

Supporting Information

Integration of acetylenic carbon clusters and silver clusters: template synthesis and stability enhancement

Xin He, Hai-Xia Liu, and Liang Zhao*

*The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education),
Department of Chemistry, Tsinghua University, Beijing 100084, China*

zhaolchem@mail.tsinghua.edu.cn

Materials and Methods

General Information. All commercially available chemicals were used without further purification. **TMS-TEE**, **TMS-HEB** and **TMS-PEB** were prepared according to the published methods.¹⁻³ The solvents used in this study were processed by standard procedures. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. ¹H and ¹³C NMR experiments were carried out on a JEOL ECX-400MHz instrument. The morphology of as-prepared clusters was determined on a Hitachi H-7650 transmission electron microscope and a FEI Tecnai G2 20 high resolution transmission electron microscope. Raman spectra were collected using a Renishaw inVia Raman Microscopy at 633 or 532 nm excitation. TGA measurements were conducted on a TGA Q50 analyzer of TA Instrument. UV-Vis-NIR absorption spectra were measured in THF solution at room-temperature on a PerkinElmer Lambda35 spectrophotometer. Photoluminescent property was recorded on a PerkinElmer LS55 spectrophotometer. Lifetime measurements were conducted on an Edinburgh FLS920 instruments.

CAUTION! Silver acetylide complexes are potentially explosive and should be handled with care and in small amounts.

Synthesis of 1. **TMS-TEE** (4.1 mg, 0.01 mmol) was added to a CH₃CN (0.5 ml) solution of AgCO₂CF₃ (220 mg, 1 mmol) under vigorous stirring for half an hour. The reaction mixture was filtered and the filtrate was then diffused by diethyl ether in the dark. After two days, yellow crystals of **1** were deposited in 85% yield (27.7 mg) based on **TMS-TEE**. Elemental analysis for [Ag₁₄(**TEE**)(CF₃CO₂)₁₀(CH₃CN)₆]: C₄₂H₁₈Ag₁₄F₃₀N₆O₂₀, found (calcd): C, 16.46 (16.78); H, 0.58 (0.60); N, 3.15 (2.80).

Synthesis of 2 and 3. The method was similar to that for synthesizing **1**. DMSO was used as the solvent and **TMS-HEB** and **TMS-PEB** were employed instead. The final filtrates were left without disturbing in the dark to produce yellow crystals of **2** and **3** in 75% (42.4 mg) and 64% (27.6 mg) yield, respectively. Elemental analysis for [Ag₂₂(**HEB**)(CF₃CO₂)₁₆·(DMSO)₈]: C₆₆H₄₈Ag₂₂F₄₈O₄₀S₈, found (calcd): C, 15.77 (15.78); H, 1.16 (0.96). Elemental analysis for [Ag₃₄(**PEB**)₂(CF₃CO₂)₂₄·(DMSO)₂₄·(H₂O)₂]: C₁₂₈H₁₅₀Ag₃₄F₇₂O₇₄S₂₄, found (calcd): C, 17.75 (17.72); H, 1.42 (1.74).

X-ray Crystallographic Analysis

Data for complexes **1**, **2** and **3** were collected at 173K with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Rigaku Saturn 724+ CCD diffractometer with frames of oscillation range 0.5° . All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. Non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL program unless otherwise noticed.^{4,5}

Crystal data for $\{[\text{Ag}_{12}\{(\text{C}\equiv\text{C})_2\text{C}=\text{C}(\text{C}\equiv\text{C})_2\}(\text{CF}_3\text{CO}_2)_{10}(\text{CH}_3\text{CN})_4]\cdot[\text{Ag}(\text{CH}_3\text{CN})_4]_2\}_{2/n}$ (**1**) (CCDC-1045345): $\text{C}_{27}\text{H}_{18}\text{Ag}_7\text{F}_{15}\text{N}_6\text{O}_{10}$ $M = 1626.56$, triclinic, space group $P-1$ (No. 2), $a = 8.7316(17) \text{ \AA}$, $b = 15.311(3) \text{ \AA}$, $c = 16.873(3) \text{ \AA}$, $\alpha = 72.77(3)^\circ$, $\beta = 82.43(3)^\circ$, $\gamma = 86.08(3)^\circ$, $V = 2134.8(7) \text{ \AA}^3$, $Z = 2$, $T = 173 \text{ K}$, $D_c = 2.530 \text{ g cm}^{-3}$. The structure, refined on F^2 , converged for 7453 unique reflections ($R_{\text{int}} = 0.0466$) and 6285 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0637$ and $wR_2 = 0.1191$ and a goodness-of-fit = 1.159. Fluorine atoms F11, F31 and F41 are all disordered at two positions owing to the rotation of C-C bond in trifluoroacetate group and their occupancy ratios are 0.9:0.1, 0.92:0.8 and 0.52:0.48, respectively. Packing view of **1** is shown in Fig. S16.

Crystal data for $[\text{Ag}_{22}\{\text{C}_6(\text{C}\equiv\text{C})_6\}(\text{CF}_3\text{CO}_2)_{16}(\text{DMSO})_{16}]\cdot(\text{H}_2\text{O})_{0.5}$ (**2**) (CCDC-1045451): $\text{C}_{82}\text{H}_{96}\text{Ag}_{22}\text{F}_{48}\text{O}_{48.5}\text{S}_{16}$, (excluding the hydrogen atoms of water molecules) $M = 5655.69$, monoclinic, space group $P2_1/n$ (No. 14), $a = 20.700(4) \text{ \AA}$, $b = 23.694(5) \text{ \AA}$, $c = 31.929(6) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 92.38(3)^\circ$, $V = 15646(5) \text{ \AA}^3$, $Z = 4$, $T = 173 \text{ K}$, $D_c = 2.401 \text{ g cm}^{-3}$. The structure, refined on F^2 , converged for 35826 unique reflections ($R_{\text{int}} = 0.0653$) and 31563 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0845$ and $wR_2 = 0.2293$ and a goodness-of-fit = 1.161. Silver atoms Ag2 (Ag23), Ag3 (Ag24), Ag6 (Ag25), Ag10 (Ag26), Ag13 (Ag29), Ag14 (Ag30), Ag16 (Ag31) and Ag22 (Ag32) are disordered at two positions with site occupancy ratios of 0.59:0.41, 0.62:0.38, 0.86:0.14, 0.74:0.26, 0.50:0.50, 0.59:0.41, 0.54:0.46 and 0.78:0.22, respectively. Silver atom Ag11 (Ag27 and Ag28) was disordered at three positions with site occupancy ratio of 0.53:0.37:0.1. Two trifluoromethyl groups C63 and C67 were disordered at two rotation positions with the occupancy ratios of 0.48:0.52 and 0.66:0.34, respectively. Several sulfur atoms in DMSO including S2 (S3), S6 (S7), S8 (S9), S10 (S11), S17 (S18) and S20 (S21) are disordered at two separation positions with site occupancy ratios of 0.48:0.52, 0.22:0.78, 0.81:0.19, 0.78:0.22, 0.14:0.86 and 0.72:0.28, respectively. Packing view of complex **2** is shown in Fig. S17.

Crystal data for $[\text{Ag}_{34}\{\text{C}_6(\text{C}\equiv\text{C})_5\text{H}\}_2(\text{CF}_3\text{CO}_2)_{24}\cdot(\text{DMSO})_{22}\cdot(\text{H}_2\text{O})_2]\cdot(\text{DMSO})_2$ (**3**) (CCDC-1415064): $\text{C}_{128}\text{H}_{150}\text{Ag}_{34}\text{F}_{72}\text{O}_{74}\text{S}_{24}$, $M = 8677.50$, monoclinic, space group $P2_1/c$ (No. 14), $a = 26.341(5) \text{ \AA}$, $b = 13.125(3) \text{ \AA}$, $c = 36.552(7) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 105.85(3)^\circ$, $V = 12157(4) \text{ \AA}^3$, $Z = 2$, $T = 173 \text{ K}$, $D_c = 2.371 \text{ g cm}^{-3}$. The structure, refined on F^2 , converged for 21364 unique reflections ($R_{\text{int}} = 0.0635$) and 18238 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.1011$ and $wR_2 = 0.2327$ and a goodness-of-fit = 1.198. Silver atom Ag6 is disordered at two positions with site occupancy ratio of 0.87:0.13. Sulfur atoms

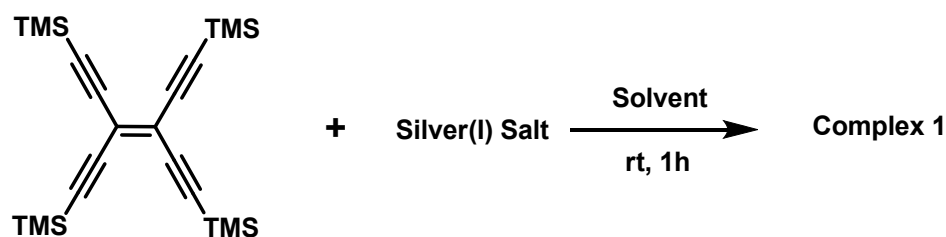
S1 (S13), S4 (S14) and S8 (S15) are disorder at to separated positions with site occupancy ratios of 0.82:0.18, 0.75:0.25 and 0.80:0.20, respectively. Oxygen atoms in CO₂⁻ group (C45) disordered at two sets of rotation sites with occupancy ratio of 0.7:0.3. Trifluoromethyl groups including C20, C28, C34, C42, C44 and C58 are all disordered resulting from C-C bond rotation with site occupancy ratios equals 0.45:0.55, 0.41:0.59, 0.8:0.2, 0.44:0.56, 0.7:0.3 and 0.7:0.3, respectively. Packing view of complex **3** is shown in Fig. S18.

References

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2. M. Sonoda, A. Inaba, K. Itahashi and Y. Tobe, *Org. Lett.*, 2001, **3**, 2419.
3. P. Ehlers, A. Neubauer, S. Lochbrunner, A. Villinger and P. Langer, *Org. Lett.*, 2011, **13**, 1618.
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5. G. M. Sheldrick, SHELXL-97 (Univ. Göttingen, 1997).

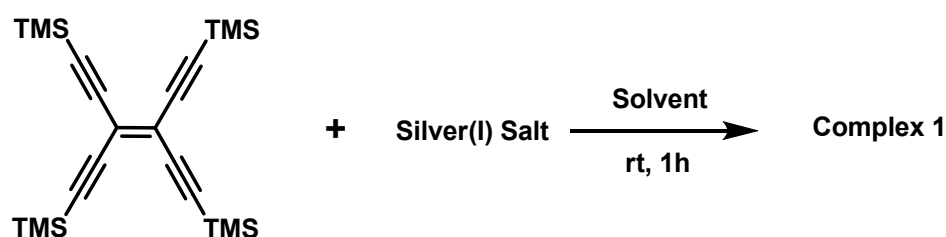
Supporting Tables

Table S1. Screening of silver salt concentration for the preparation of **1**.



