Supplementary Information

Doping Effect on the Structure and Properties of Eight-Electron Silver Nanoclusters

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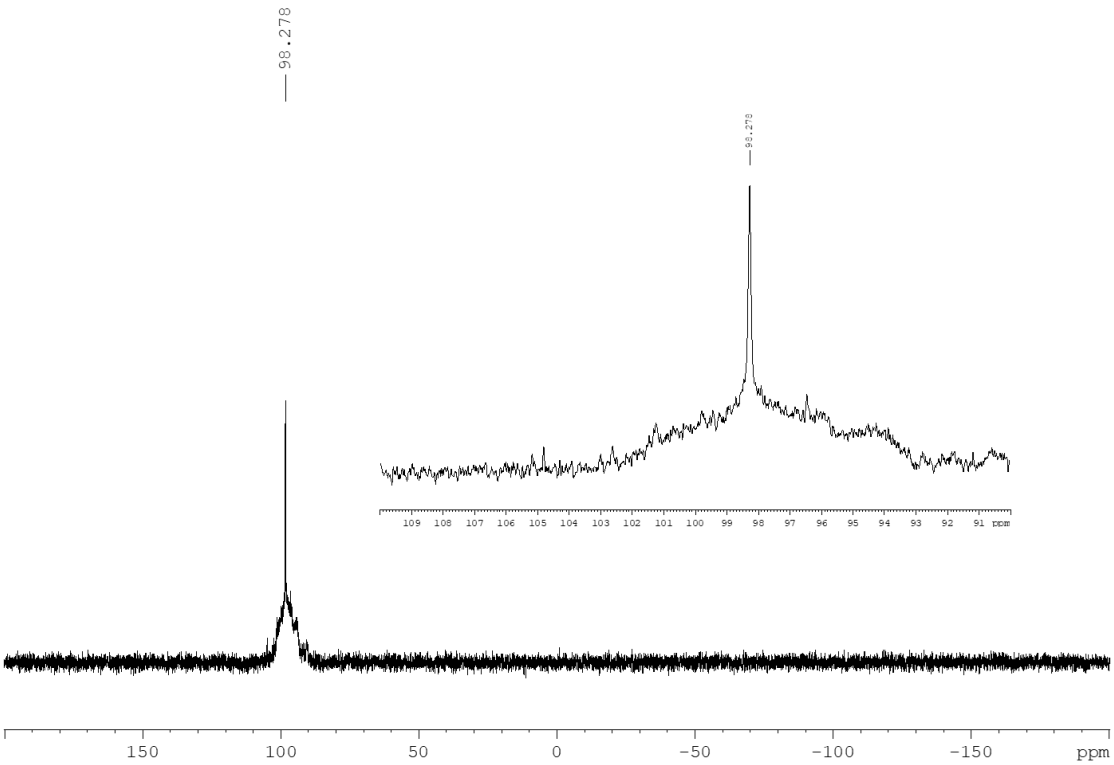

FIG. S1. The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **1**.

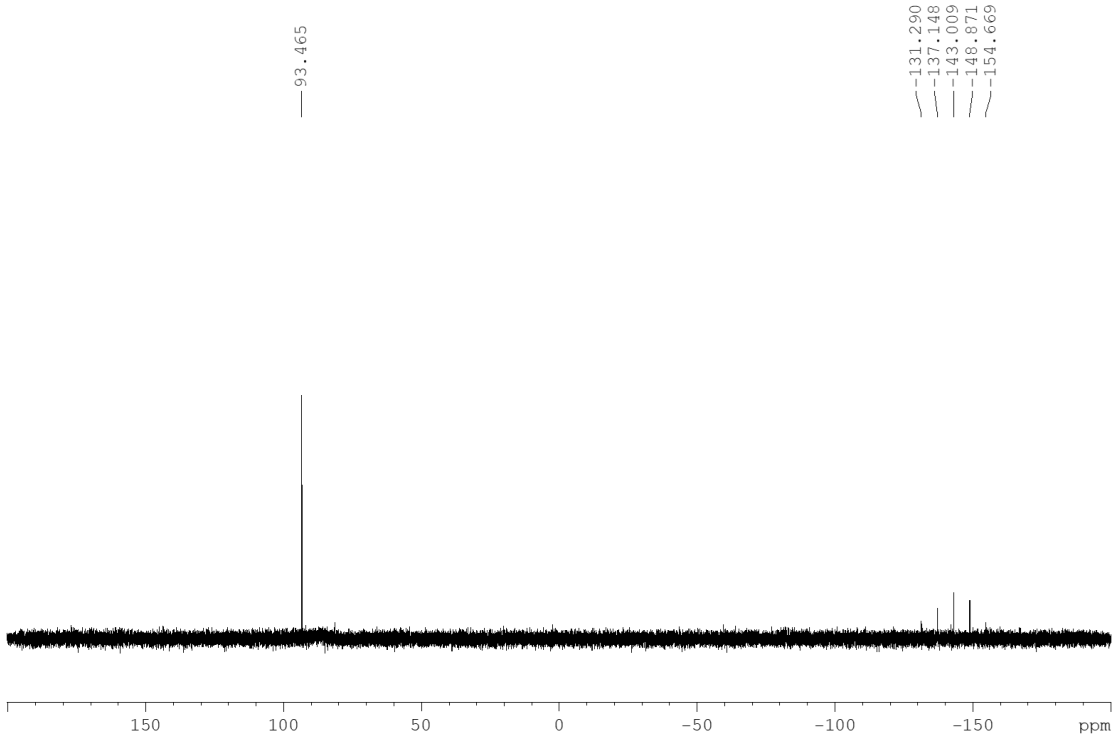

FIG. S2. The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2**.

