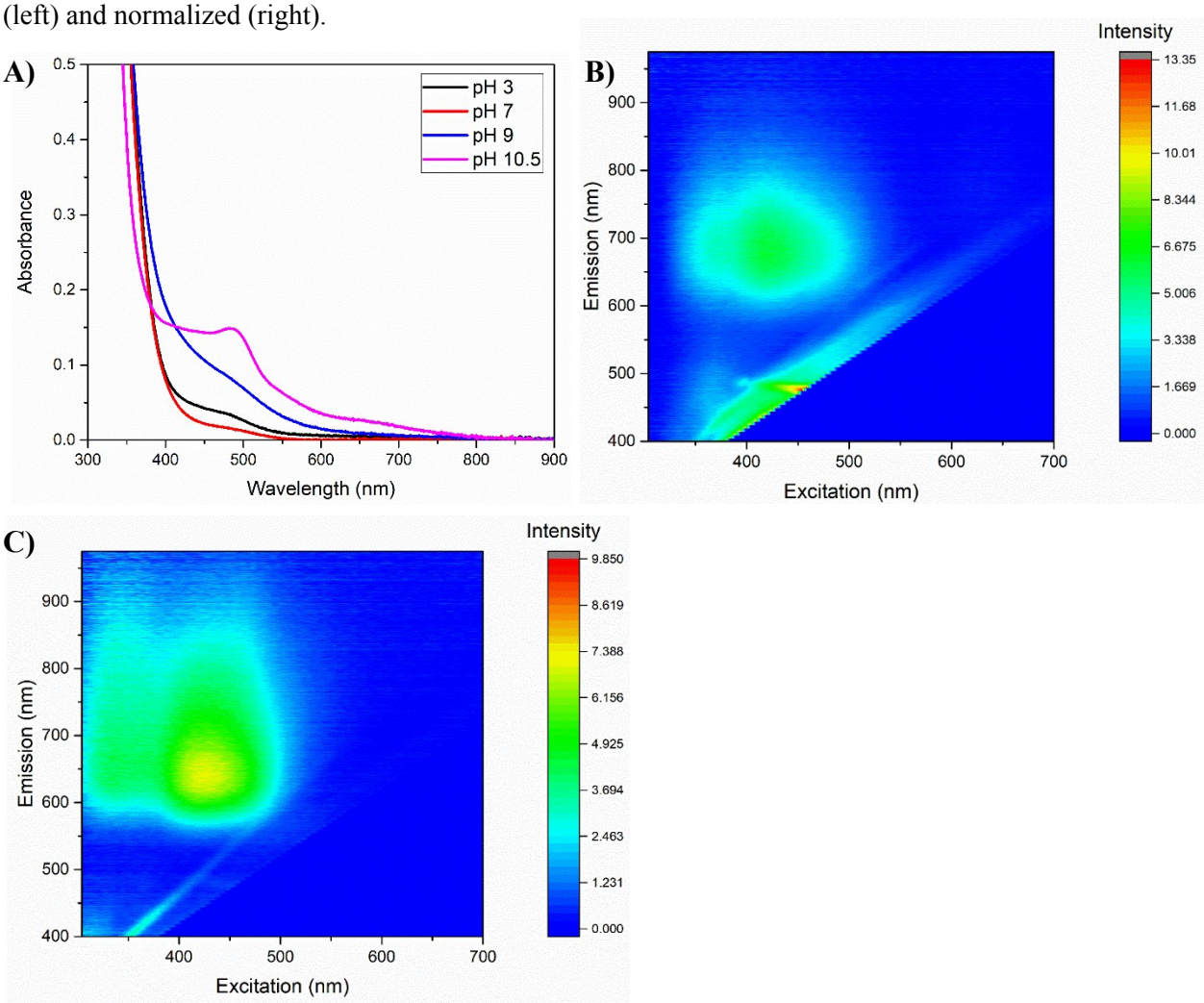

Figure S6. A) Absorbance spectra of clusters formed when captopril stock solution brought to a pH of 3, 7, 9 or 10.5, and fluorescence EEM of B) pH 9 product and C) pH 10.5 product.

