

Supplementary information

Synthesis, Structural Characterization and Transformation of an Eight-Electron Superautomic Alloy, Au@Ag₁₉(dtp)₁₂

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EXPERIMENTAL SECTION

Materials and Methods. All the reactions were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under nitrogen. All chemicals were purchased from commercial sources and were used as received. [Ag(CH₃CN)₄](PF₆),¹ and NH₄(S₂P(OR)₂) (R = ⁿPr,) ² ligands were prepared as described in the literature. Melting points were measured by using a Fargo MP-2D melting point apparatus. NMR spectra were recorded on Bruker Advance DPX300 FT-NMR spectrometer that operates at 300 MHz while recording ¹H, 121.5 MHz for ³¹P. Residual solvent protons were used as a reference (δ, ppm, CDCl₃, 7.26; CD₃COCD₃, 2.05). ³¹P NMR spectra were referenced to external 85% H₃PO₄ at δ 0.00. ESI-mass spectra were recorded on a Fison Quattro Bio-Q (Fisons Instruments, VG Biotech, UK). A thin film of a solid sample was prepared on a carbon strip which was subjected to FE-SEM and EDS measurements on a JEOL JSM-7000F, JEOL Ltd. microscope from Japan. (Resolution:1.5 nm (15KV), 5 nm (1KV)). The elemental and structural information were analyzed using X-ray photoelectron spectrometer (XPS, VG Multilab 2000-Thermo Scientific Inc. UK, Kα) with a microfocus monochromated Al Kα X-ray working with high photonic energies from 0.2 to 3 KeV. UV– Visible absorption spectra were measured on a Perkin Elmer Lambda 750 spectrophotometer using quartz cells with path length of 1 cm. The emission spectra were collected using a Varian CARY Eclipse Fluorescence spectrophotometer with Oxford Instruments Superconductivity, OX135QX, UK. This system was operated using the SynerJY software. The detector heads were cooled to -90 °C and the spectrometers were purged with dry N₂

Synthesis of $[\text{AuAg}_{19}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ **1** :

In a Flame-dried Schlenk tube, nanocluster $[\text{Ag}_{20}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ (0.080 g, 0.017 mmol) was dissolved in THF (30 mL), and was cooled at -20°C for 20 minutes. In another Schlenk tube, 1 eq. of $\text{Au}(\text{PPh}_3)\text{Cl}$ (0.008 g, 0.017 mmol) was dissolved in THF (5 mL) and was transferred into Schlenk tube containing $[\text{Ag}_{20}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ using a cannula. The resulting reaction mixture was stirred for 2 h. The reaction mixture was allowed to come to RT, and was dried under reduced pressure. The residue was thoroughly washed with DCM/Water mixture. The DCM layer was separated and dried under vacuum to yield $[\text{AuAg}_{19}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$, (Yield% : 0.067 g, 84 %). Mp: 145°C (dec.). EDS for (Au:Ag:S:P) atomic %, Calcd: (1.79:35.71:42.86:21.43); Found: (1.75:35.21:42.23:20.81). ESI-MS ($\text{M}+\text{Ag}^+$ Calc. 4913.27) : m/z 4913.28. Anal. Calcd for $\text{C}_{72}\text{H}_{168}\text{Ag}_{19}\text{AuO}_{24}\text{P}_{12}\text{S}_{24} \cdot 8(\text{C}_3\text{H}_6\text{O})$: C, 21.88; H, 4.13; S, 14.60 Found: C, 21.93; H, 3.84; S, 13.70 %. ^{31}P NMR (121.49 MHz, acetone- d_6 , δ , ppm, r.t.): 105.6. UV-vis [λ_{max} in nm, (ϵ in $\text{M}^{-1}\text{cm}^{-1}$)] 375(8800), 420(9500). Emission (nm) at 77K : 782.