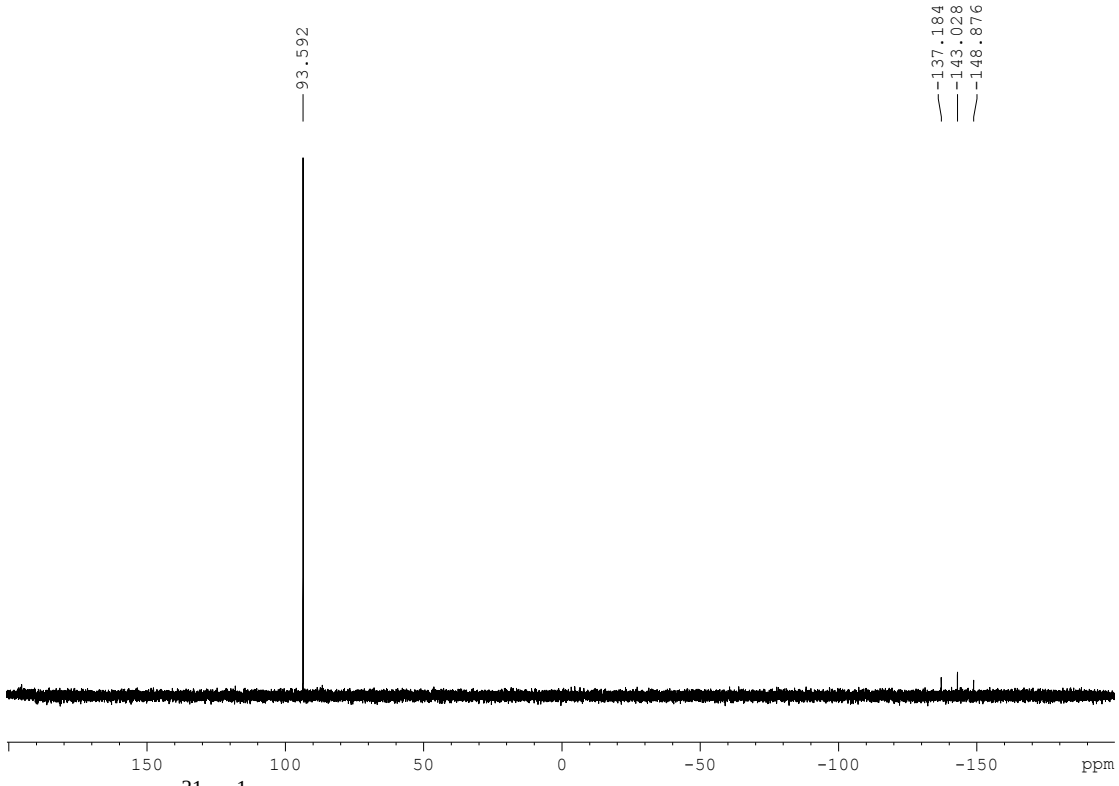

FIG. S3. The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **3**.

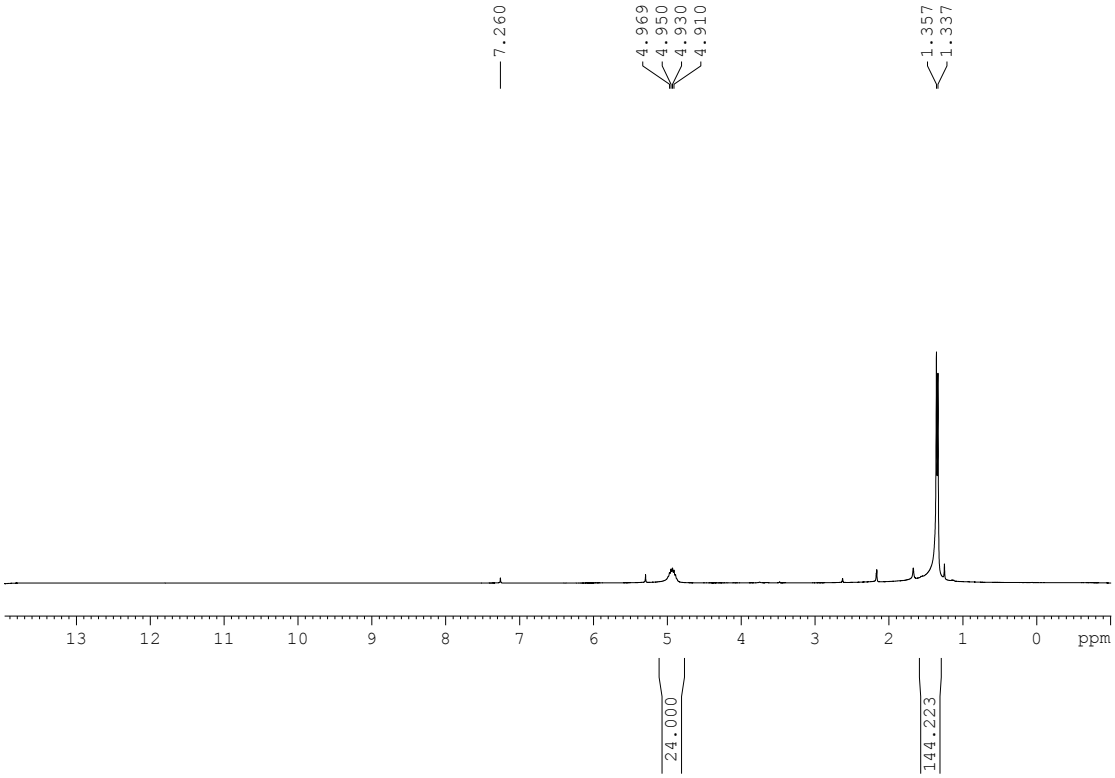

FIG. S4. The ^{1}H NMR ($CDCl_3$) spectrum of **1**.