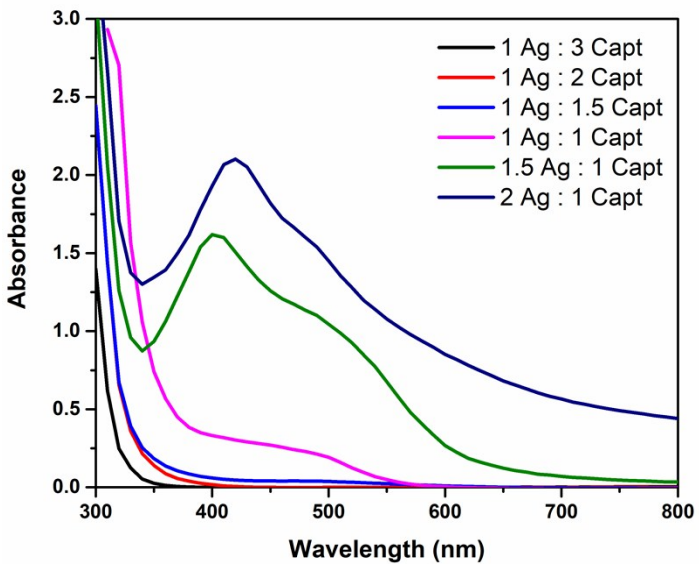

Figure S7. Absorbance of products formed using different relative concentrations of silver nitrate and captopril.

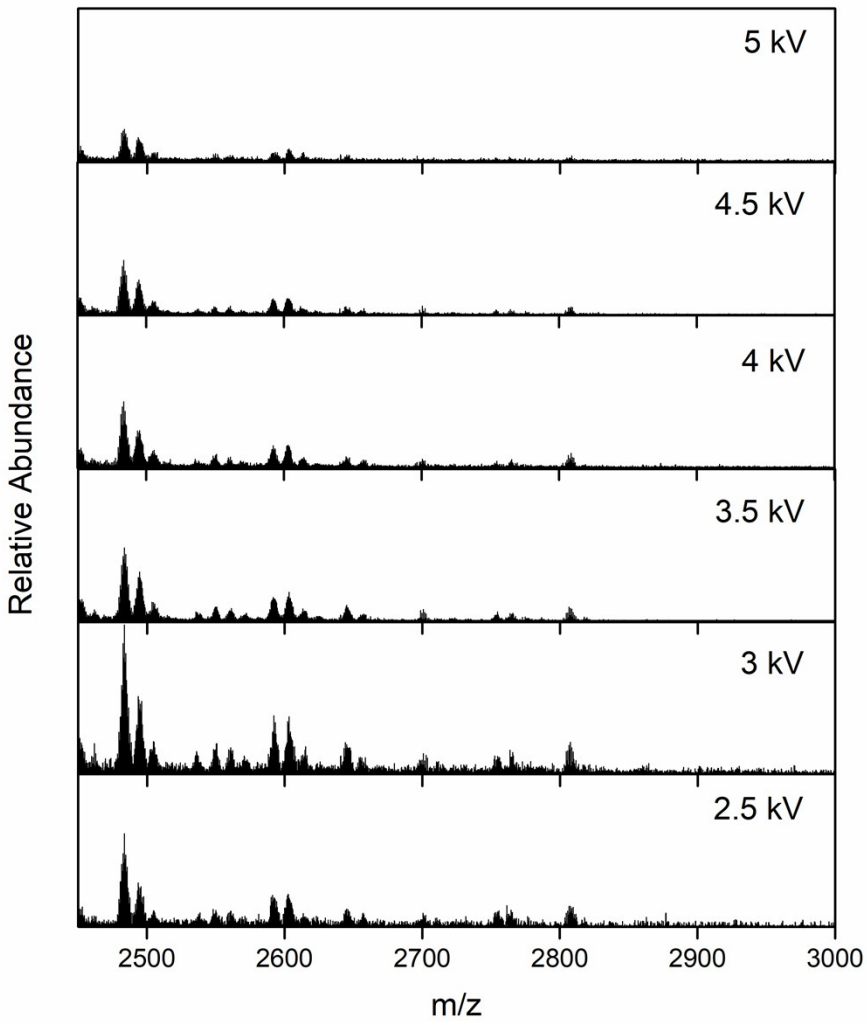

Figure S8. ESI-MS of silver clusters (AgNCs) performed using a spray voltage of 2.5 to 5 kV.