Entry	Silver(I) Salt	Solvent	Result
1	4.4 mg AgCO ₂ CF ₃ (2 equiv.)	CH ₃ CN	Dark Red Precipitation
2	13.2 mg AgCO ₂ CF ₃ (6 equiv.)	CH ₃ CN	Dark Red Precipitation
3	26.4 mg AgCO ₂ CF ₃ (12 equiv.)	CH ₃ CN	Dark Red Precipitation
4	39.6 mg AgCO ₂ CF ₃ (18 equiv.)	CH ₃ CN	Dark Red Precipitation
5	52.8 mg AgCO ₂ CF ₃ (24 equiv.)	CH ₃ CN	Dark Red Precipitation
6	66.0 mg AgCO ₂ CF ₃ (0.6M 30 equiv.)	CH ₃ CN	Clear orange solution
7	79.2 mg AgCO ₂ CF ₃ (36 equiv.)	CH ₃ CN	Clear orange solution
8	110 mg AgCO ₂ CF ₃ (1M 50 equiv.)	CH ₃ CN	Clear orange solution
9	220 mg AgCO ₂ CF ₃ (2M 100 equiv.)	CH ₃ CN	Clear yellow solution

Table S2. Screening of solvent for the preparation of **1**.



Entry	Silver(I) Salt	Solvent	Result
1	2M AgCO ₂ CF ₃	CH ₃ CN	Clear yellow solution
2	2M AgCO ₂ CF ₃	DMSO	Clear yellow solution
3	2M AgCO ₂ CF ₃	H ₂ O	No obvious dissolution
4	2M AgCO ₂ CF ₃	DMSO : H ₂ O = 1 : 1 (v : v)	No obvious dissolution
5	2M AgCO ₂ CF ₃	CH ₃ CN : H ₂ O = 1 : 1 (v : v)	No obvious dissolution
6	2M AgCO ₂ CF ₃	CH ₃ OH	Clear yellow solution

Table S3. Screening of silver salts for the preparation of **1**.



Entry	Silver(I) Salt	Solvent	Time	Result
1	2M AgCO ₂ CF ₃	DMSO	1 h	Clear yellow solution
2	1M AgNO ₃	DMSO	24 h	Partial dissolution
3	1M AgSO ₃ CF ₃	DMSO	24 h	Partial dissolution
4	1M AgBF ₄	DMSO	24 h	No obvious dissolution
5	2M AgCO ₂ CF ₃	CH ₃ CN	1 h	Clear yellow solution
6	2M AgNO ₃	CH ₃ CN	24 h	Light yellow solution
7	2M AgSO ₃ CF ₃	CH ₃ CN	24 h	Light yellow solution
8	2M AgBF ₄	CH ₃ CN	24 h	Colorless solution

Supporting Figures

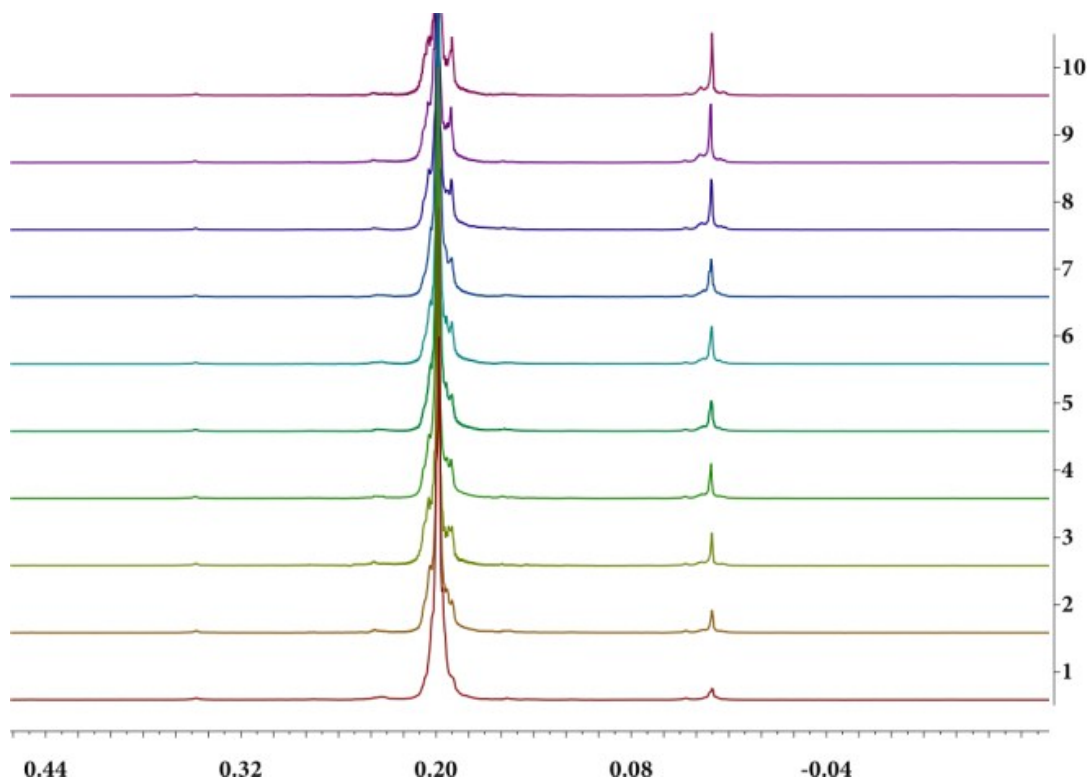


Fig. S1 ¹H-NMR spectra (400 MHz, CD₃CN) of the mixture of 0.4 equiv. AgCO₂CF₃ and (4.1 mg, 0.01 mmol, 0.02 M). 5 min interval for each spectrum from entry 1 to 10.

When insufficient AgCO₂CF₃ (0.4 equiv.) was mixed with **TMS-TEE** in acetonitrile, a red solution was acquired. ¹H-NMR spectrum revealed two sets of signals at the regions of 0.20 and 0.03 ppm. The former signal can be assigned to the trimethylsilyl species of the remaining C≡C-TMS on **TEE** skeleton ($\delta = 0.20$ ppm for **TMS-TEE**). The latter set may be ascribed to Me₃SiOH or (Me₃Si)₂O that arises from the hydrolysis of Me₃SiOCOCF₃. Me₃SiOCOCF₃ could be generated in the AgCO₂CF₃-mediated desilylation step. These results evidenced the occurrence of partial desilylation of **TMS-TEE** and supported our hypothesis that the partially TMS-protected silver acetylide intermediates [R(C≡CAg)_m(C≡CTMS)_n] are soluble.

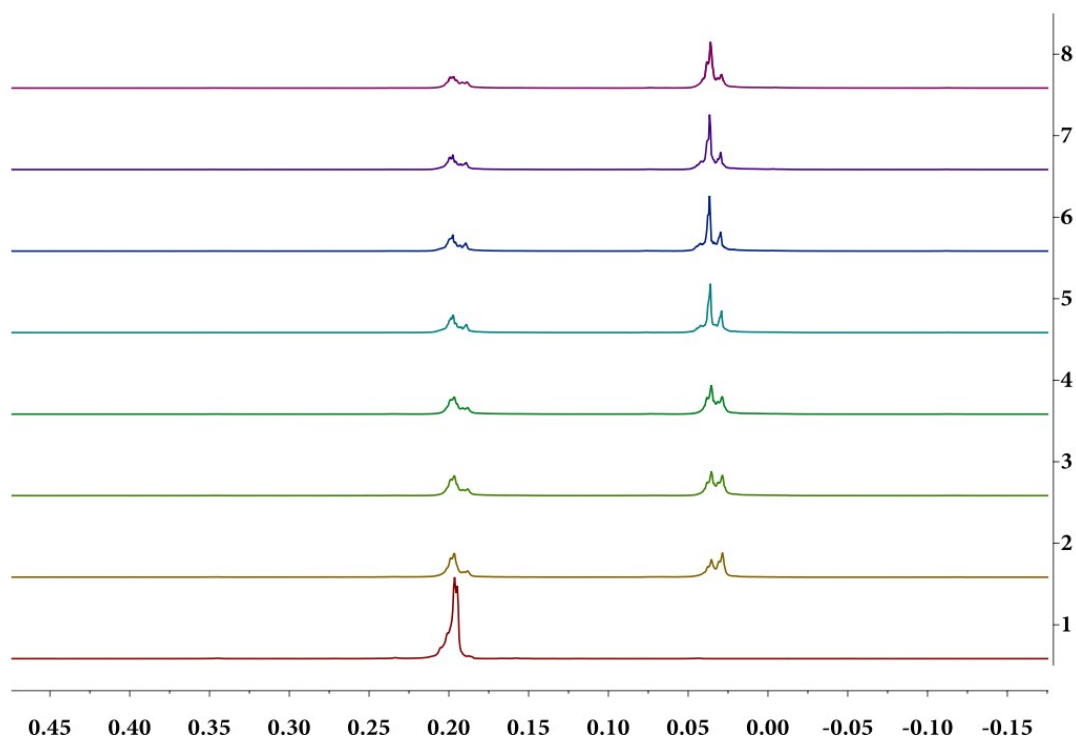


Fig. S2 $^1\text{H-NMR}$ spectra (400 MHz, CD_3CN) of the mixture of 4 molar equiv. AgCO_2CF_3 and **TMS-TEE** (4.1 mg, 0.01 mmol, 0.02 M). 5 min interval for each spectrum.

Upon increasing the ratio of $\text{AgCO}_2\text{CF}_3/\text{TMS-TEE}$ to 4:1, a dark red powder was obtained. Monitoring this titration process by $^1\text{H-NMR}$ explored the gradual diminishing of the signal at 0.20 ppm and the increasing of the peaks around 0.03 ppm. Raman spectrum of the dark red solid exhibited a peak at 1968 cm^{-1} (Fig. 1C), which is red-shifted relative to the peak at 2141 cm^{-1} for the carbon-carbon triple bond of **TMS-TEE**. The absence of the band within the $2900\text{-}3000\text{ cm}^{-1}$ range confirmed that the solid has been completely desilylated.