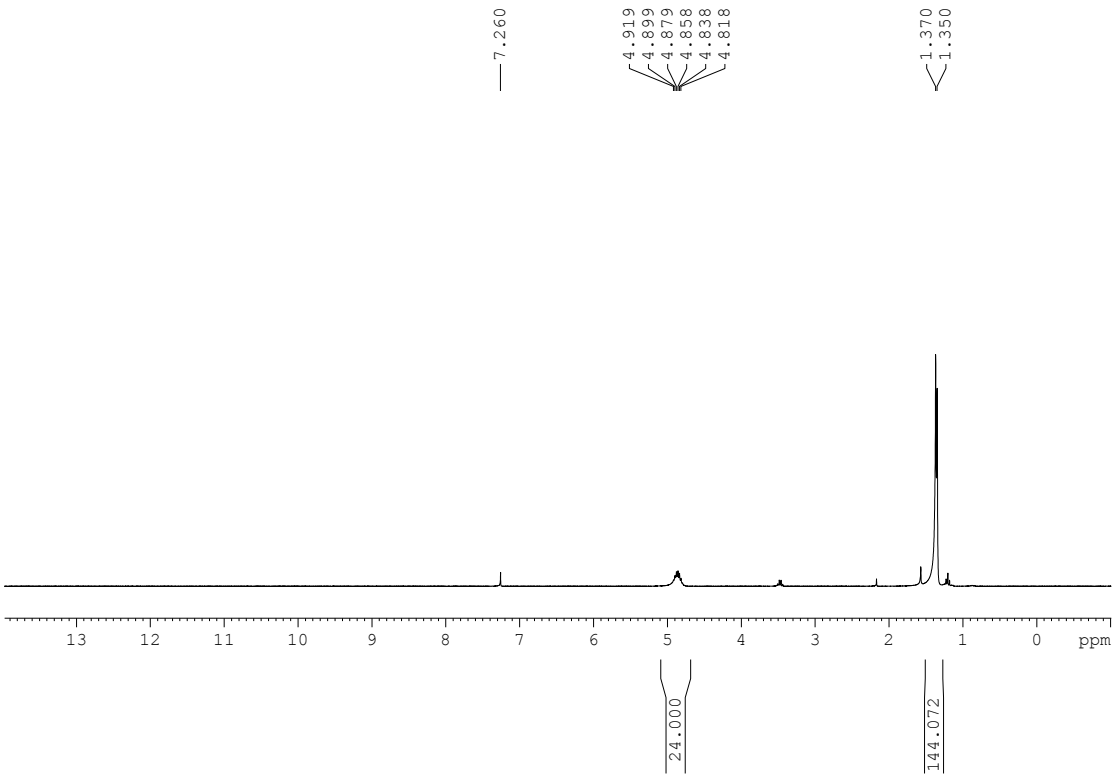

FIG. S5. The ^{1}H NMR ($CDCl_3$) spectrum of **2**.

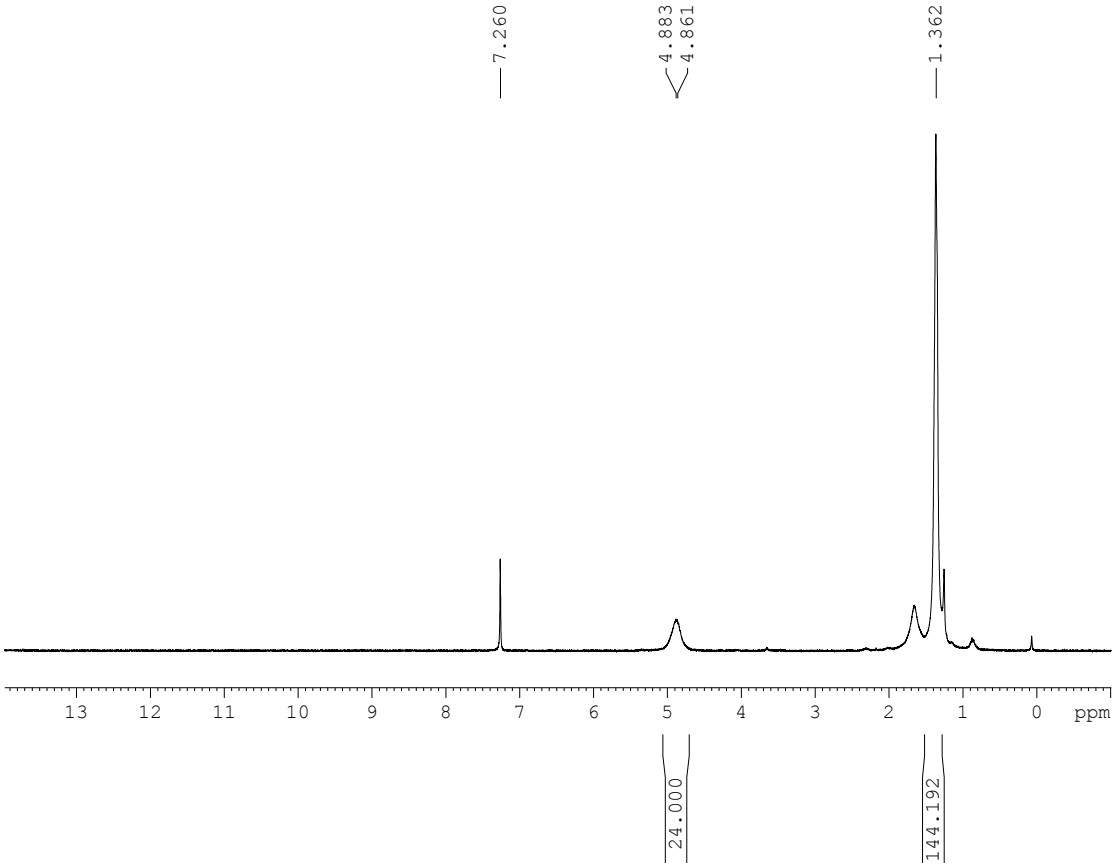

FIG. S5. The ^{1}H NMR ($CDCl_3$) spectrum of **3**.