Synthesis of $[\text{AuAg}_{20}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]^+$ **2** :

In a Flame-dried Schlenk tube, nanocluster $[\text{AuAg}_{19}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ (0.100 g, 0.02 mmol) was dissolved in THF (30 mL), and was cooled at -20°C for 20 minutes. In another Schlenk tube, 1 eq. of $\text{Ag}(\text{CH}_3\text{CN})_4(\text{PF}_6)$ (0.0087 g, 0.02 mmol) was dissolved in THF (5 mL) and was transferred into Schlenk tube containing $[\text{AuAg}_{19}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ using a cannula. The resulting reaction mixture was stirred for 2 h. The reaction mixture was allowed to come to RT, and was dried under reduced pressure. The residue was thoroughly washed with DCM/Water mixture. The DCM layer was separated and dried under vacuum to yield $[\text{AuAg}_{20}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]^+$. EDS for (Au:Ag:S:P) atomic %, Calcd: (1.75:35.09:42.11:21.05);

Found: (1.74:35.00:42.32:20.94). ESI-MS (M+Ag⁺ Calc. 4913.27) : m/z 4913.23. ³¹P NMR (121.49 MHz, acetone-d₆, δ, ppm, r.t.): 103.7 (br), -143.0 (multiplet). UV-vis [λ_{max} in nm, (ε in M⁻¹cm⁻¹)] 359(8421), 427(8957). Emission (nm) at 77K : 835.