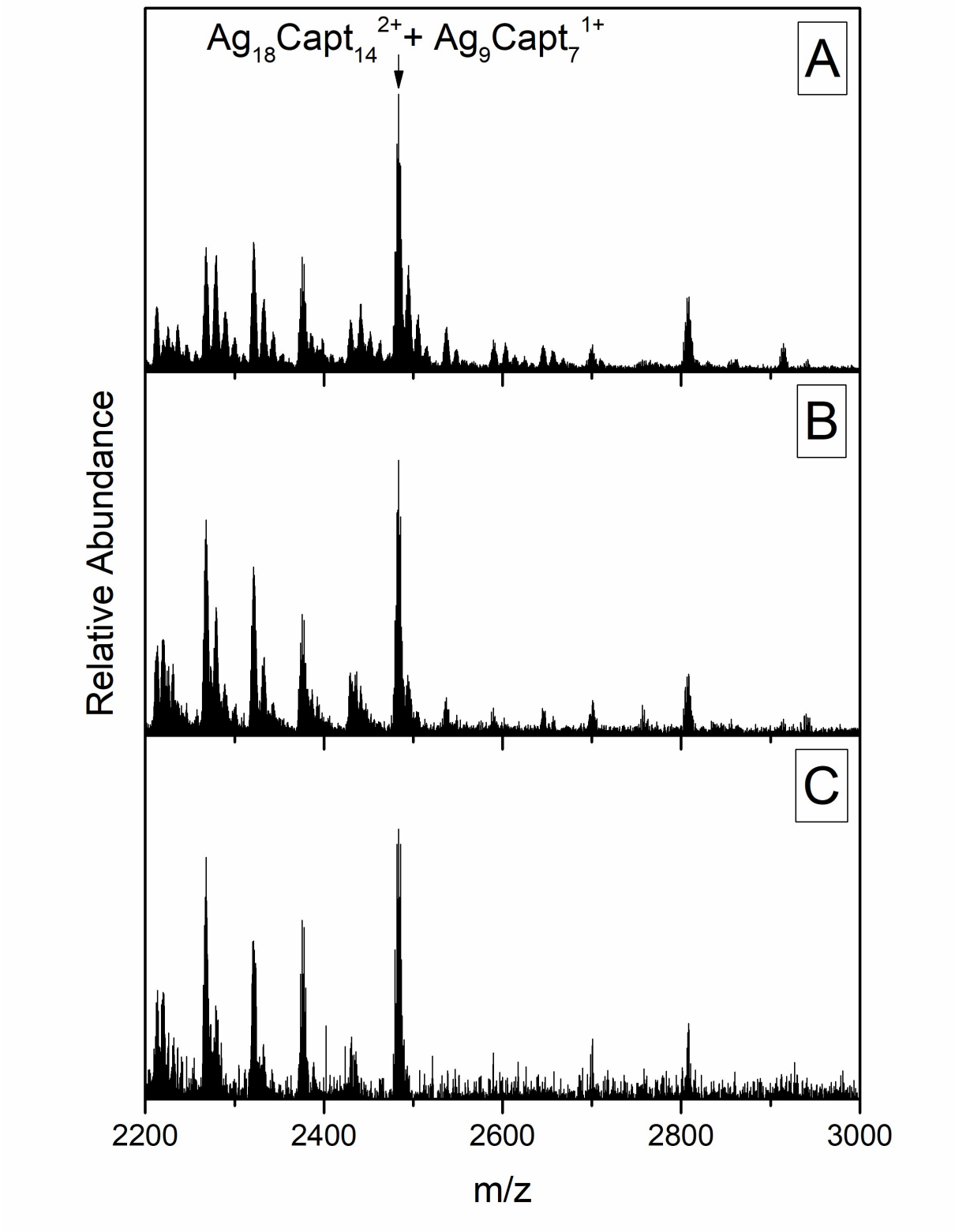

Figure S9. ESI-MS of silver clusters (AgNCs) performed under increasingly dilute conditions through dilution with water, from A (most concentrated) to C (least concentrated).