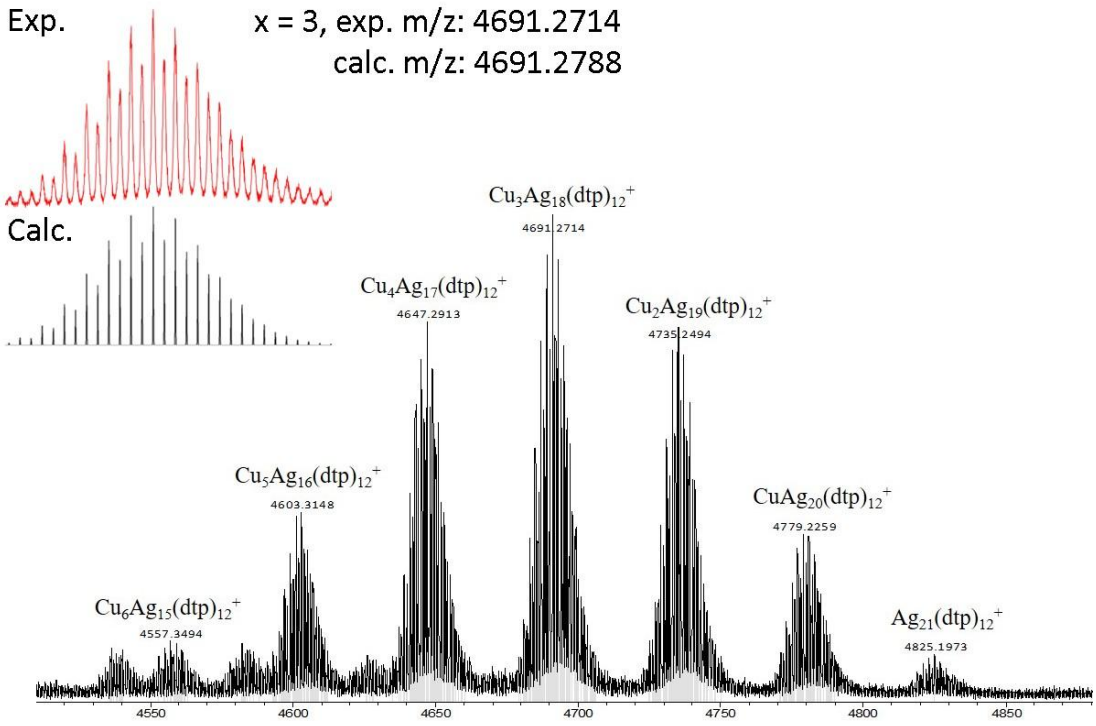

FIG. S7. ESI-MS spectrum of **2**. The distribution of molecular ion peaks is corresponding to $[Cu_xAg_{21-x}\{S_2P(O^iPr)_2\}_{12}]^+$ (x = 0-6).

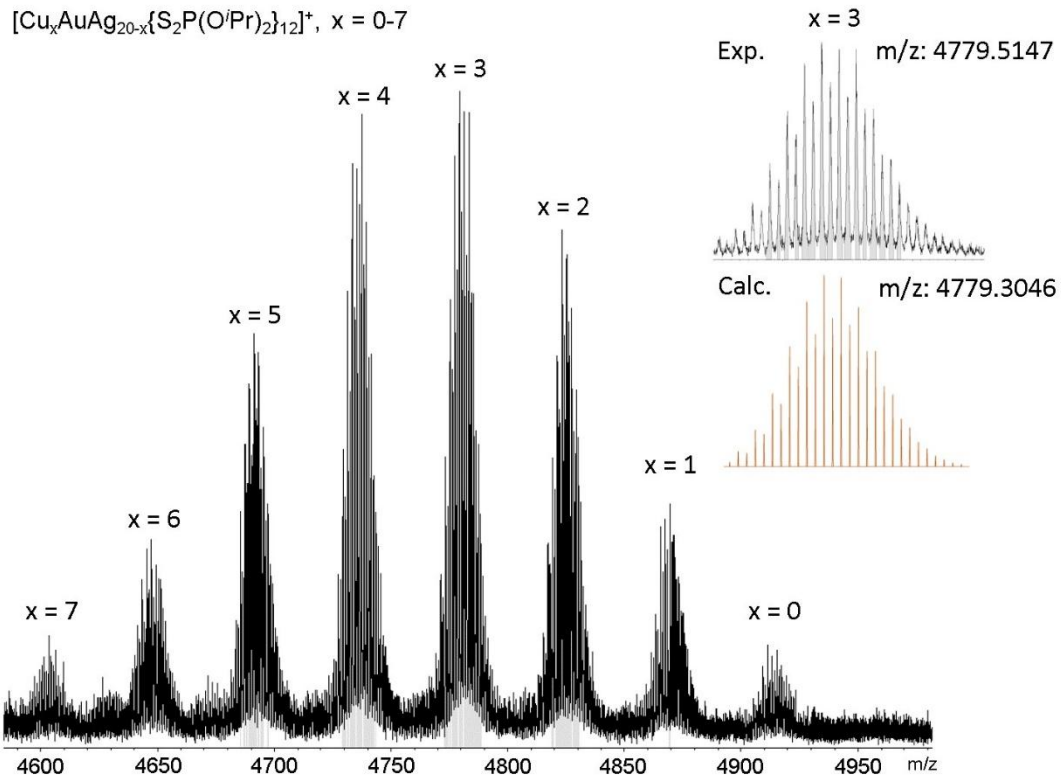

FIG. S8. ESI-MS spectrum of **3**. The distribution of molecular ion peaks is corresponding to $[Cu_xAuAg_{20-x}\{S_2P(O^iPr)_2\}_{12}]^+$ (x = 0-7).