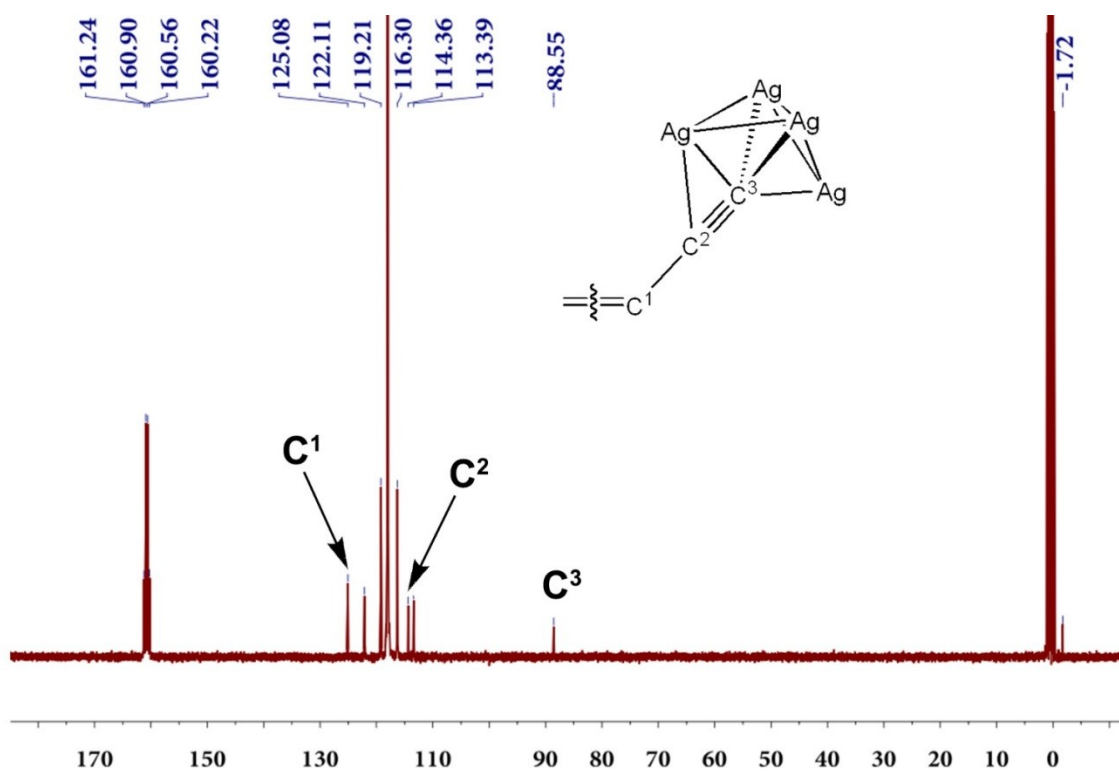


Fig. S3 ^{13}C -NMR spectrum (100 MHz, CD_3CN) of the solution for preparing complex **1**. ^{13}C -NMR (CD_3CN): $\delta = 160.73$ (q, $^2J_{\text{FC}} = 34$ Hz, CO_2CF_3^-), 125.08 (s, $\text{C}=\text{C}$), 117.75 (q, $^1J_{\text{FC}} = 290$ Hz, CO_2CF_3^-), 114.36 (s, $\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{Ag}$), 88.55 (s, $\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{Ag}$).

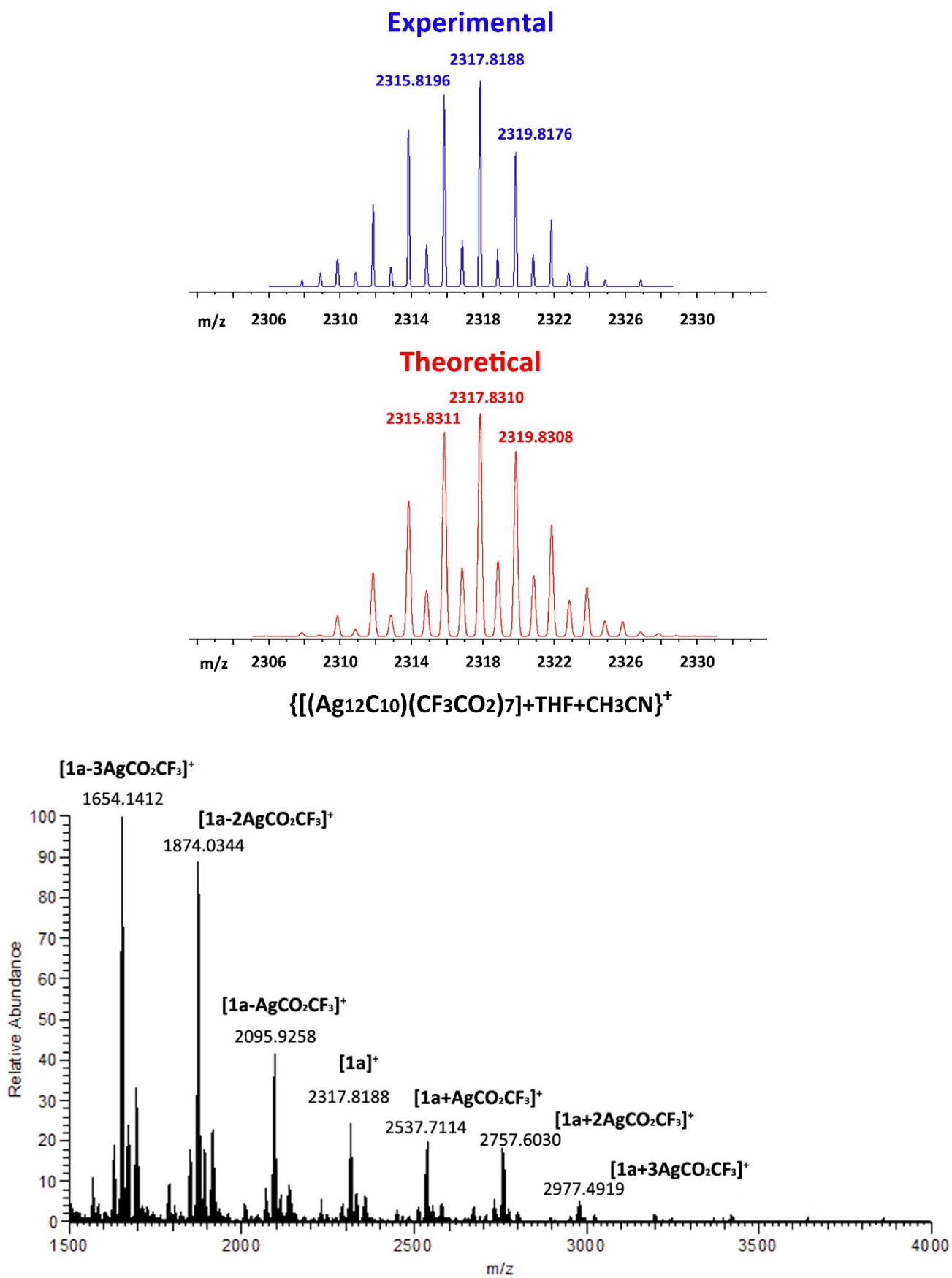
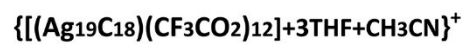
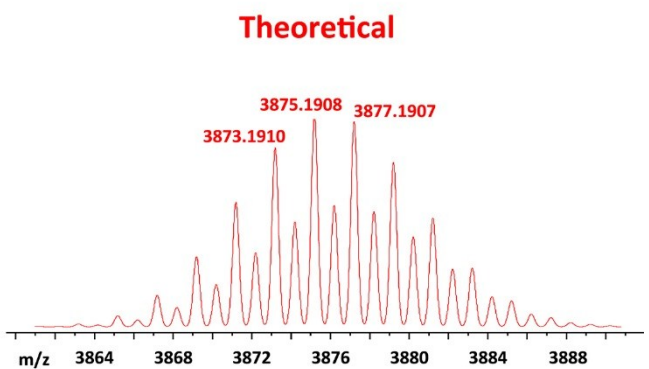
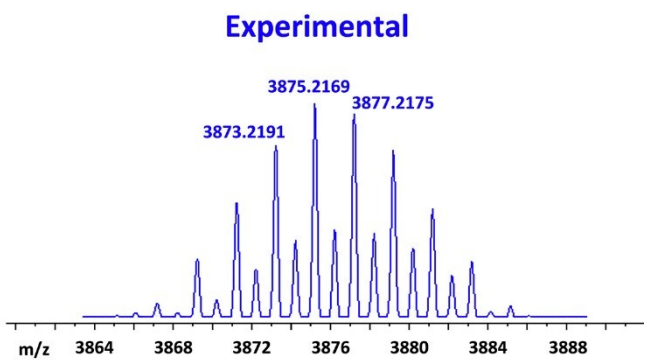
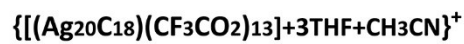
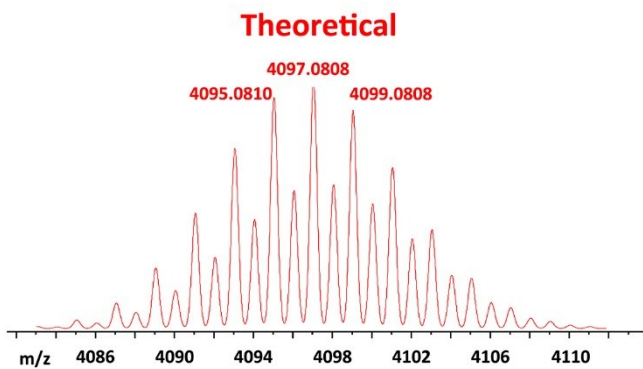
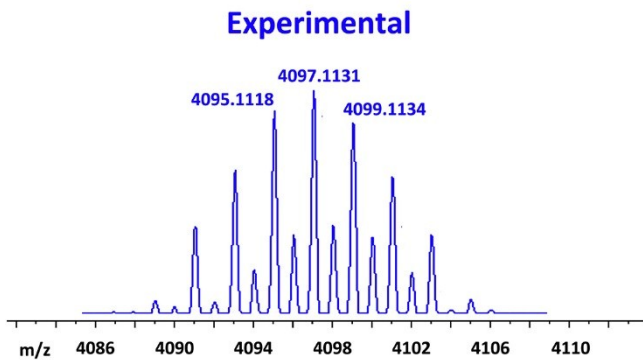
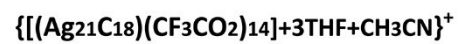
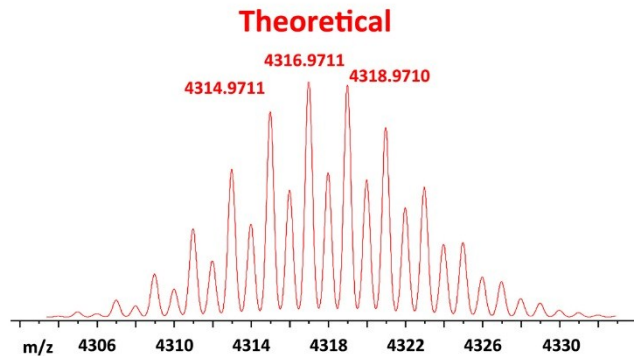
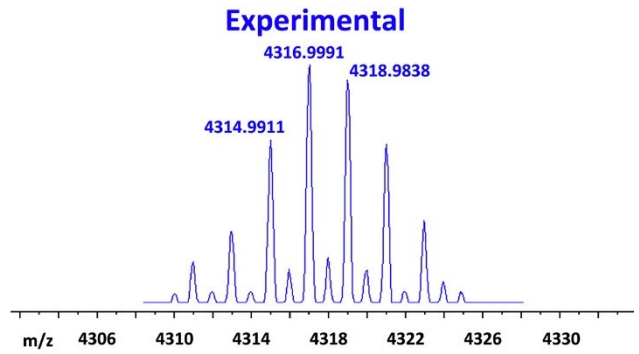
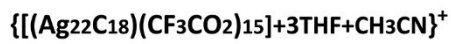
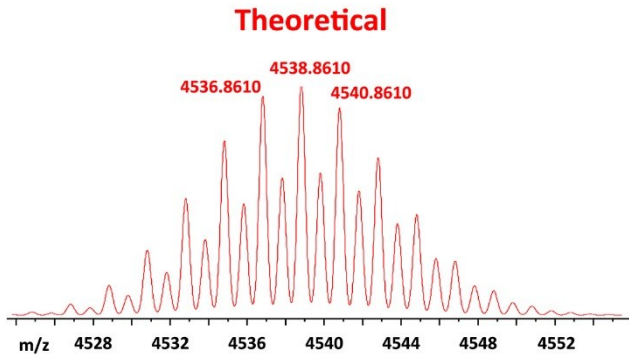
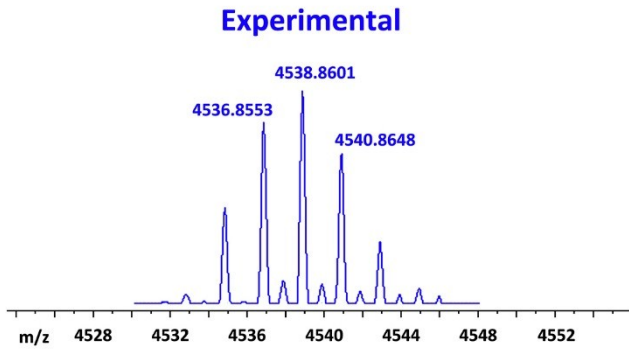
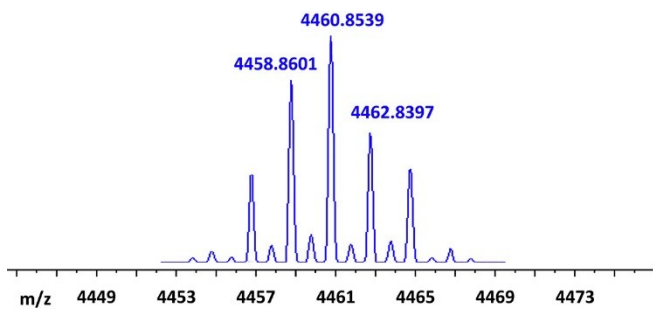