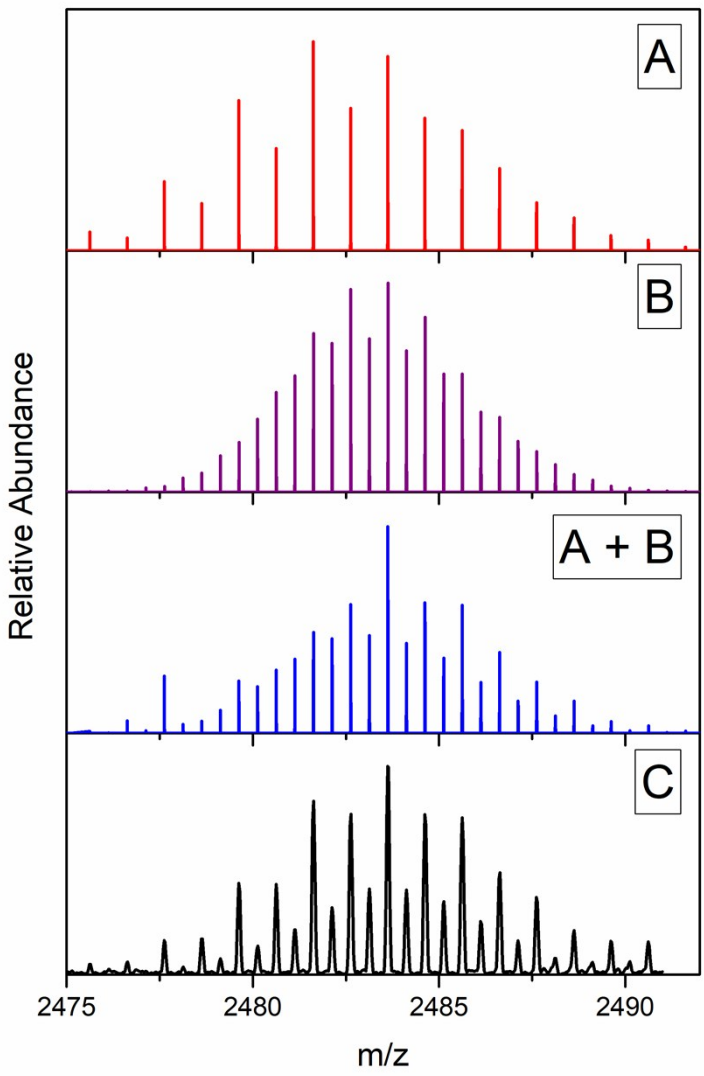

Figure S10. Simulated isotope patterns of A) $Ag_9(Capt)_7^{1+}$, B) $Ag_{18}(Capt)_{14}^{2+}$, A+B) the simulated isotope pattern of $Ag_9(Capt)_7^{1+}$ added to that of $Ag_{18}(Capt)_{14}^{2+}$; C) experimental data.

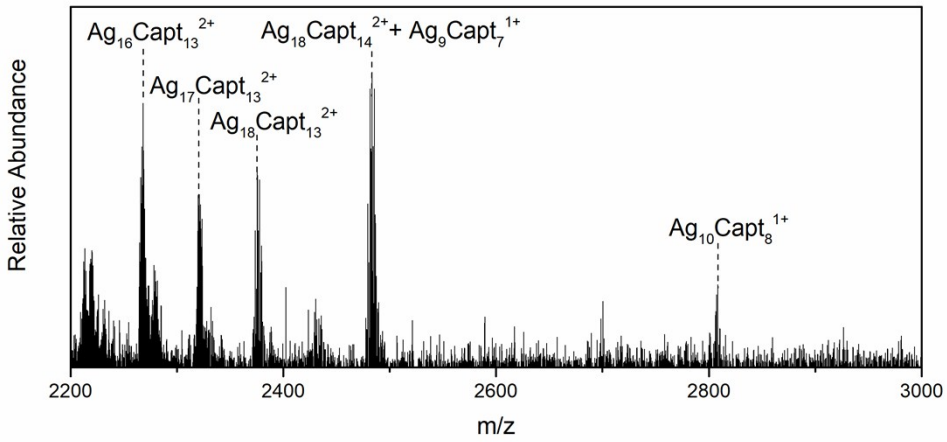

Figure S11. Isotopes observed and identified from 2200-3000 m/z in ESI-MS experiments.