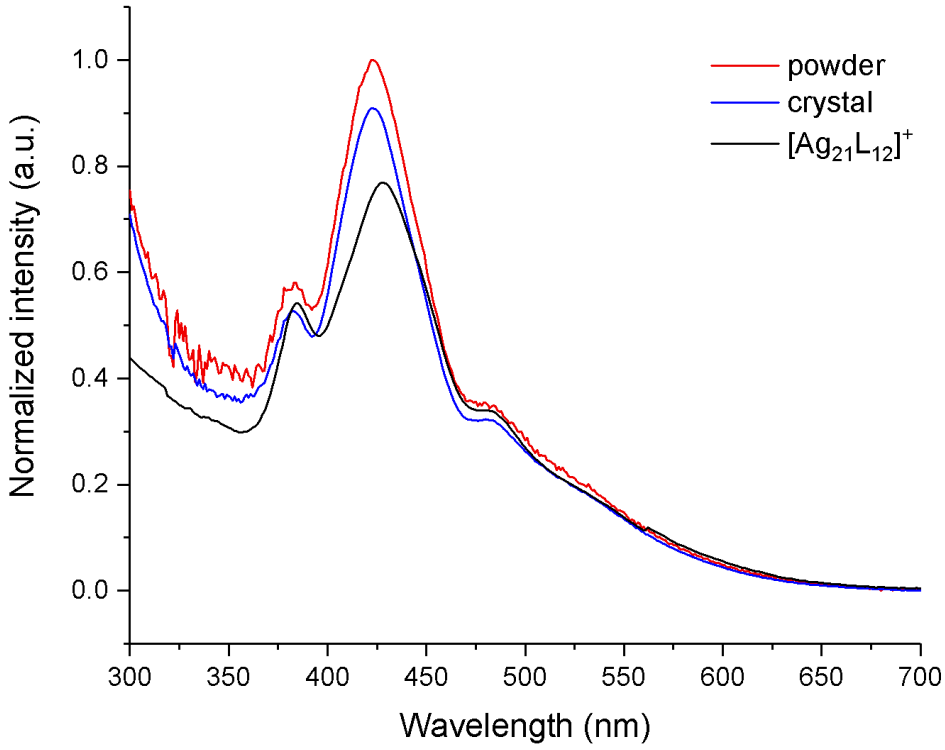

FIG. S9. The absorption spectra of **2** in powder (ref line), crystal (blue line), and $[Ag_{21}\{S_2P(O^iPr)_2\}_{12}]^+$ (black line) in 2-MeTHF.

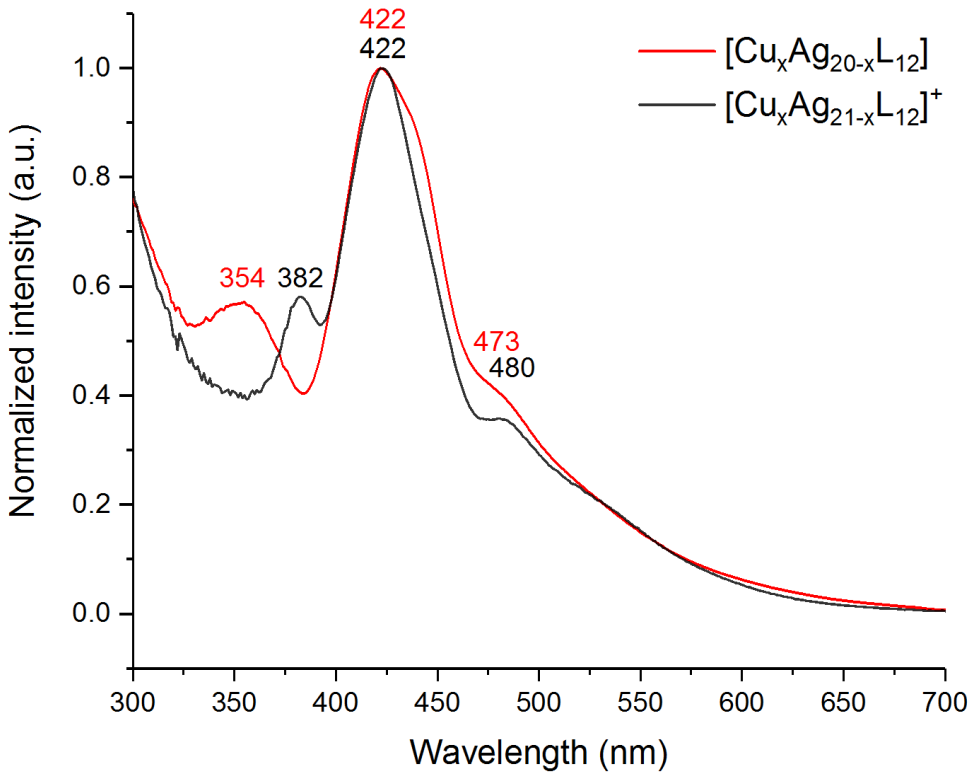

FIG. S10. The absorption spectrum of **1** (red line) and **2** (black line) in 2-MeTHF.