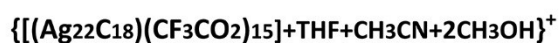
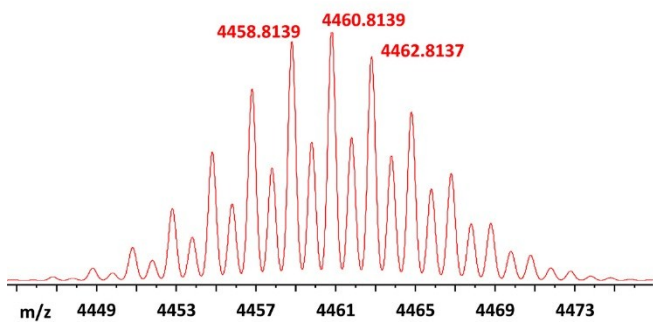
Fig. S4 ESI-MS spectra of complex **1** ($[(\text{Ag}_{12}\text{C}_{10})(\text{CF}_3\text{CO}_2)_7(\text{THF})(\text{CH}_3\text{CN})]^+$) was denoted as **1a**). Sample for ESI-MS measurements was prepared by dissolving crystals of complex **1** in THF.



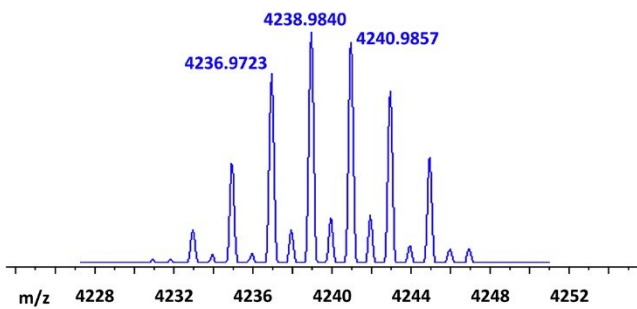
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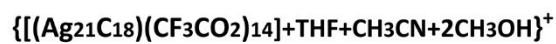
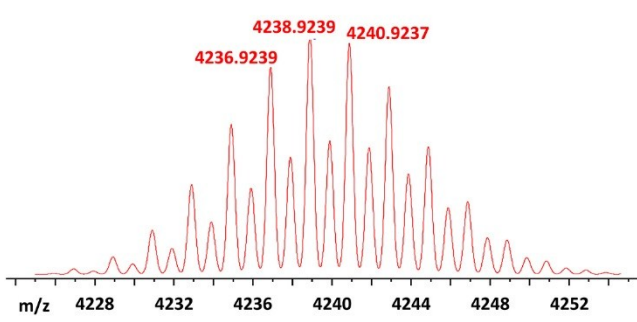
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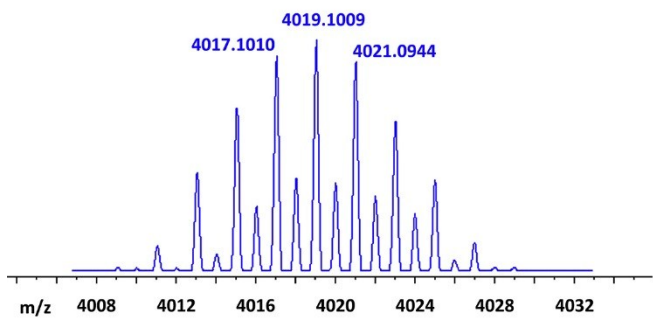
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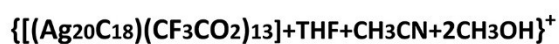
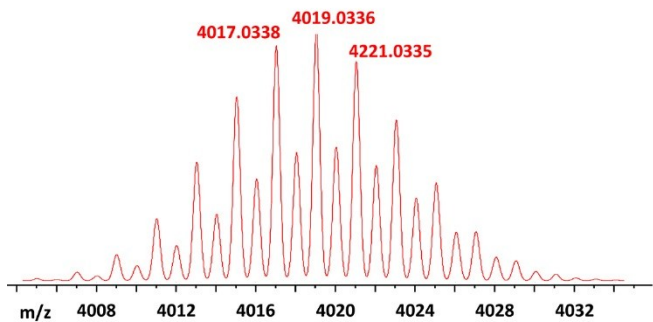
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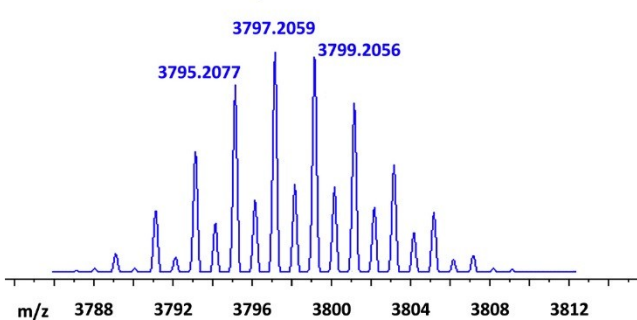
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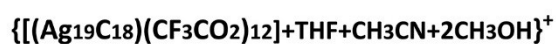
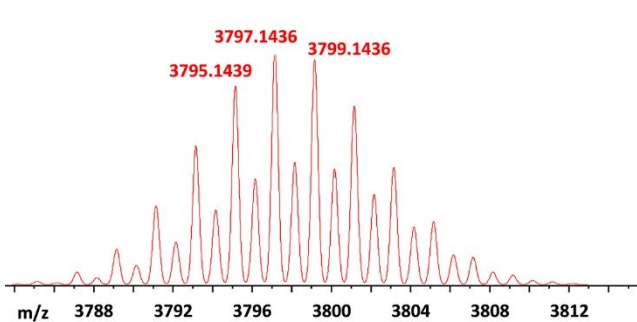
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Experimental



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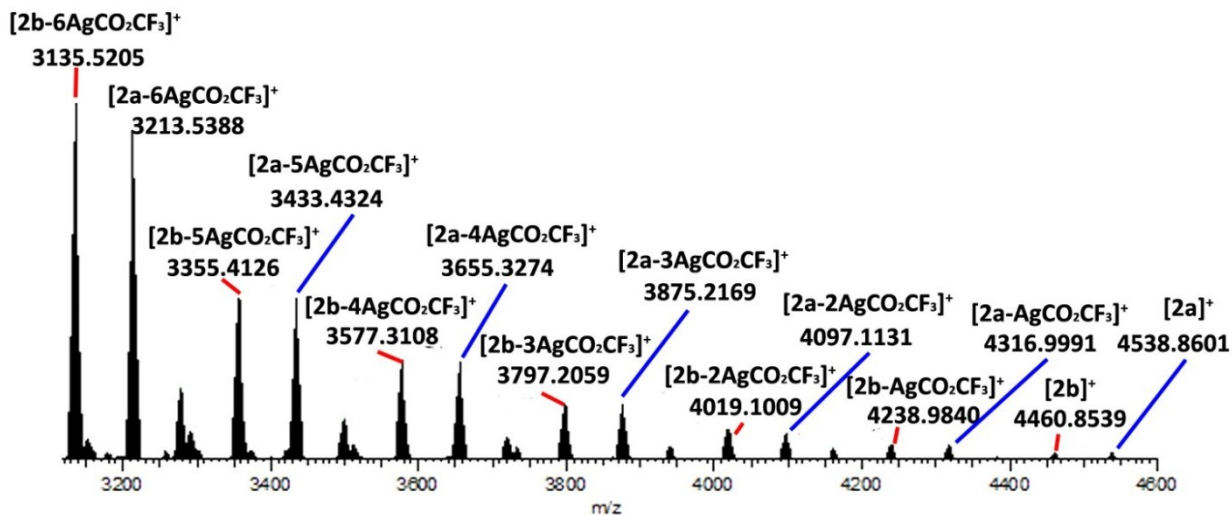


Fig. S5 ESI-MS spectra of complex **2** ($[(\text{Ag}_{22}\text{C}_{18})(\text{CF}_3\text{CO}_2)_{15}(\text{THF})_3(\text{CH}_3\text{CN})]^+$ and $[(\text{Ag}_{22}\text{C}_{18})(\text{CF}_3\text{CO}_2)_{15}(\text{THF})(\text{CH}_3\text{CN})(\text{CH}_3\text{OH})_2]^+$ were denoted as **2a** and **2b**, respectively). The sample for ESI-MS measurement was prepared by dissolving crystals of complex **2** in THF and diluted by a mixed solvent of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ ($v : v = 1 : 1$).

