Supporting Information

Soluble Silver Acetylide for the Construction and Structural Conversion of All-Alkynyl-Stabilized High-Nuclearity Homoleptic Silver Clusters

Rui Zhang,[a] Xiang Hao,[b] Xiumin Li,[a] Zhengyang Zhou,[c] Junliang Sun[c]

and Rui Cao*[,a,d]

[a] Department of Chemistry, Renmin University of China, Beijing 100872, China.

[b] Center for Physicochemical Analysis and Measurement, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[c] College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

[d] School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China.

*To whom correspondence should be addressed, Email: ruicao@ruc.edu.cn

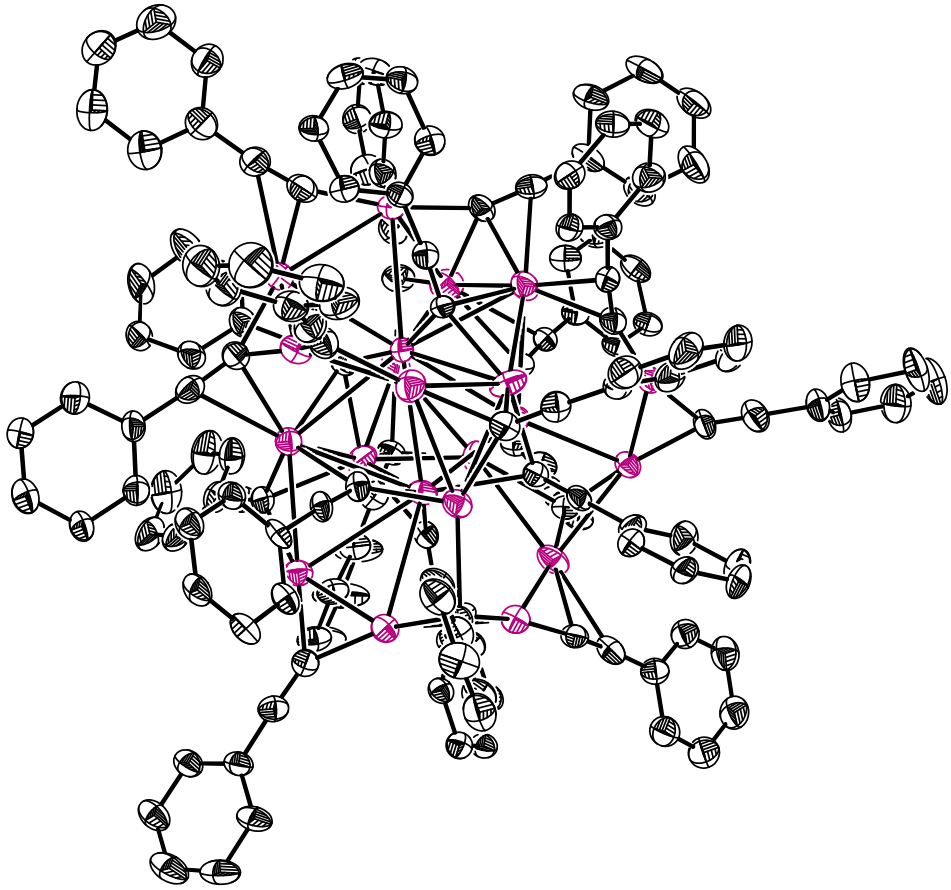

Figure S1. Thermal ellipsoid plot (50% probability) of the [Ag_{21}] cluster of complex **1**. All hydrogen atoms and *tert*-butyl moieties are omitted for clarity.