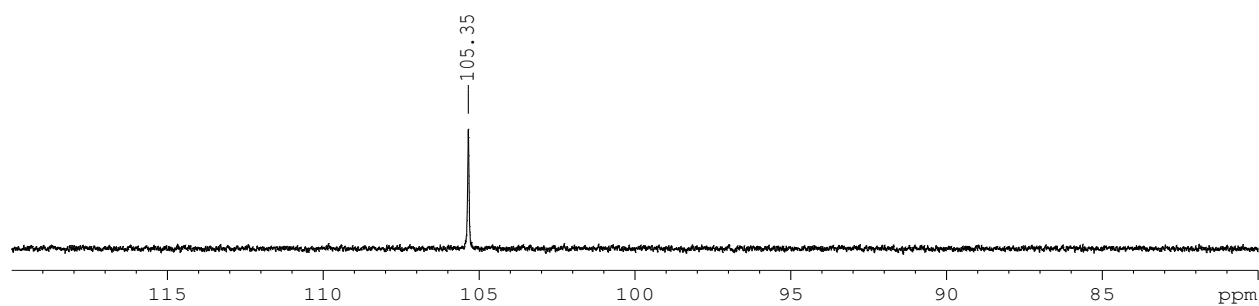


Figure S1 : ³¹P NMR spectrum of **1**

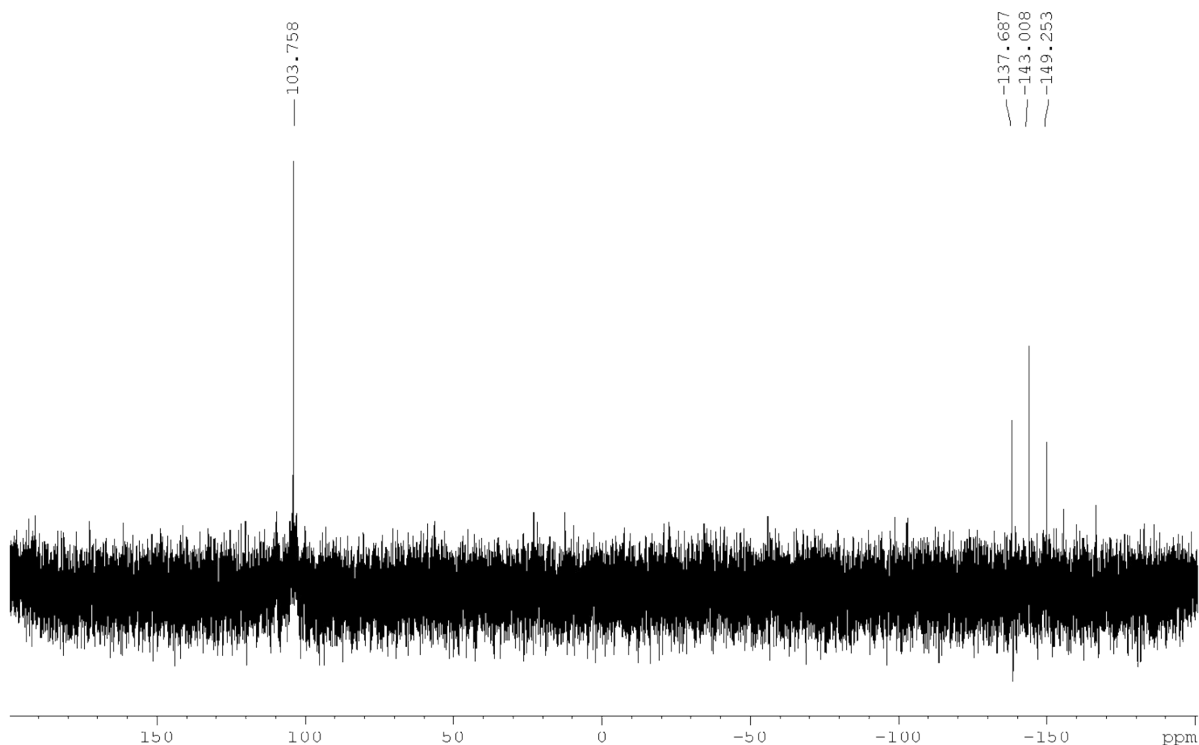
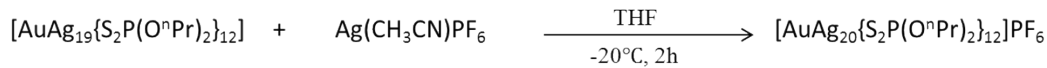


Figure S2 : ^{31}P NMR spectrum of **2**

X-ray Crystallography: Single crystals suitable for X-ray diffraction analysis of **1** were obtained by diffusing hexane into concentrated acetone solution. The single crystal was mounted on the tip of glass fiber coated in paratone oil, then frozen at 150 K. Data were collected on a Bruker APEX II CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections for area detector were performed with SADABS. The structure was solved by direct methods and refined by least-squares against F^2 using the SHELXL-97 package, incorporated in SHELXTL/PC V6.14. All non-hydrogen atoms were refined anisotropically.

CCDC 1584458 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 1: X-ray crystal parameters

Compound	[AuAg ₁₉ {S ₂ P(O ⁿ Pr) ₂ } ₁₂]
Formula	C75 H175 Ag19 Au O24 P12 S24
fw	4848.72
crystal symmetry	Monoclinic
space group	P2(1)/c
a, b, c (Å)	29.6903(7), 17.3784(4), 30.3868(6)
α, β, γ deg	90, 110.3727(6), 90
V, Å ³	14697.9(6)
Z	4
T, K	150(2)
ρ _{calcd} , g/cm ³	2.191
μ, mm ⁻¹	3.984
Reflection collected	86192
Independent reflections	25525 (R _{int} = 0.0273)
Data/restraints/parameters	25855 / 440 / 1396
Final R indices [I > 2σ(I) ^{a,b}]	R1 = 0.0426 wR2 = 0.1012
R indices (all data)	R1 = 0.0574 wR2 = 0.1153
GOF	1.033
Largest diff. peak and hole, e Å ⁻³	2.711 and -1.634