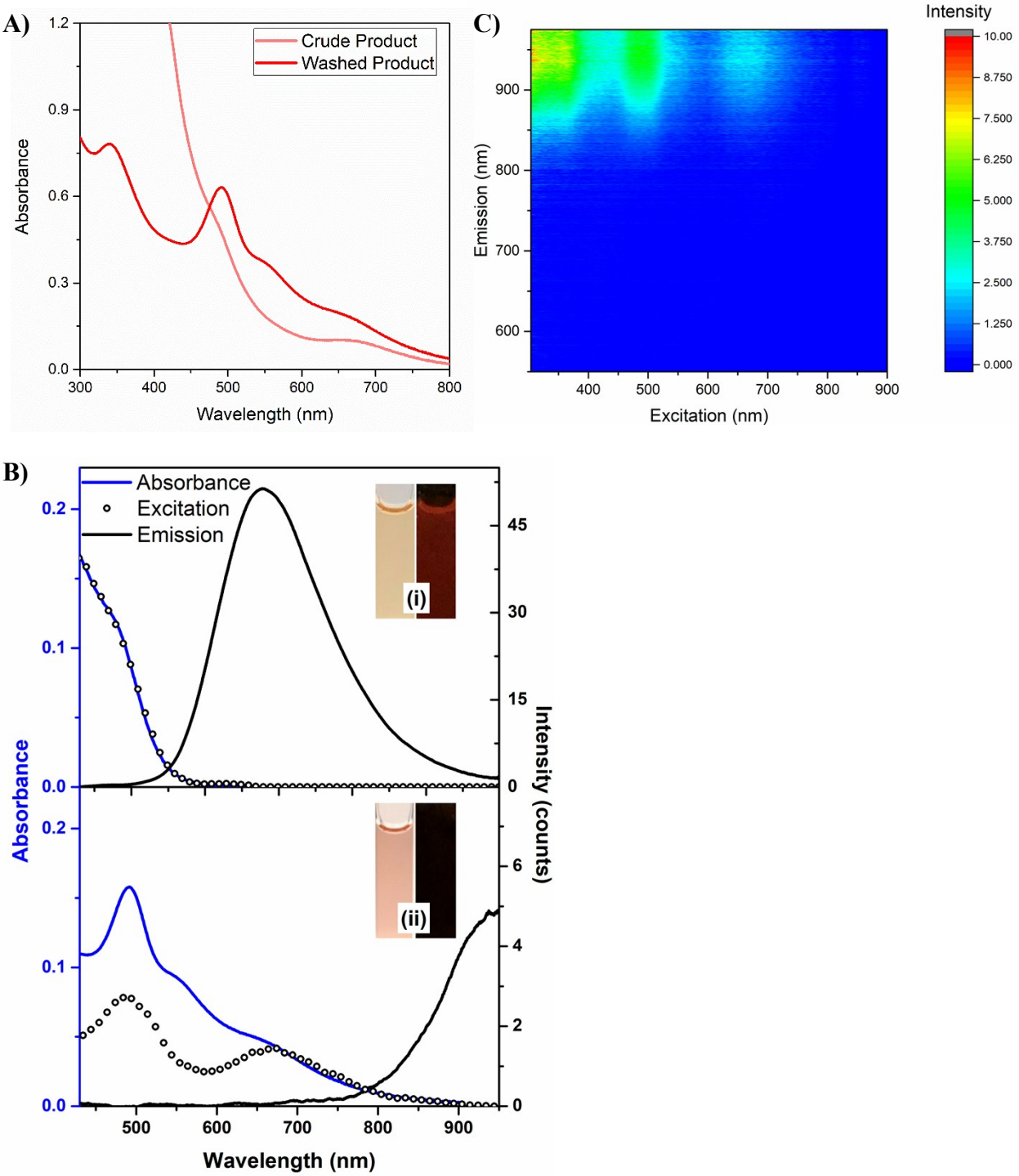

Figure S12. A) Absorbance spectra of thermally synthesized silver-captopril clusters directly after synthesis (crude product) and after washing and precipitating (washed product). B) TOP: Absorbance spectra of photochemical AgNC along with its emission spectra (λ_{exc}= 424 nm) and excitation spectra (λ_{ems}= 680 nm); inset (i): appearance of AgNC solution in (left) visible and (right) UVA light. BOTTOM: Absorbance spectra of thermal AgNC along with its