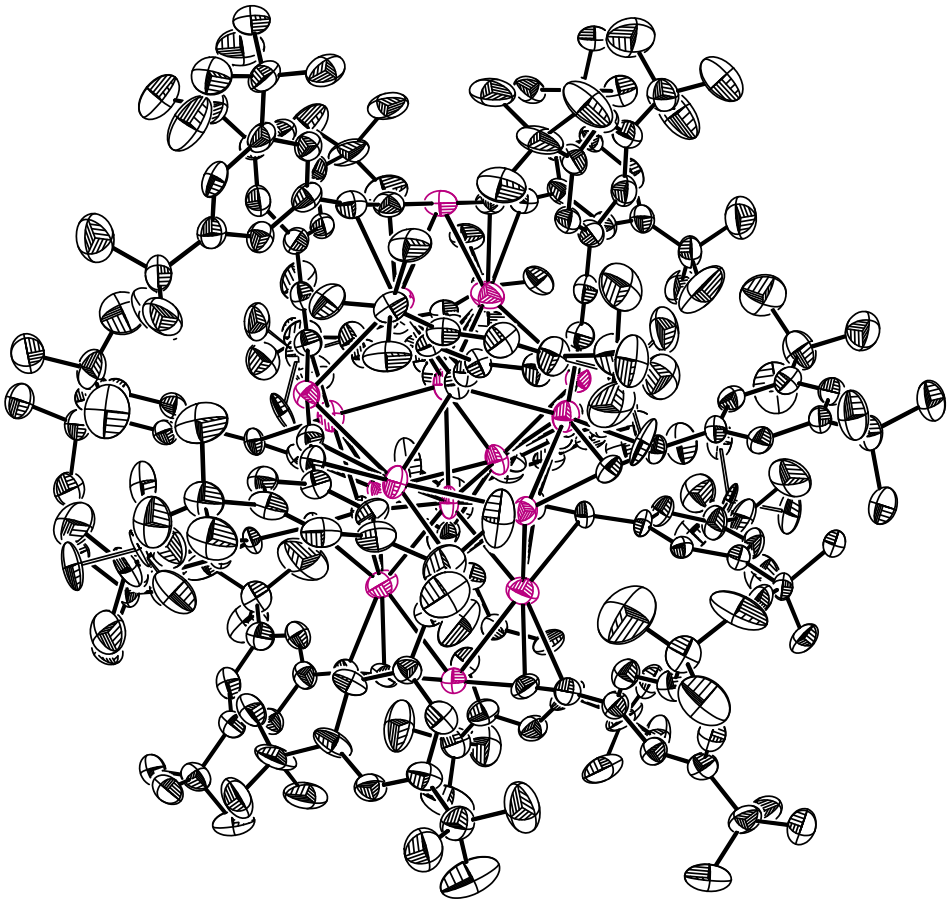

Figure S2. Thermal ellipsoid plot (50% probability) of the [Ag_{16}] cluster of complex **2**. All hydrogen atoms are omitted for clarity.