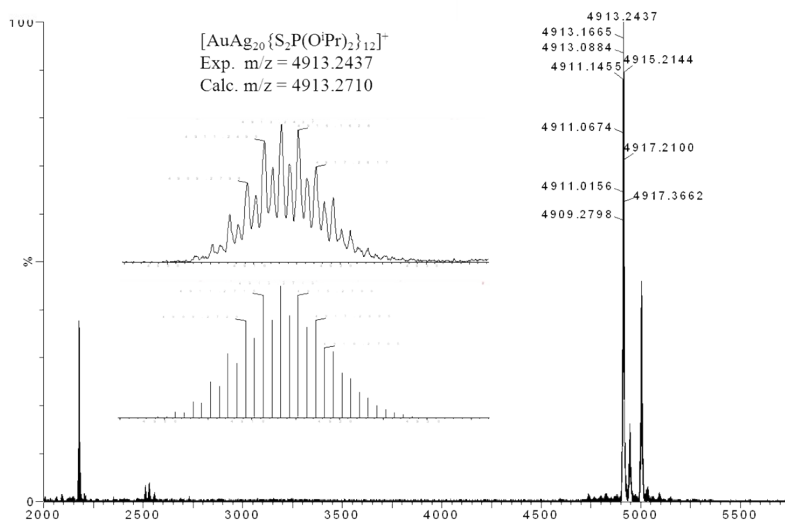
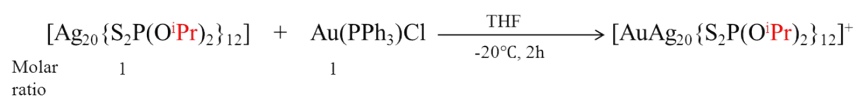
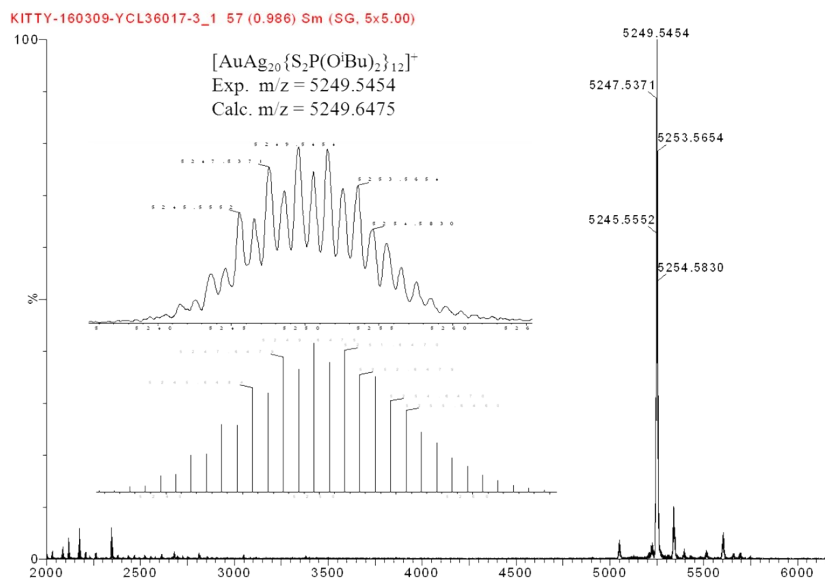
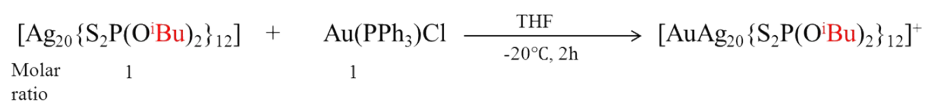


Figure S3. Positive ESI-MS of spectrum of $[\text{Au}@\text{Ag}_{20}\{\text{S}_2\text{P}(\text{O}^i\text{Bu})_2\}_{12}]^+$ and $[\text{Au}@\text{Ag}_{20}\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_{12}]^+$