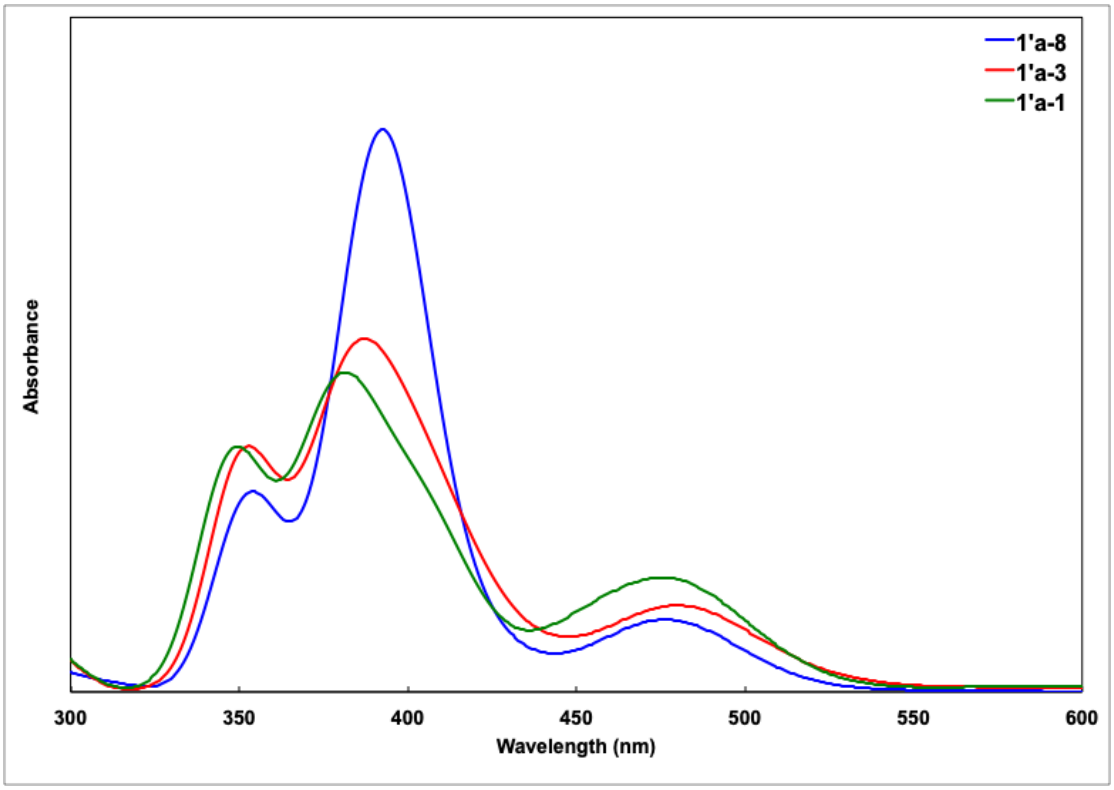

FIG. S11. The TD-DFT-simulated absorption spectra of a selection of positional isomers of **1a'** (see main text).

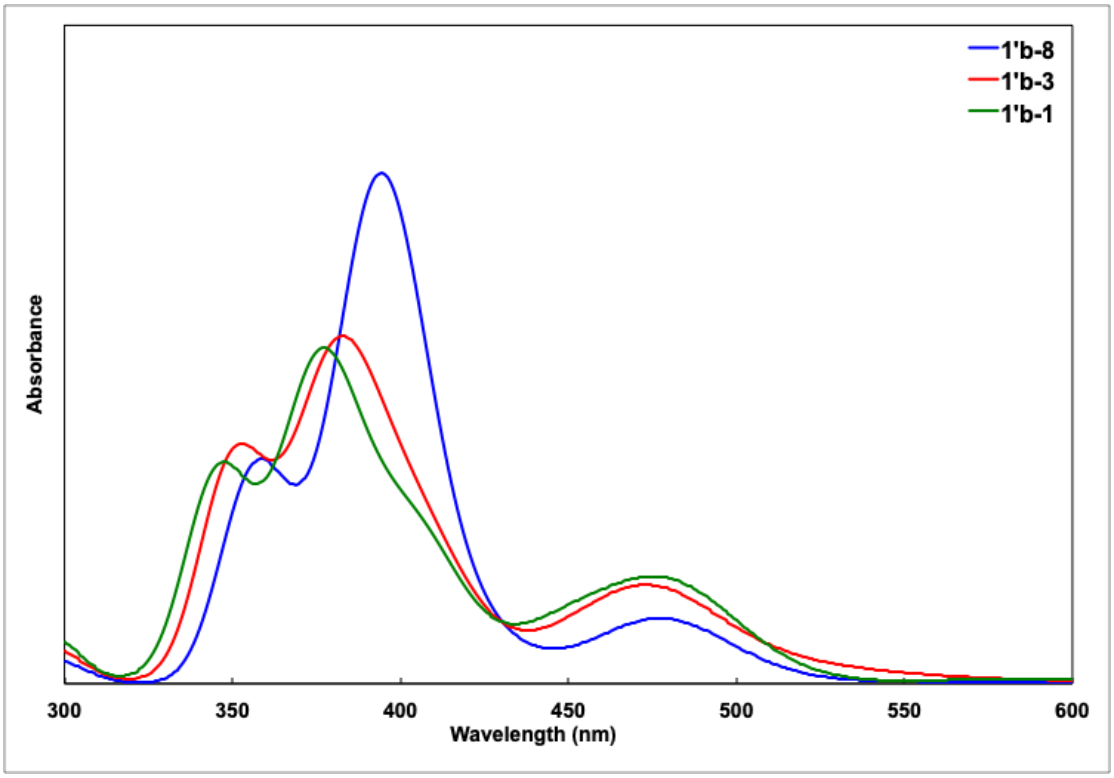

FIG. S12. The TD-DFT-simulated absorption spectra of a selection of positional isomers of **1b'** (see main text).