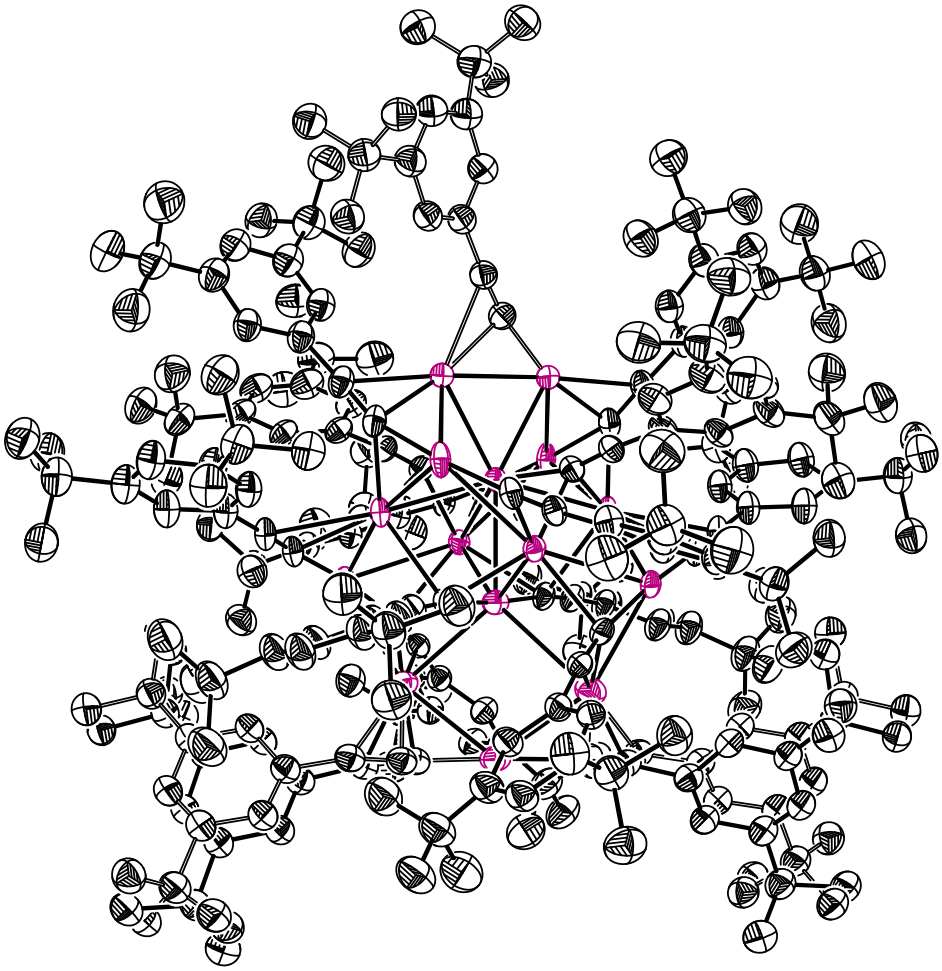

Figure S3. Thermal ellipsoid plot (50% probability) of the [Ag_{15}] cluster of complex **3**. All hydrogen atoms are omitted for clarity.

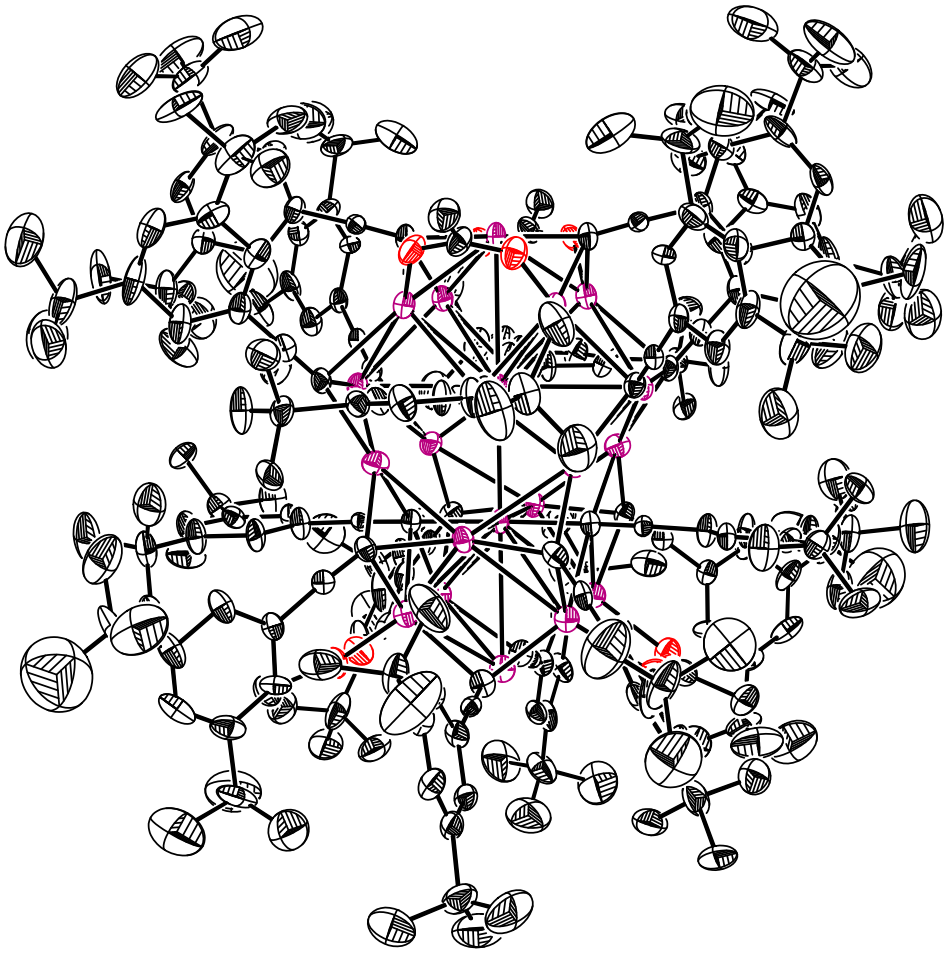

Figure S4. Thermal ellipsoid plot (50% probability) of the [Ag_{20}] cluster of complex **4**. All hydrogen atoms and acetate groups are omitted for clarity.