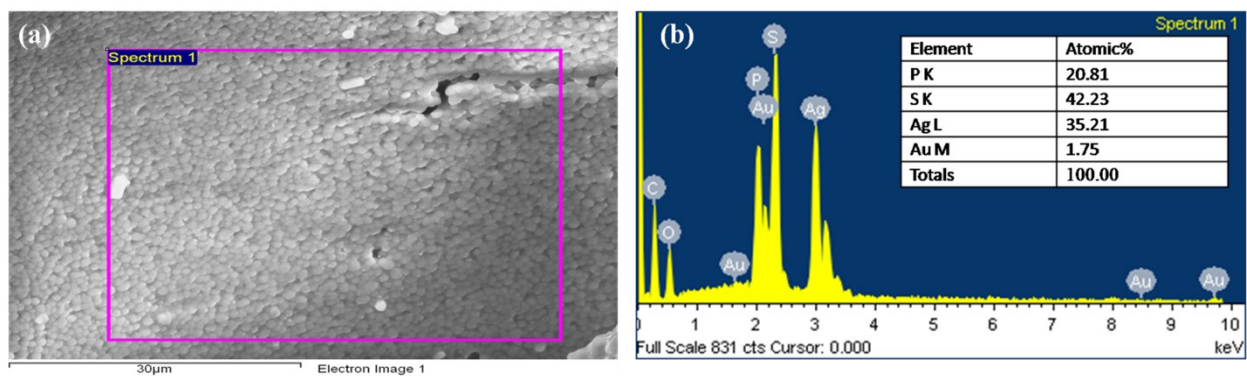


Figure S4. FE-SEM image and EDS spectrum of **1**

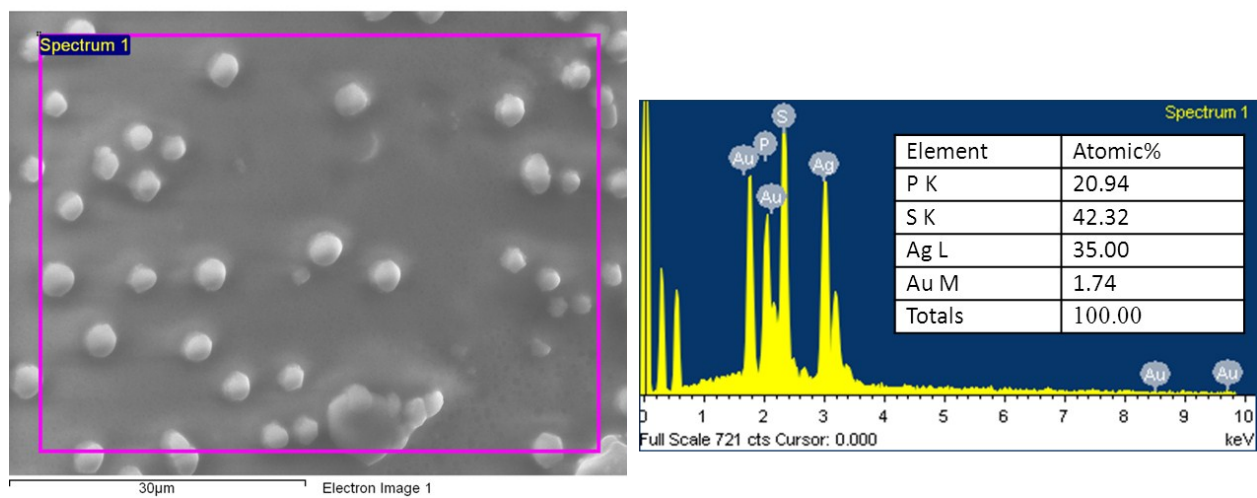


Figure S5. FE-SEM image and EDS spectrum of **2**

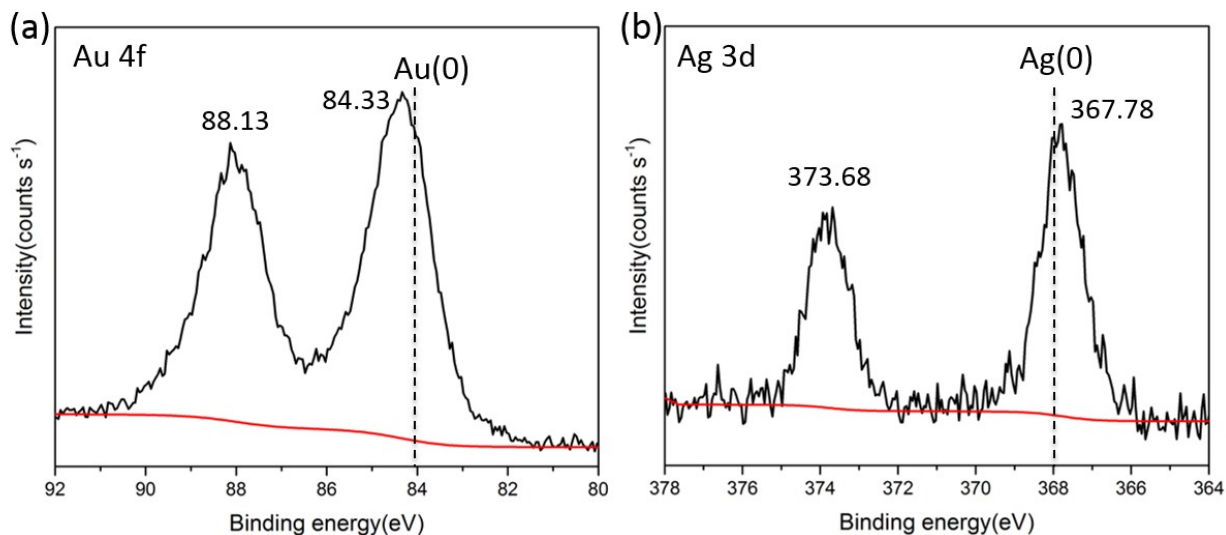


Figure S6. (a) Au 4f, (b) Ag 3d in X-ray photoelectron spectroscopy (XPS) spectrum of **1**

Table 2. EDS data for Au/Ag nanoclusters.

Compound	Ag/S atomic ratio [Calculated]	Ag/S atomic ratio [observed]
$[\text{AuAg}_{20}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]^+$	Au: 1.75 % Ag: 35.09 % S: 42.11 % P: 21.05 %	Au: 1.74 % Ag: 35.00 % S: 42.32 % P: 20.94 %
$[\text{AuAg}_{19}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$	Au: 1.79 % Ag: 35.71 % S: 42.86 % P: 21.43 %	Au: 1.75 % Ag: 35.21 % S: 42.23 % P: 20.81%