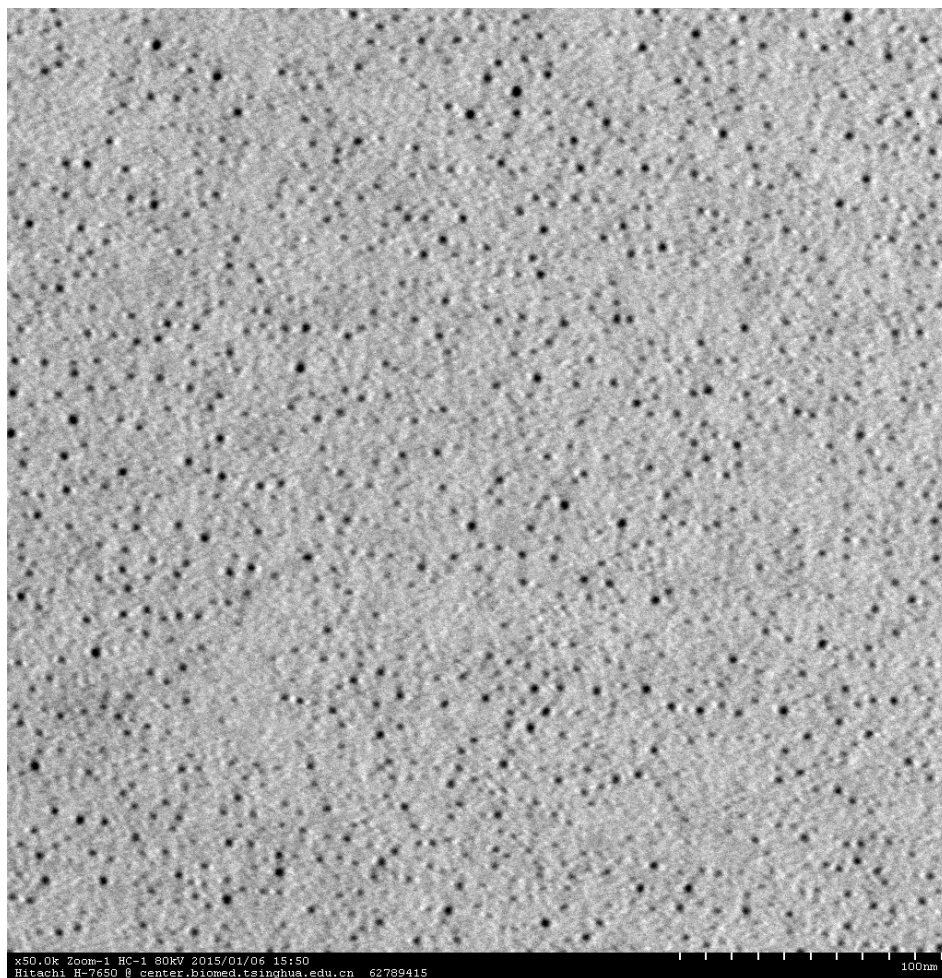


Fig. S6 TEM image of complex 2.

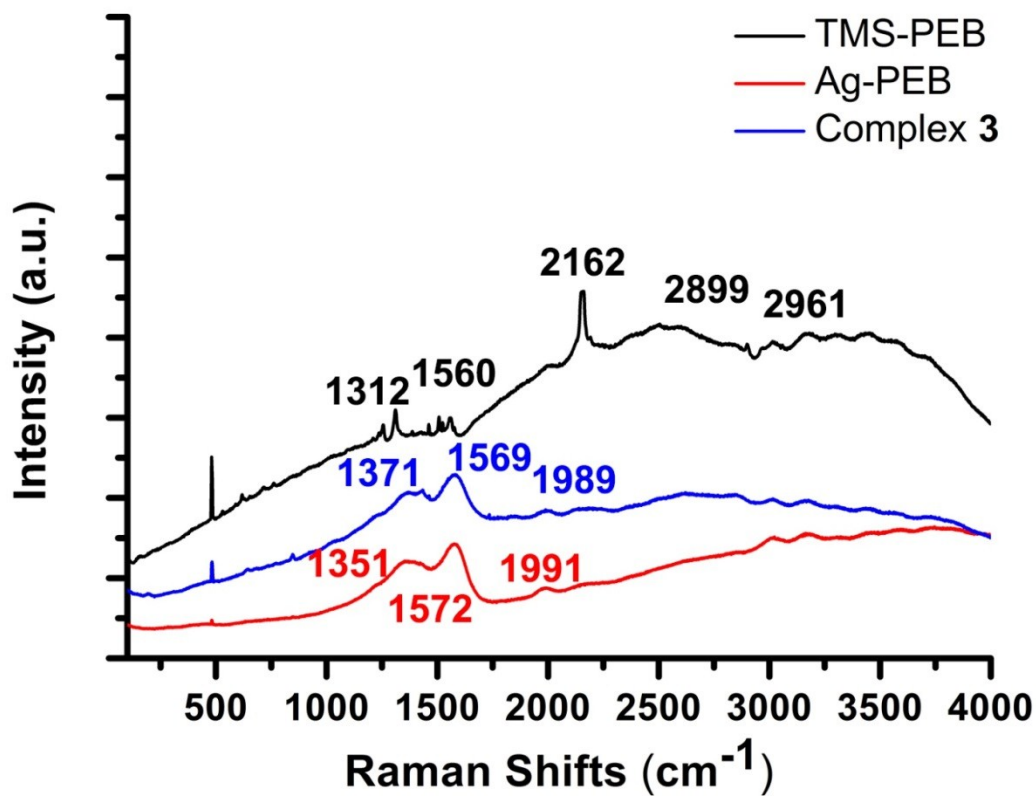


Fig. S7 Raman spectrum of TMS-PEB, Ag-PEB and complex 3 under the laser excitation line at 532 nm.

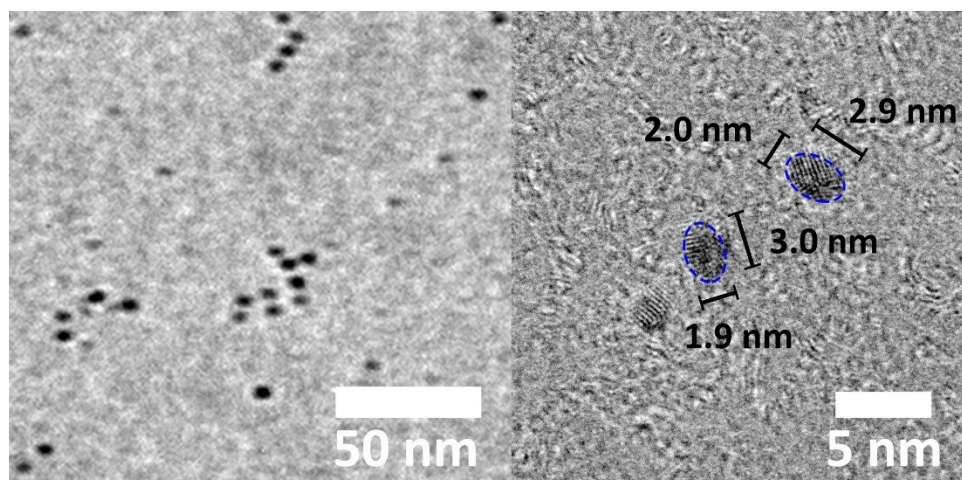


Fig. S8 TEM image of complex 3.

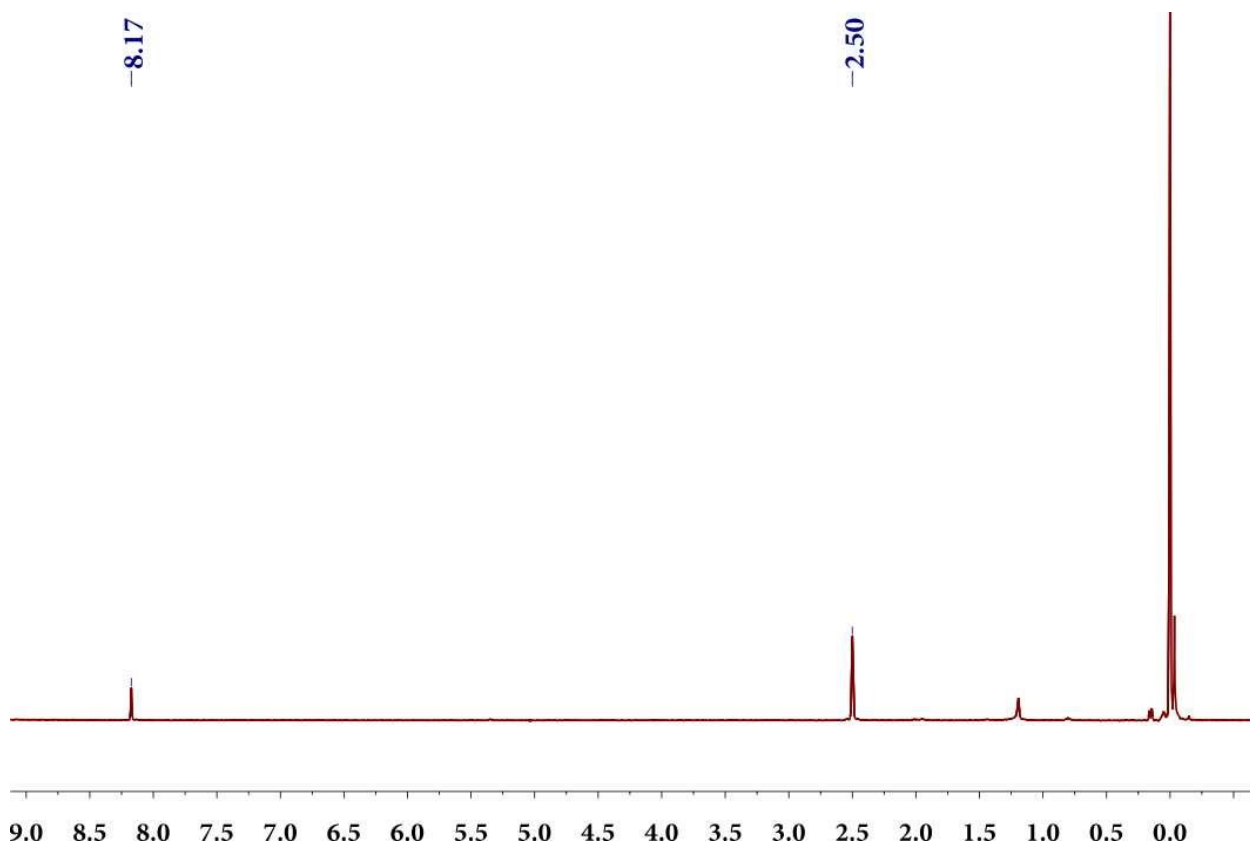


Fig. S9 $^1\text{H-NMR}$ spectrum (400 MHz, $\text{DMSO-}d_6$) of the solution for preparing complex **3**.