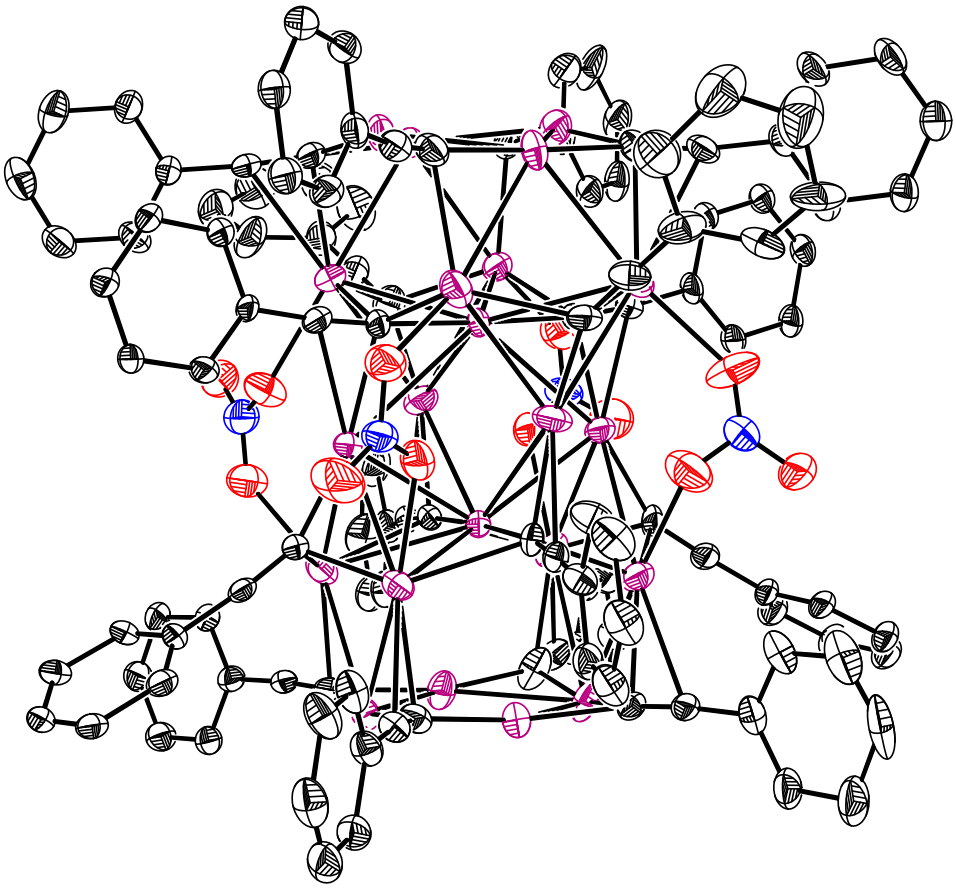

Figure S5. Thermal ellipsoid plot (50% probability) of the [Ag_{22}] cluster of complex **5**. All hydrogen atoms and *tert*-butyl groups are omitted for clarity.