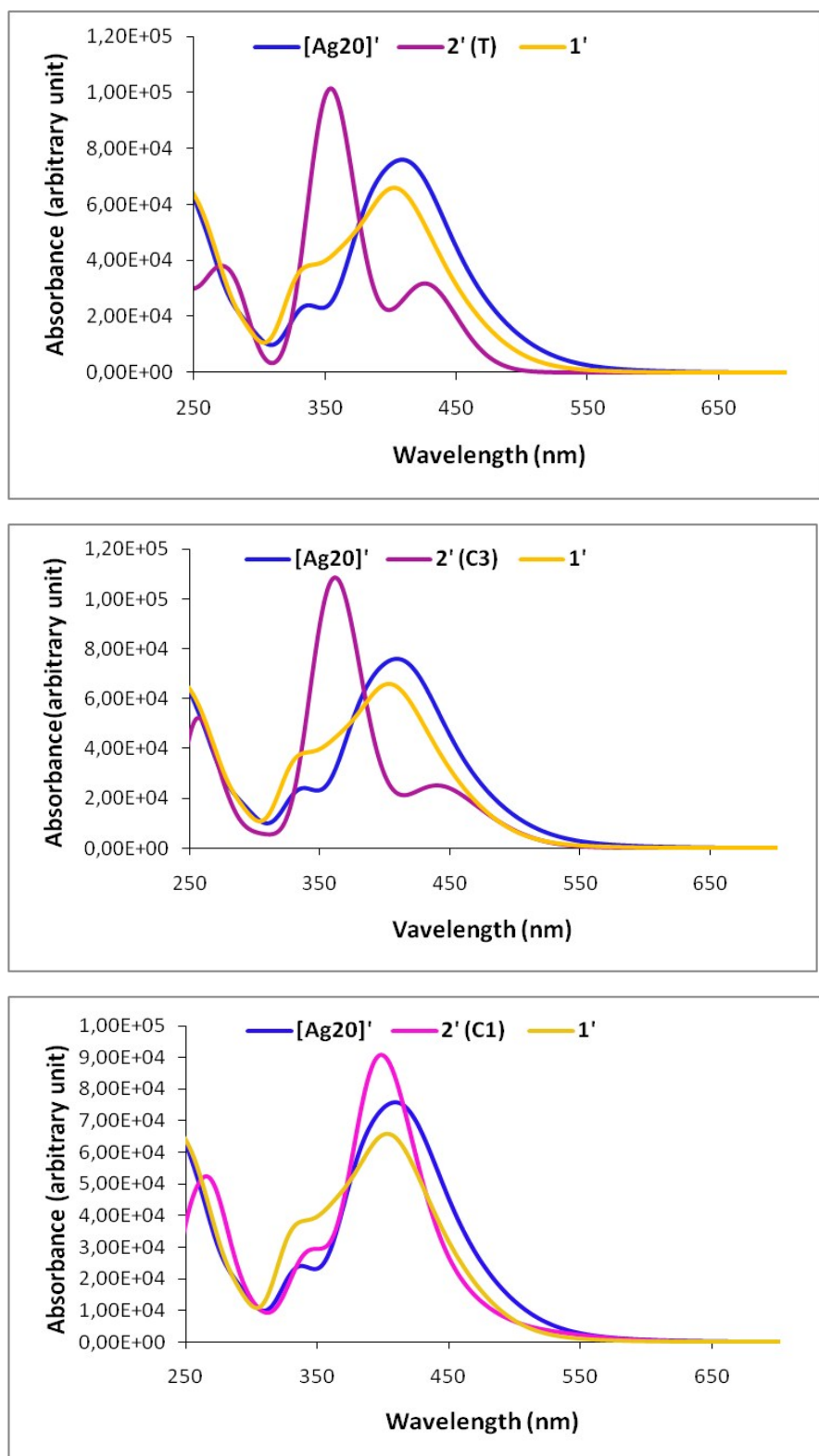


Figure S7. The TD-DFT simulated spectra of $[Ag_{20}]'$, $1'$ and $2'$ assuming for the latter species structures of T (top), C_3 (middle) and C_1 symmetry.

Computational Details

Geometry optimizations at the density functional theory (DFT) level were carried out using the Gaussian 09 package.³ The BP86 functional⁴ was used together with the general triple- ξ polarized Def2-TZVPbasis set from EMSL basis set exchange library, with an all-electron basis set on silver.⁵ All optimized geometries were fully characterized as true minima via analytical frequency calculations (no imaginary values). Natural atomic orbital (NAO) populations were computed with the NBO 5.0 program.⁶ The energy of reaction $\mathbf{1}' + \text{AgCl} \rightarrow \mathbf{2}' + \text{Cl}^-$ was computed assuming THF as implicit solvent using the PCM model.⁷ The UV-visible transitions were calculated by means of TD-DFT calculations⁸ on the optimized geometries with the CAM-B3LYP functional⁹ which is more appropriate than BP86 for computing charge-transfer excitation energies.

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