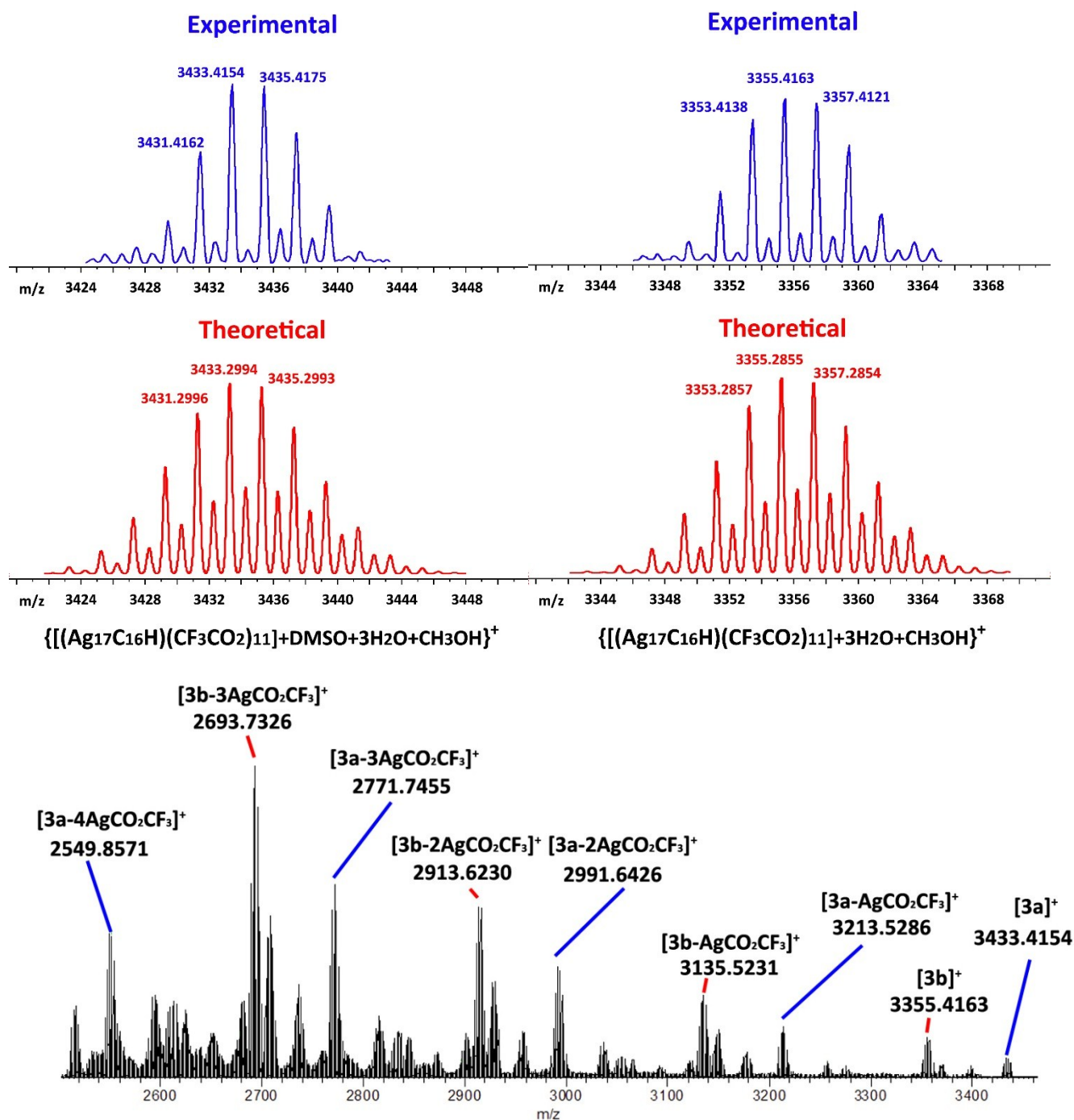


Fig. S10 ESI-MS spectra of complex **3** ($\{[(\text{Ag}_{17}\text{C}_{16}\text{H})(\text{CF}_3\text{CO}_2)_{11}](\text{DMSO})(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})\}^+$ and $\{[(\text{Ag}_{17}\text{C}_{16}\text{H})(\text{CF}_3\text{CO}_2)_{11}](\text{H}_2\text{O})_3(\text{CH}_3\text{OH})\}^+$ were detonated as **3a** and **3b**, respectively). The sample for ESI-MS measurement was prepared by dissolving crystals of complex **3** in THF and diluted by CH_3OH .

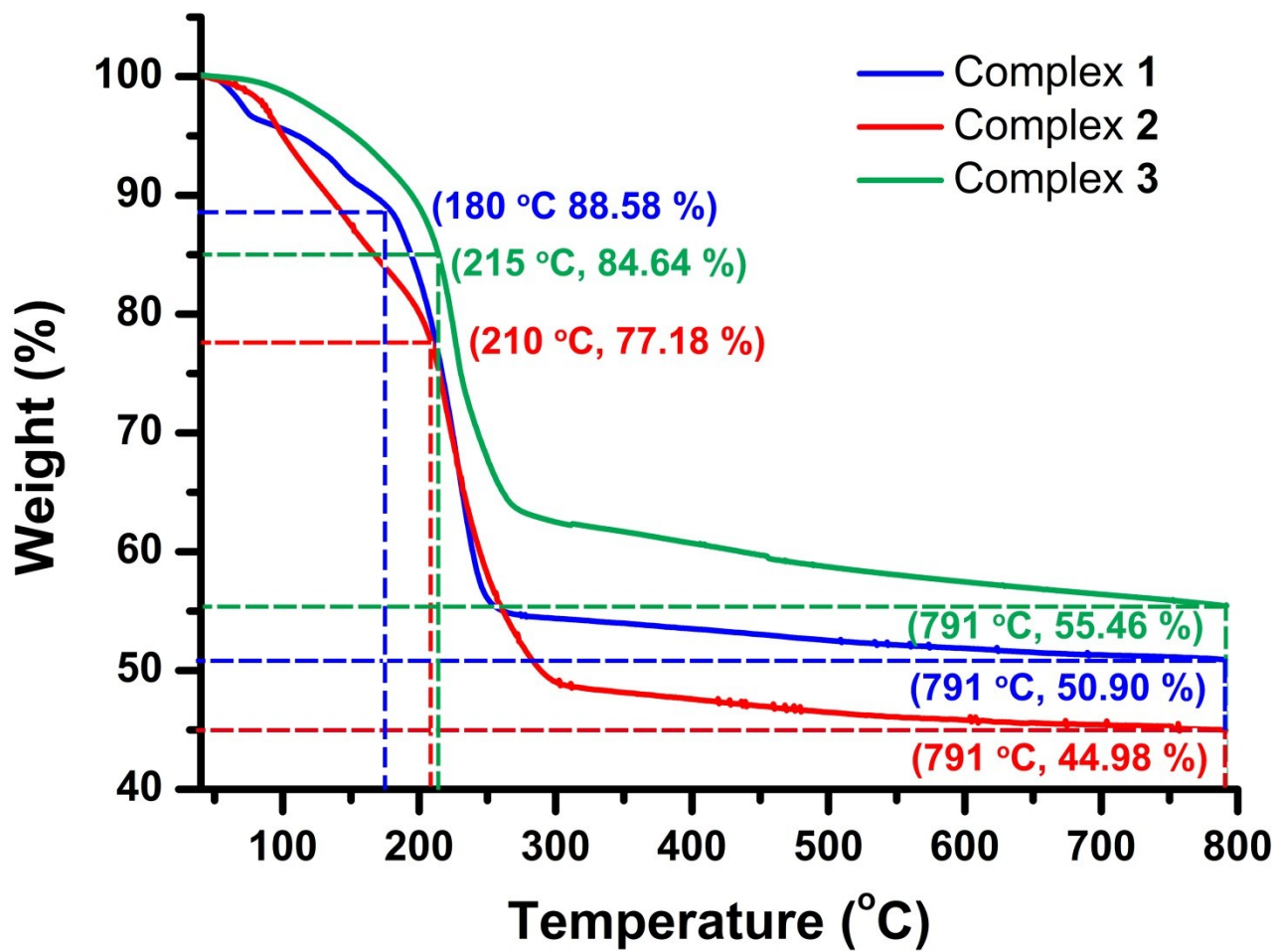


Fig. S11 TGA of complexes 1, 2 and 3.

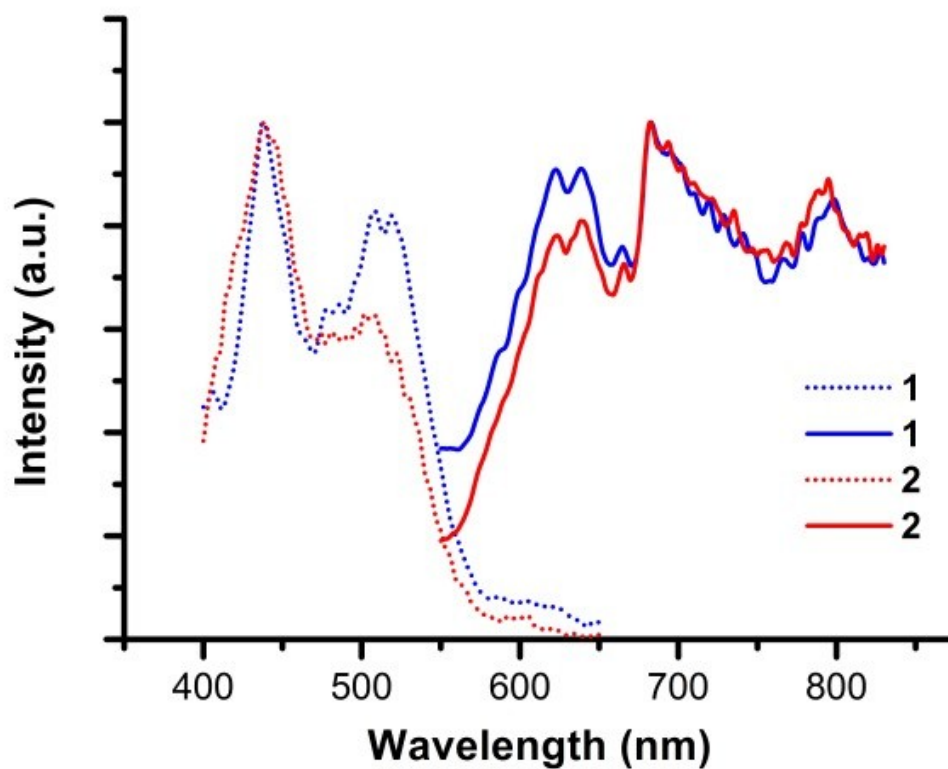


Fig. S12 Excitation (dotted line) and emission (solid line) spectra of complex **1** ($\lambda_{\text{ex}} = 438$ nm, $\lambda_{\text{em}} = 683$ nm) and **2** ($\lambda_{\text{ex}} = 438$ nm, $\lambda_{\text{em}} = 683$ nm) (298 K, THF).