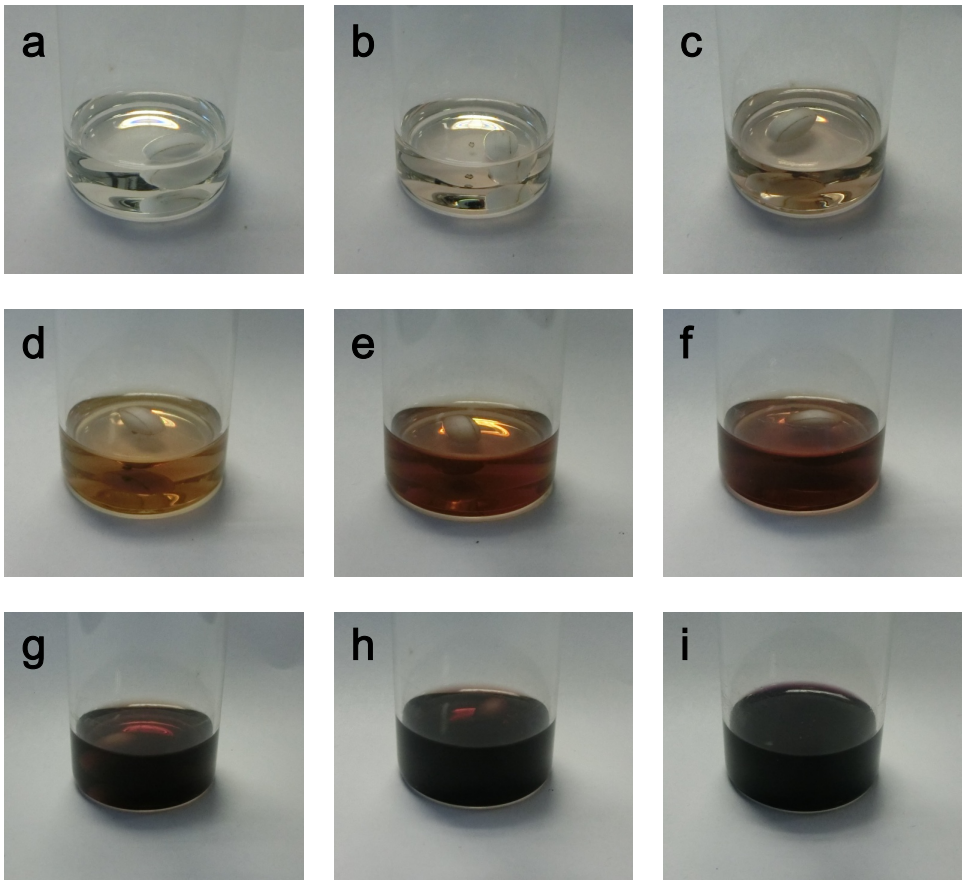

Figure S6. Photography of silver 3,5-di-*tert*-butyl-phenylacetylide in a DCM/ethanol solution (a), and with the addition of 0.05 equivalents of $NaBH_4$ after 1 min (b), 2 min (c), 5 min (d), 8 min (e), 10 min (f), 12 min (g), 15 min (h), and 2 h (i).

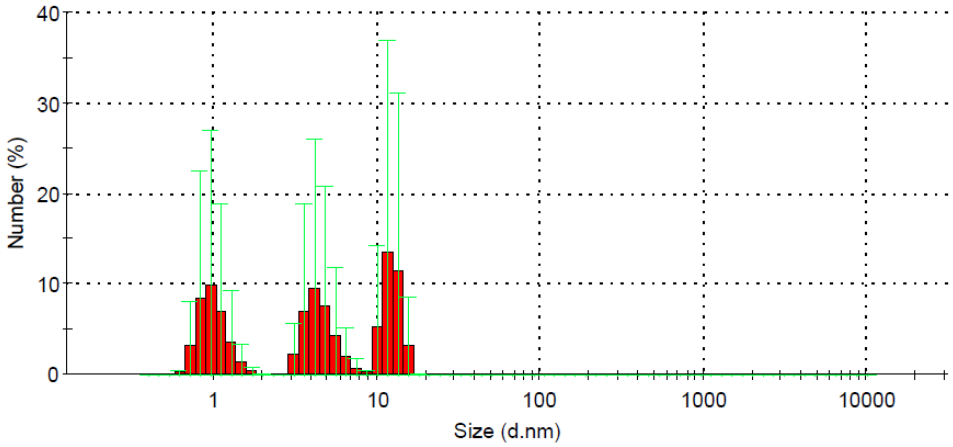

Figure S7. Dynamic light scattering of silver 3,5-di-*tert*-butyl-phenylacetylide in a DCM/ethanol solution after the addition of 0.05 equivalents of $NaBH_4$, showing the absence of aggregated silver nanoparticles.