emission spectra (λ_{exc}= 324 nm) and excitation spectra (λ_{ems}= 925 nm); inset (ii): appearance of AgNC solution in (left) visible and (right) UVA light. C) Fluorescence EEM scan of washed product.

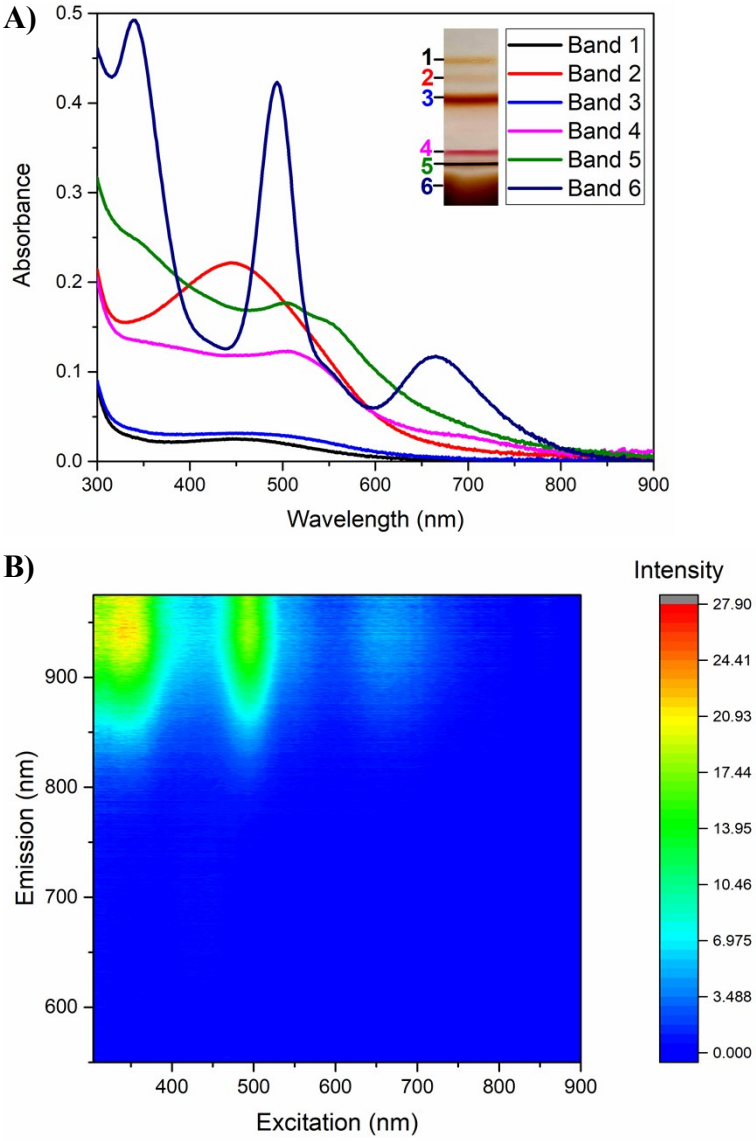

Figure S13. A) Absorbance spectra of thermally synthesized silver-captopril clusters after separation by SDS PAGE; inset: strip of SDS PAGE gel after separation with bands in gel numbered, B) fluorescence EEM scan of Band 6, the only emissive gel product.