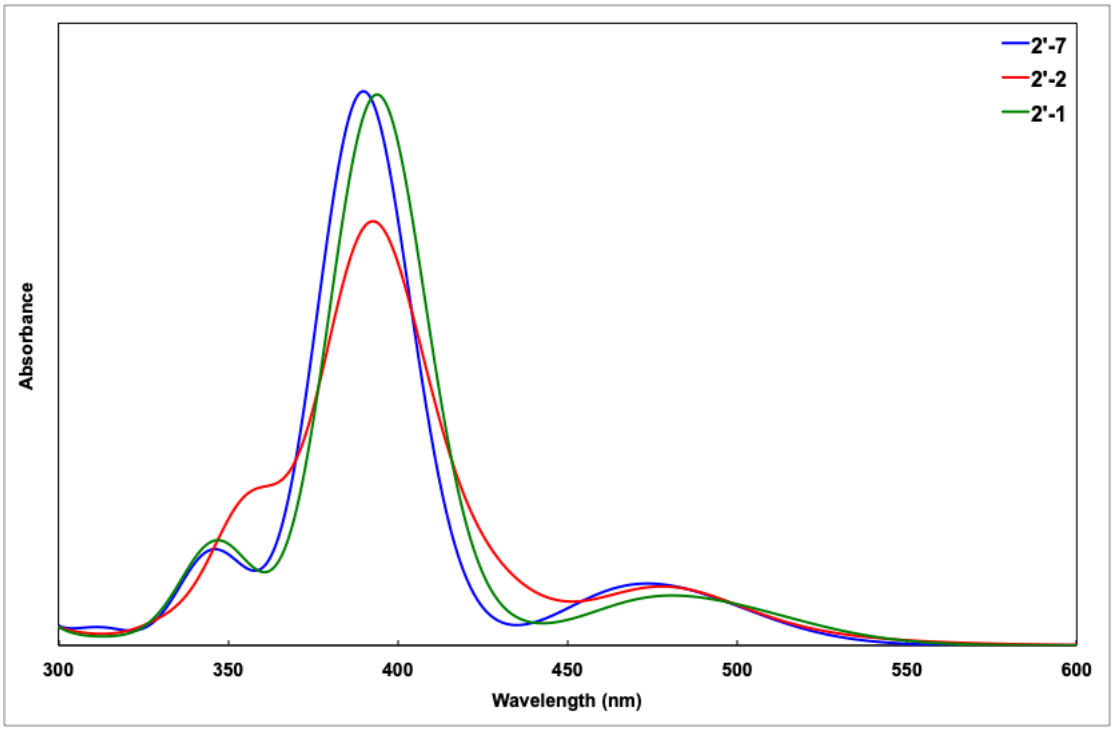

FIG. S13. The TD-DFT-simulated absorption spectra of a selection of positional isomers of **2'** (see main text).

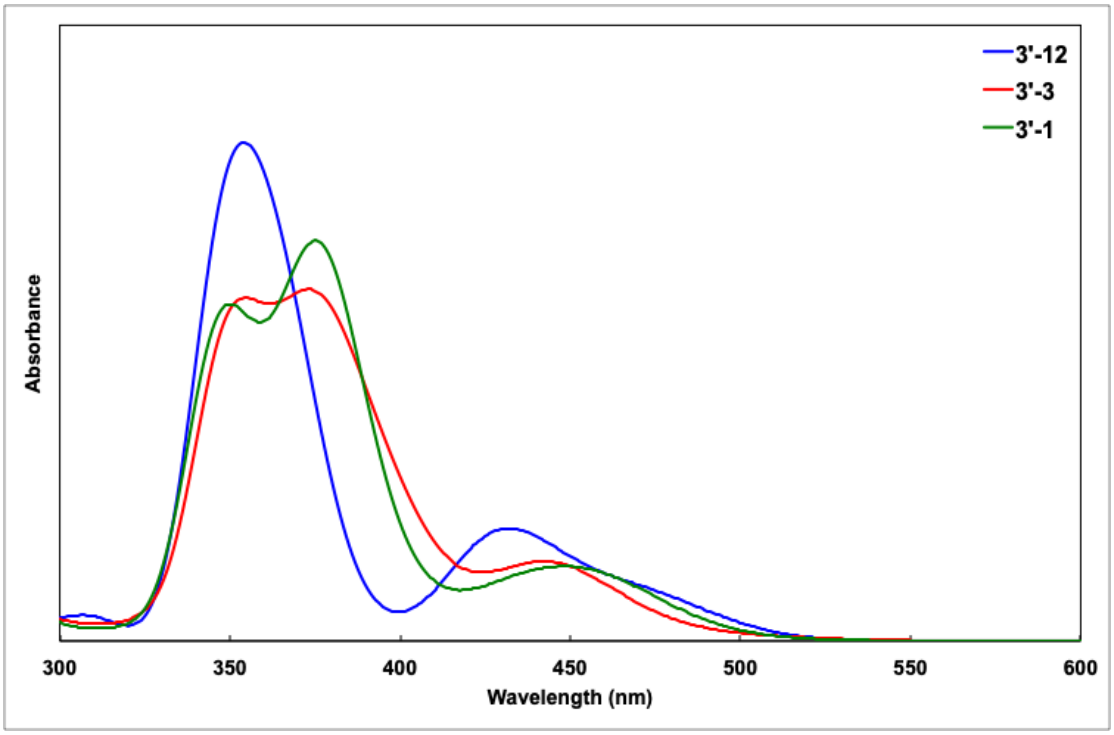

FIG. S14. The TD-DFT-simulated absorption spectra of a selection of positional isomers of **3'** (see main text).