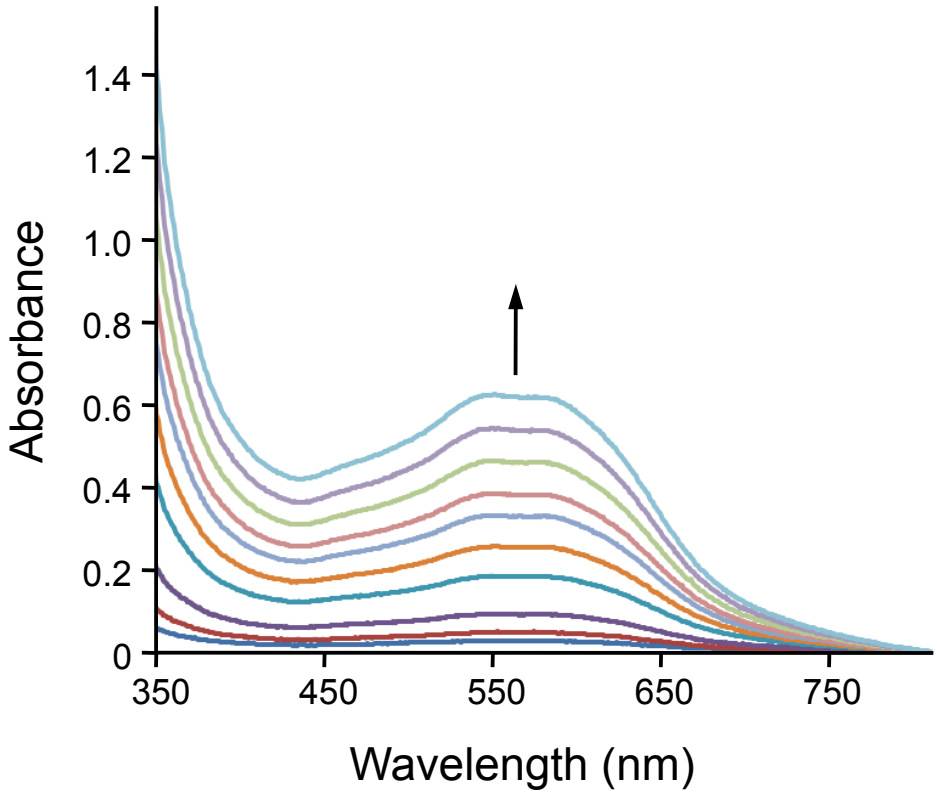

Figure S8. UV-vis absorption spectra of silver 3,5-di-*tert*-butyl-phenylacetylide in a DCM/ethanol solution after the addition of increasing amounts of $NaBH_4$, from 0.05 eq to 0.50 eq.

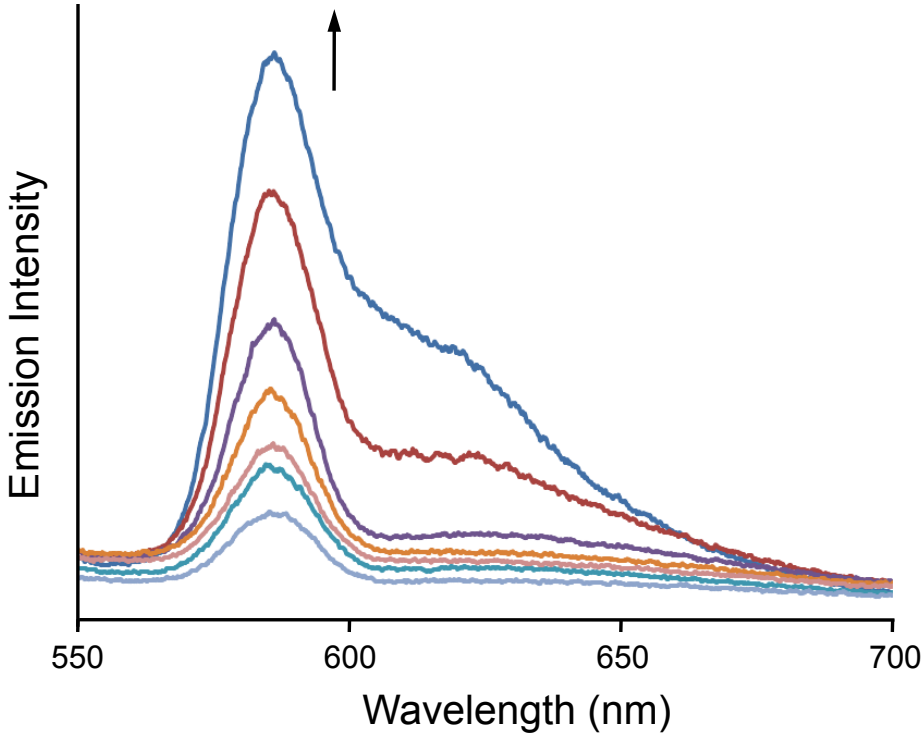

Figure S9. Emission spectra of silver 3,5-di-*tert*-butyl-phenylacetylide in a DCM/ethanol solution after the addition of increasing amounts of $NaBH_4$, from 0.05 eq to 0.50 eq. The excitation wavelength is 500 nm.