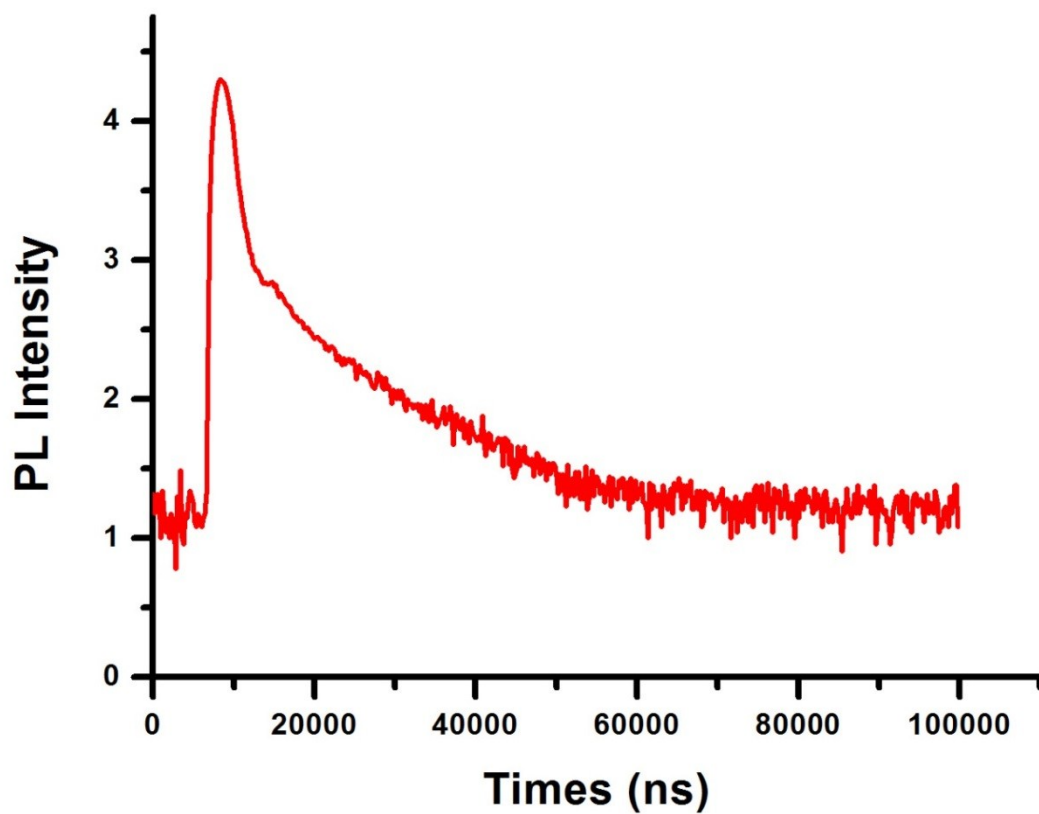


Fig. S13 Photoluminescence decay of **1** (1.8 μs).

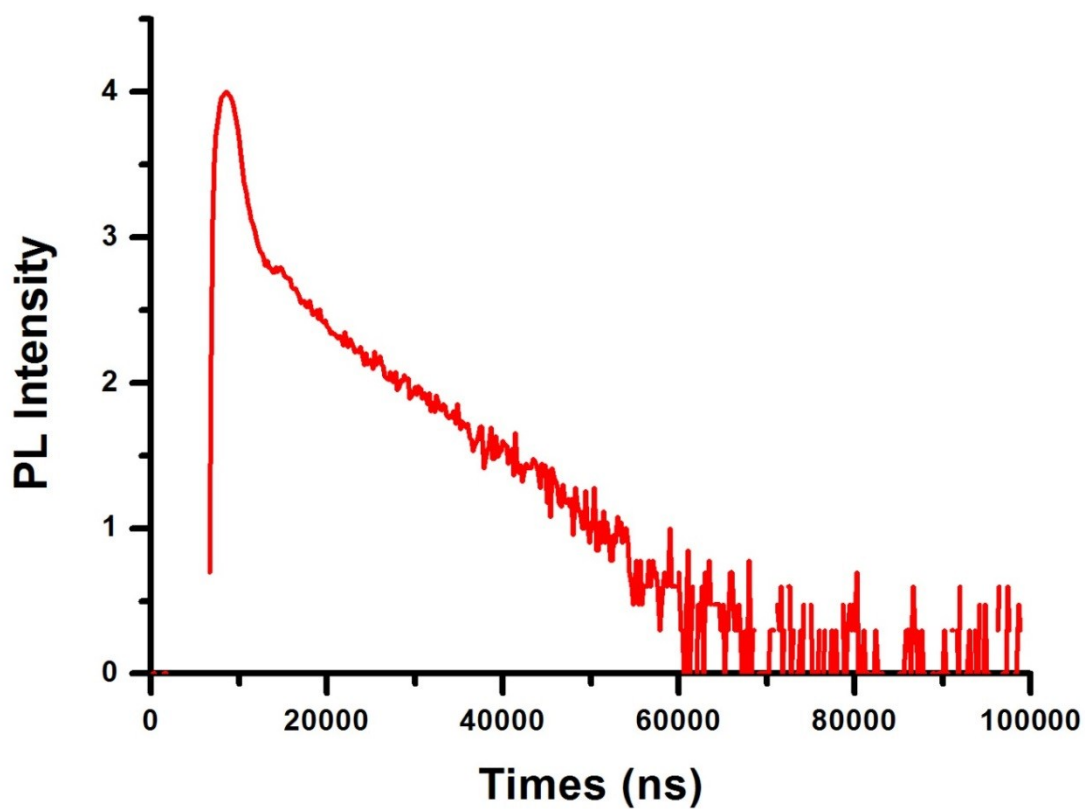


Fig. S14 Photoluminescence decay of **2** (4.4 μs).

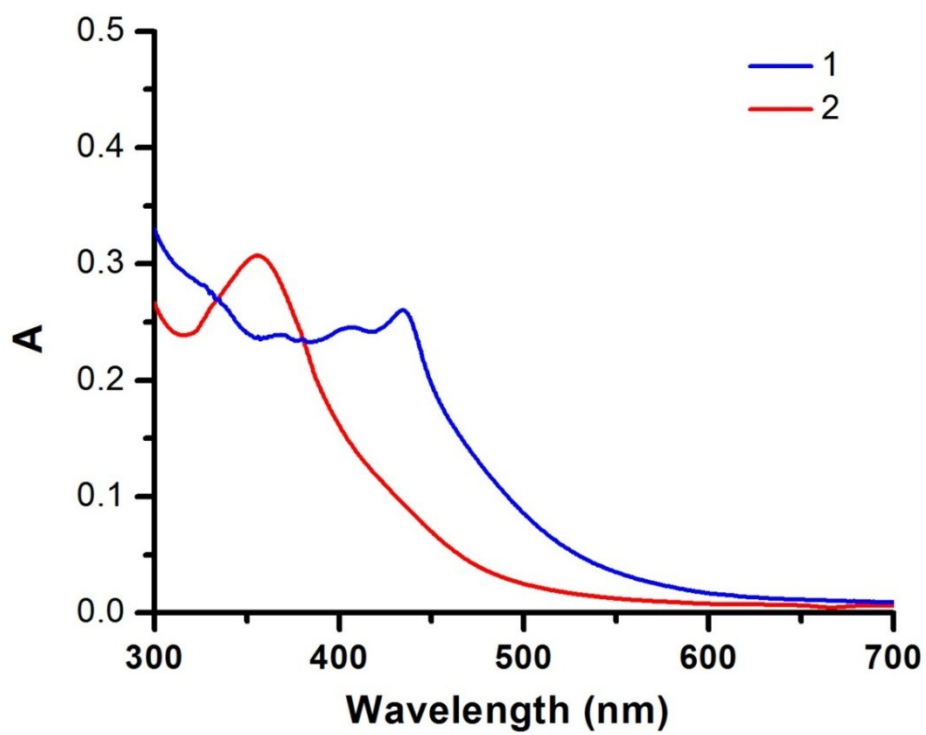


Fig. S15 Photoluminescence of complex **1** ($\lambda_{\text{max}} = 435$ nm) and **2** ($\lambda_{\text{max}} = 356$ nm) (298 K, THF).