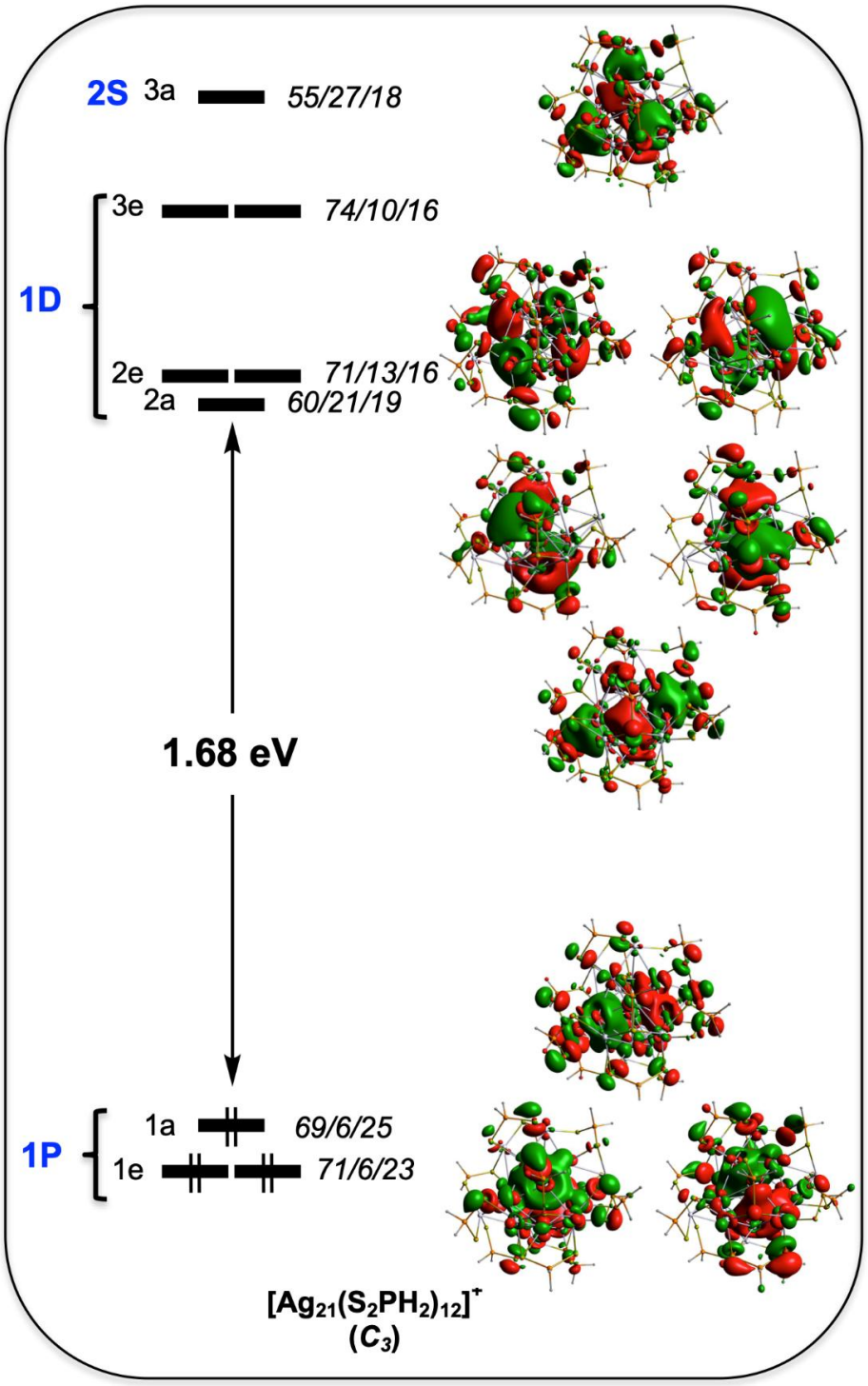

FIG. S15. Frontier Kohn-Sham MO diagram of the homometallic $[Ag_{21}(S_2PH_2)_{12}]^+$ model of C_3 symmetry. The MO localizations are given in % as Ag_{13}(icosahedron)/Ag_8(caps)/ligands.

TABLE SI. UV-vis absorption data of M_{20} and M_{21} nanoclusters.

M_{20} nanoclusters	*UV-vis (λ, nm; ε, $M^{-1}cm^{-1}$)*
$[Ag_{20}\{S_2P(O^iPr)_2\}_{12}]$ [a]	354 (4400), 422 (7700), 473 (3300)
$[Cu_xAg_{20-x}\{S_2P(O^iPr)_2\}_{12}]$ (**1**, powder)	354 (4000), 422 (6100), 473 (2600)
$[Cu_3Ag_{17}\{S_2P(O^iPr)_2\}_{12}]_{0.5}[Cu_4Ag_{16}\{S_2P(O^iPr)_2\}_{12}]_{0.5}$ ($[\mathbf{1a}]_{0.5}[\mathbf{1b}]_{0.5}$, crystal)	355 (4000), 422 (6100), 473 (2600)
M_{21} nanoclusters	
$[Ag_{21}\{S_2P(O^iPr)_2\}_{12}]PF_6$ [b]	385 (4900), 428 (6900), 480 (3000)
$[Cu_xAg_{21-x}\{S_2P(O^iPr)_2\}_{12}]PF_6$ (**2**, powder)	382 (3900), 422 (5600), 480 (2400)
$[Cu_4Ag_{17}\{S_2P(O^iPr)_2\}_{12}]PF_6$ (**2**, crystal)	382 (3900), 422 (5600), 480 (2400)
$[AuCu_xAg_{20-x}\{S_2P(O^iPr)_2\}_{12}]PF_6$ (**3**)	373 (4100), 413 (4700), 464 (2100)

[a] Chem. Eur. J. **22**, 9943-9947 (2016). [b] Angew. Chem. Int. Ed. **54**, 3702-3706 (2015).

Table SII. Selected crystallographic data of [**1a**]$_{0.5}$[**1b**]$_{0.5}$ and **2**.

Compound	$[Cu_3Ag_{17}\{S_2P(O^iPr)_2\}_{12}]_{0.5}$-$[Cu_4Ag_{16}\{S_2P(O^iPr)_2\}_{12}]_{0.5}$ [**1a**]$_{0.5}$[**1b**]$_{0.5}$	$[Cu_4Ag_{17}\{S_2P(O^iPr)_2\}_{12}]PF_6$ (**2**)
CCDC Number	2073787	2057371
Chemical formula	$C_{144}H_{336}Ag_{33}Cu_7O_{48}P_{24}S_{48}$	$C_{72}H_{168}Ag_{17}Cu_4F_6O_{24}P_{13}S_{24}$
Formula weight	9122.76	4792.05
Wavelength, Å	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	16.7730(18)	16.8518(4)
b, Å	30.745(3)	30.8520(7)
c, Å	29.873(3)	30.5757(7)
α, deg.	90	90
β, deg.	94.371(2)	97.1300(7)
γ, deg.	90	90
V, Å^3	15360(3)	15773.7(6)
Z	4	4
Temperature, K	100(2)	150(2)
ρ_{calcd}, g/cm^3	1.972	2.018
μ, mm^{-1}	3.023	3.088
θ_{max}, deg.	25.165	24.999
Completeness, %	99.3	99.9
Reflection collected / unique	80382 / 27352 [R_{int} = 0.0698]	93791 / 27744 [R_{int} = 0.0471]
Restraints / parameters	432 / 1417	529 / 1516
[a] $R1$, [b] $wR2$ [I > 2σ(I)]	0.0668, 0.1310	0.0504, 0.1202
[a] $R1$, [b] $wR2$ (all data)	0.0907, 0.1413	0.0739, 0.1345
GOF	1.127	1.087
Largest diff. peak and hole, e/Å^3	1.780 and -1.623	2.419 and -0.982

[a] $R1 = \Sigma \mid\mid F_o \mid - \mid Fc \mid\mid / \Sigma \mid F_o \mid$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.