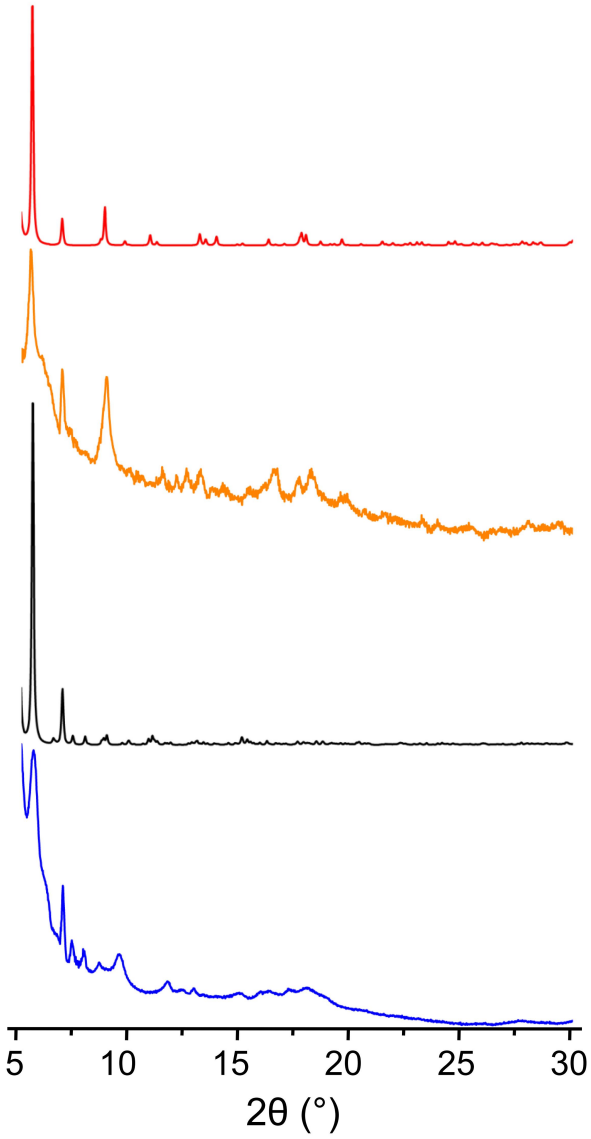

Figure S10. PXRD patterns. From top to bottom: simulated from the single crystal X-ray data of **2**; experimental pattern of **2**; simulated from the single crystal X-ray data of **3**; experimental pattern of **3**.

Table S1. Crystal data and structure refinement parameters for the X-ray structure determination of complex **1**.

complex	**1**
molecular formula	$C_{320}H_{421}Ag_{21}O$
formula wt. (g mol^{-1})	6548.81
temperature (K)	153(2)
radiation (λ, Å)	0.71073
crystal system	Monoclinic
space group	$P2_1/c$ (#14)
a (Å)	21.6397(16)
b (Å)	41.645(3)
c (Å)	41.752(3)
β (°)	99.8190(10)
Volume ($Å^3$)	37076(5)
Z	4
ρ_{calcd} (g cm^{-3})	1.173
μ (mm^{-1})	1.121
F(000)	13344
crystal size (mm^3)	0.23 × 0.20 × 0.20
Theta range for data collection	2.20 to 26.45°
reflections collected	275045
independent reflections	75952 [R(int) = 0.0701]
Completeness to theta = 26.37°	99.4%
absorption correction	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	75952 / 5917 / 3318
goodness-of-fit on F^2	1.034
final R indices	$R_1{}^a$ = 0.0733
[R > 2σ (I)]	$wR_2{}^b$ = 0.1832
R indices (all data)	$R_1{}^a$ = 0.1195
	$wR_2{}^b$ = 0.2058
largest diff. peak and hole (e $Å^{-3}$)	2.301 and -0.911

$^aR_1 = \Sigma||F_o| - |F_c|| / |F_o|$, $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$

Table S2. Crystal data and structure refinement parameters for the X-ray structure determination of complex **2**.

complex	**2**
molecular formula	$C_{256}H_{336}Ag_{16}$
formula wt. (g mol^{-1})	5139.17
temperature (K)	150(2)
radiation (λ, Å)	0.71073
crystal system	Tetragonal
space group	$I\bar{4}$ (#82)
a (Å)	25.8070(9)
c (Å)	20.5657(10)
Volume ($Å^3$)	13696.8(9)
Z	2
ρ_{calcd} (g cm^{-3})	1.246
μ (mm^{-1})	1.158
F(000)	5248
crystal size (mm^3)	0.25 × 0.24 × 0.22
Theta range for data collection	2.23 to 26.47°
reflections collected	158423
independent reflections	14097 [R(int) = 0.0650]
Completeness to theta = 26.37°	99.7%
absorption correction	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	14097 / 179 / 651
goodness-of-fit on F^2	1.041
final R indices	$R_1{}^a$ = 0.0681
[R > 2σ (I)]	$wR_2{}^b$ = 0.1889
R indices (all data)	$R_1{}^a$ = 0.0912
	$wR_2{}^b$ = 0.2105
Flack parameter	0.105(8)
largest diff. peak and hole (e $Å^{-3}$)	2.386 and -1.157