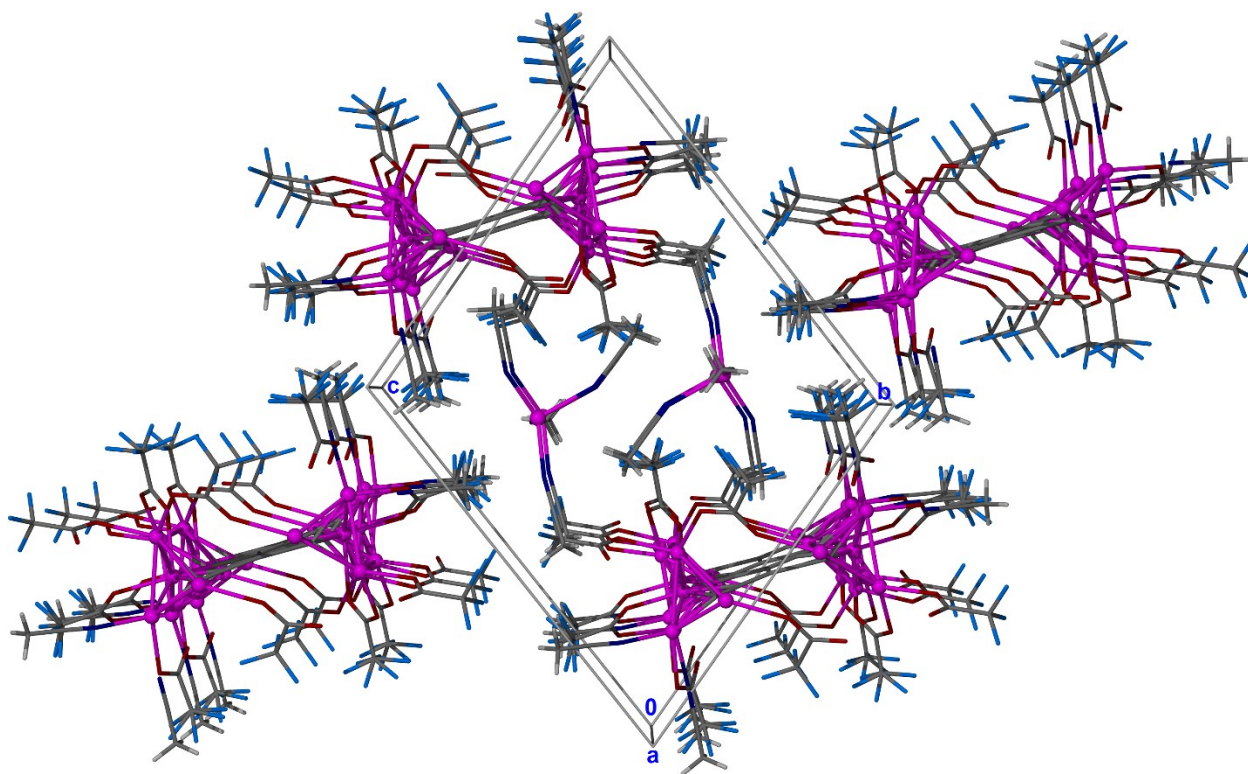


Fig. S16 Packing view of $\{[Ag_{12}\{(C\equiv C)_2C=C(C\equiv C)_2\}(CF_3CO_2)_{10}(CH_3CN)_4]\cdot[Ag(CH_3CN)_4]_2\}_n$ (**1**). The infinite silver-carbide ladder was packed along the [100] direction. Color scheme for atoms: Ag purple, C gray, O red, F cyan, N blue.

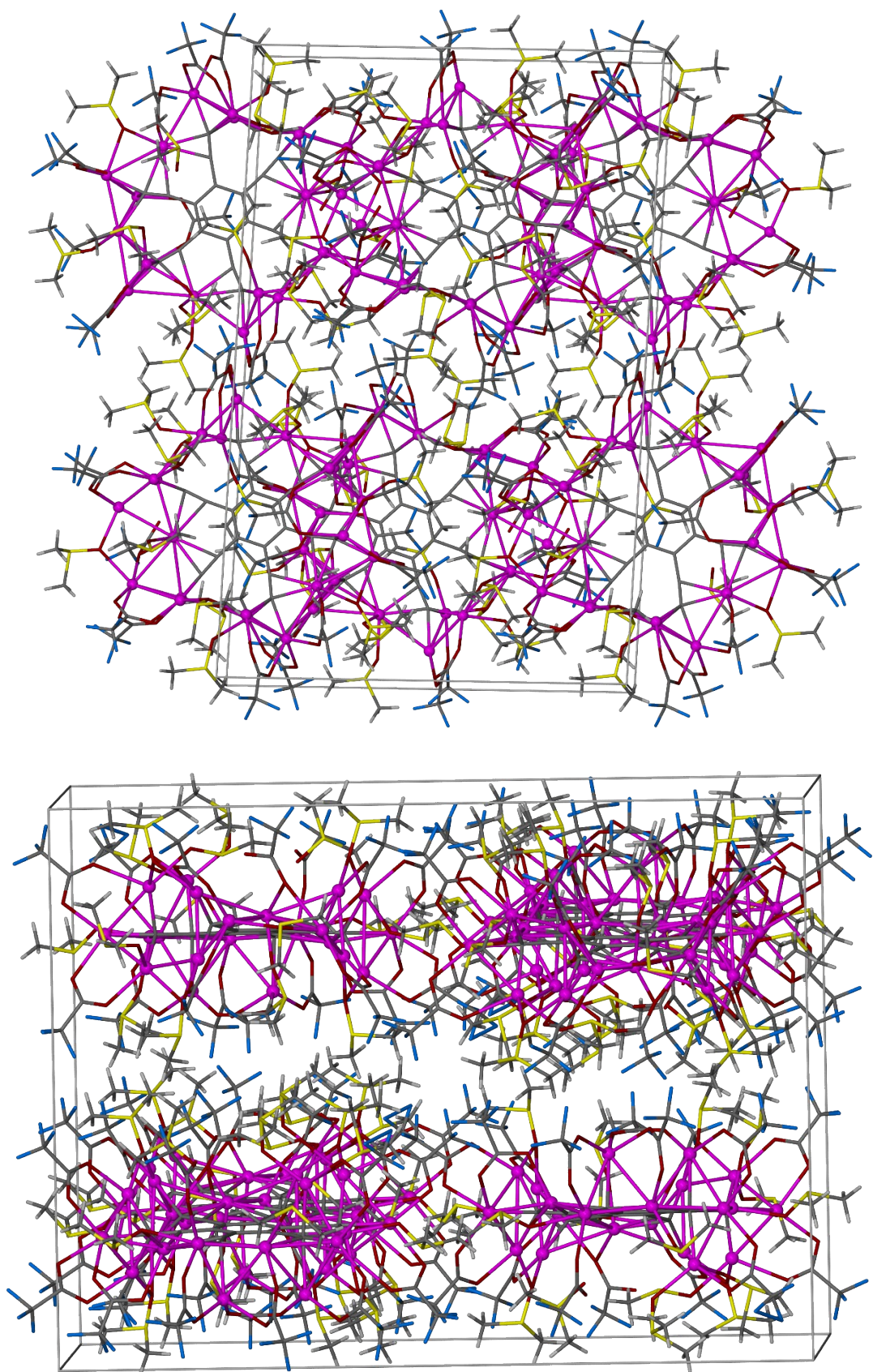


Fig. S17 Packing view of $[\text{Ag}_{22}\{\text{C}_6(\text{C}\equiv\text{C})_6\}(\text{CF}_3\text{CO}_2)_{16}(\text{DMSO})_{16}]\cdot(\text{H}_2\text{O})_{0.5}$ (**2**). Color scheme for atoms: Ag purple, C gray, H white, O red, F cyan, S yellow.

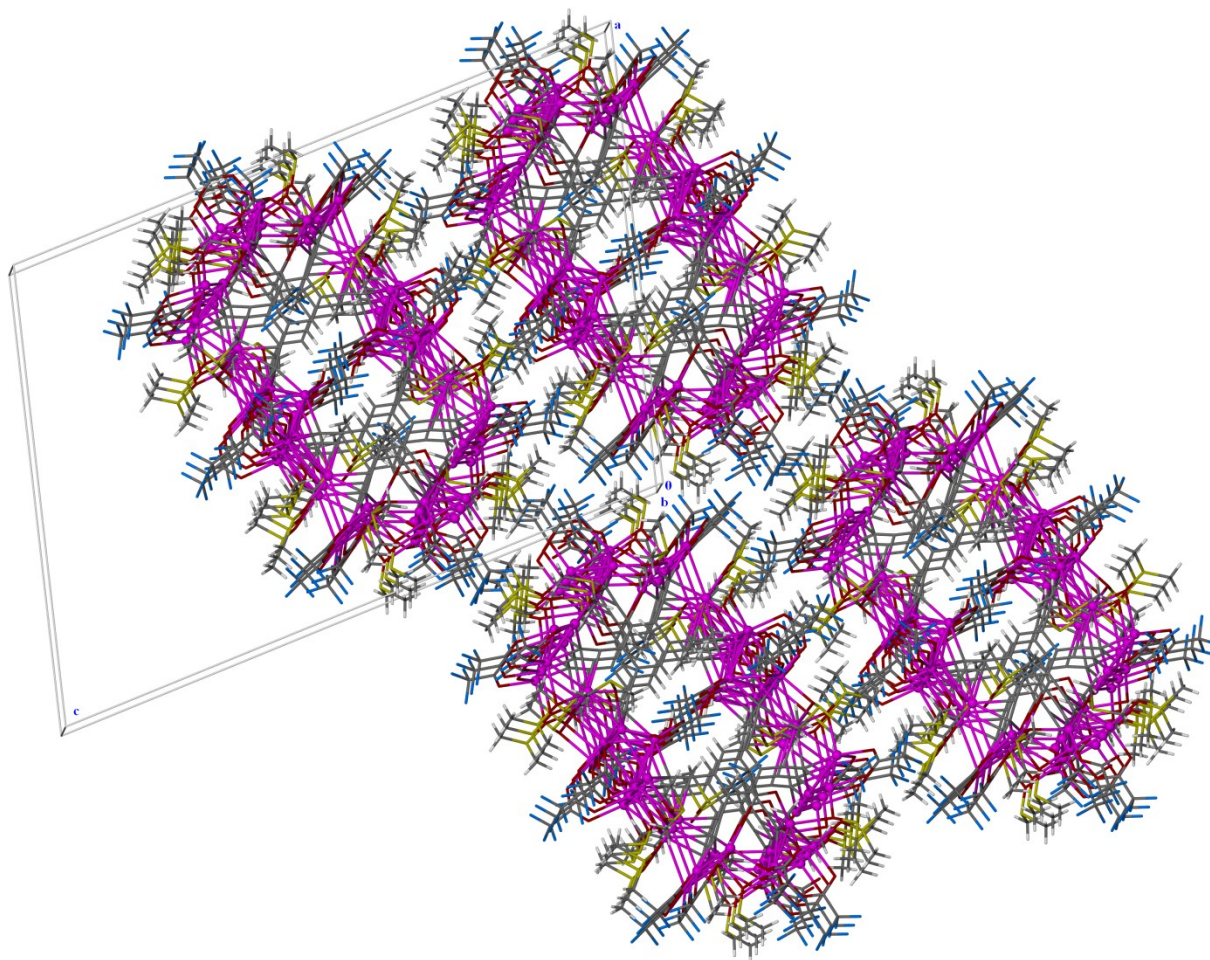


Fig. S18 Packing view of $[\text{Ag}_{34}\{\text{C}_6(\text{C}\equiv\text{C})_5\text{H}\}_2(\text{CF}_3\text{CO}_2)_{24}\cdot(\text{DMSO})_{24}\cdot(\text{H}_2\text{O})_2]$ (**3**). Color scheme for atoms: Ag purple, C gray, H white, O red, F cyan, S yellow.