$^aR_1 = \Sigma||F_o| - |F_c|| / |F_o|$, $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$

Table S3. Crystal data and structure refinement parameters for the X-ray structure determination of complex **3**.

complex	**3**
molecular formula	$C_{240}H_{315}Ag_{15}$
formula wt. (g mol^{-1})	4817.97
temperature (K)	150(2)
radiation (λ, Å)	0.71073
crystal system	Orthorhombic
space group	*C*cca (#68)
a (Å)	35.961(4)
b (Å)	36.933(4)
c (Å)	40.933(5)
Volume (Å^3)	54364(11)
Z	8
ρ_{calcd} (g cm^{-3})	1.177
μ (mm^{-1})	1.094
F(000)	19680
crystal size (mm^3)	0.35 × 0.30 × 0.25
Theta range for data collection	2.17 to 26.38°
reflections collected	278541
independent reflections	27696 [R(int) = 0.0581]
Completeness to theta = 26.37°	99.5%
absorption correction	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	27696 / 2740 / 1367
goodness-of-fit on F^2	1.034
final R indices	$R_1{}^a$ = 0.0967
[R > 2σ (I)]	$wR_2{}^b$ = 0.2582
R indices (all data)	$R_1{}^a$ = 0.1476
	$wR_2{}^b$ = 0.3043
largest diff. peak and hole (e Å^{-3})	4.071 and -2.621

$^aR_1 = \Sigma||F_o| - |F_c|| / |F_o|$, $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$

Table S4. Crystal data and structure refinement parameters for the X-ray structure determination of complex **4**.

complex	**4**
molecular formula	$C_{264}H_{348}Ag_{20}O_8$
formula wt. (g mol^{-1})	5806.82
temperature (K)	150(2)
radiation (λ, Å)	0.71073
crystal system	Tetragonal
space group	$I\bar{4}$ (#82)
a (Å)	27.3816(7)
c (Å)	19.3573(6)
Volume (Å^3)	14513.2(7)
Z	2
ρ_{calcd} (g cm^{-3})	1.329
μ (mm^{-1})	1.360
F(000)	5872
crystal size (mm^3)	0.15 × 0.05 × 0.05
Theta range for data collection	2.35 to 26.43°
reflections collected	44076
independent reflections	14870 [R(int) = 0.0794]
Completeness to theta = 26.37°	99.7%
absorption correction	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	14870 / 205 / 659
goodness-of-fit on F^2	0.987
final R indices	$R_1{}^a$ = 0.0541
[R > 2σ (I)]	$wR_2{}^b$ = 0.1173
R indices (all data)	$R_1{}^a$ = 0.1113
	$wR_2{}^b$ = 0.1368
Flack parameter	-0.01(2)
largest diff. peak and hole (e Å^{-3})	0.796 and -0.426

$^a R_1 = \Sigma||F_o| - |F_c|| / |F_o|$, $^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$

Table S5. Crystal data and structure refinement parameters for the X-ray structure determination of complex **5**.

complex	**5**
molecular formula	$C_{264}H_{362}Ag_{22}N_4O_{18}$
formula wt. (g mol^{-1})	6252.72
temperature (K)	153(2)
radiation (λ, Å)	0.71073
crystal system	Monoclinic
space group	*C*2/c (#15)
a (Å)	80.349(10)
b (Å)	20.033(2)
c (Å)	40.226(5)
β (°)	112.8040(10)
Volume ($Å^3$)	59687(12)
Z	8
ρ_{calcd} (g cm^{-3})	1.392
μ (mm^{-1})	1.456
F(000)	25216
crystal size (mm^3)	0.50 × 0.20 × 0.15
Theta range for data collection	2.23 to 26.36°
reflections collected	191913
independent reflections	60246 [R(int) = 0.0439]
Completeness to theta = 26.37°	98.8%
absorption correction	semi-empirical from equivalents
refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	60246 / 5448 / 3004
goodness-of-fit on F^2	1.037
final R indices	$R_1{}^a$ = 0.0820
[R > 2σ (I)]	$wR_2{}^b$ = 0.2236
R indices (all data)	$R_1{}^a$ = 0.1355
	$wR_2{}^b$ = 0.2687
largest diff. peak and hole (e $Å^{-3}$)	3.529 and -1.186

$^aR_1 = \Sigma||F_o| - |F_c|| / |F_o|$, $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{0.5}$