Electronic Supplementary Information (ESI)

The solvent-induced isomerization of silver thiolate clusters with symmetry transformation

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General procedures. The TabHPF$_6$ was prepared according to the literature methods.[S1] All other chemicals and reagents were commercially available and used without further purification. The C, H and N elemental analyses were carried out on an EA1110 elemental analyzer, whereas the S elemental analysis was carried out on a Vario micro organic elemental analyzer. The IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks in the range of 4000-400 cm^{-1}. The UV-Vis spectra and optical diffuse reflectance spectra were obtained with a Shimadzu UV-2600 spectrometer. The thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA851 thermal analyzer under an N_2 atmosphere with a heating rate of 10 °C min^{-1}. The powder X-ray diffraction (PXRD) patterns were collected by using a PANalytical Aeris diffractometer with Cu-Kα radiation (λ = 1.5406 Å) over the 2θ range of 5-50° at room temperature.

Synthesis of Tab (4–(trimethyl–ammonio)benzenethiolate) ligand. The solution of TabHPF$_6$ (156.5 mg, 0.5 mol) in 5 mL acetonitrile was mixed with 1 mL Et_3N under stirring for 5 minutes at ambient temperature. Then the white precipitate of Tab was isolated by filtration, washed by 2 mL acetonitrile and 5 mL Et_2O, and dried in air: Yield: 93%.

Synthesis of Ag12a. A mixture of Tab (16.7 mg, 0.1 mmol) and AgTFA (44 mg, 0.2 mmol) was dissolved in a mixed CH_3CN-DMF solvent (5 mL, $v : v = 4 : 1$) under ultrasonic. Then about 0.25 mL deionized water was added dropwise. The resulting clear solution was diffused by Et_2O in the dark at room temperature. After about five days the colorless needle-like crystals were collected and washed by Et_2O. Yield: 15.3% (based on AgTFA). Ana. Calcd (%) for $C_{90}H_{100}Ag_{12}F_{36}N_{12}O_{26}S_6$: C 27.46, H 2.56, N 4.27, S 4.89; found: C 27.75, H 2.63, N 4.31, S 5.24. IR (KBr disk, cm^{-1}): 3438 (s), 1678 (vs), 1487 (s), 1431 (m), 1208 (vs), 956 (w), 836 (s), 802 (m), 722 (s), 549 (m).

Synthesis of Ag12b. A mixture of Tab (16.7 mg, 0.1 mmol) and AgTFA (44 mg, 0.2 mmol) was dissolved in a mixed CH_3OH-DMF solvent (5 mL, $v : v = 4 : 1$) under ultrasonic. The resulting clear solution was diffused by Et_2O in the dark at room temperature. After about five days the colorless block crystals were collected and washed by Et_2O. Yield: 20.7% (based on AgTFA). Ana. Calcd (%) for $C_{84}H_{92}Ag_{12}F_{36}N_8O_{26}S_6$: C 26.55, H 2.44, N 2.95, S 5.06; found: C 26.10, H 2.39, N 3.12, S 5.53. IR (KBr disk, cm^{-1}): 3438 (s), 1678 (vs), 1488 (s), 1431 (m), 1208 (vs), 1125 (s), 956 (w), 836 (s), 802 (m), 722 (s), 549 (m), 517 (w).

Synthesis of Ag12c. A mixture of Tab (16.7 mg, 0.1 mmol) and $AgOOCCF_3$ (44 mg, 0.2 mmol) was dissolved in 5 mL CH_3CN under ultrasonic. The resulting clear solution was diffused by anhydrous Et_2O in the dark at room temperature. After about five days the colorless block crystals were collected and washed by Et_2O. Product yield was 35.4% (based on AgTFA). Ana. Calcd (%)

for $C_{82}H_{84}Ag_{12}F_{36}N_8O_{24}S_6$: C 26.36, H 2.27, N 3.00, S 5.15; found: C 26.72, H 2.34, N 3.15, S 5.60. IR (KBr disk, cm^{-1}): 3438 (s), 1678 (vs), 1488 (s), 1431 (m), 1208 (vs), 1125 (s), 956 (w), 836 (s), 802 (m), 722 (s), 549 (m), 517 (w).

X-ray diffraction crystallography. Single-crystal X-ray diffraction of **Ag12a**, **Ag12b** and **Ag12c** was performed on a Bruker D8-Quest diffractometer by using graphite monochromated Mo Kα radiation (λ = 0.7107Å). Single crystal with appropriate dimensions was mounted on the glass fiber loop and quickly and coated with paraton oil to prevent decomposition at 190 K. The cell parameters refinement and data reduction were performed using the program Bruker Apex III with absorption correction (multi-scan) applied.[S2]

The structures of **Ag12a**, **Ag12b** and **Ag12c** were solved by using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[S3] and refined by full-matrix least-squares techniques on F_o^2 using the *SHELXL* program[S4] through the *OLEX*^{2} interface.[S5] Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. A small amount of spatially delocalized electron density in the lattice was found but acceptable refinement results could not be obtained for this electron density. The solvent contribution was then modeled using *SQUEEZE* in the Platon program suite.[S6] Hydrogen atoms were placed in calculated positions and refined isotropically by using a riding model. All structures were examined using the Addsym subroutine of *PLATON*[S7] to ensure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table S1. Crystallographic data have been deposited in the Cambridge Crystallographic Data Center (CCDC) with the reference numbers of 1974330 for **Ag12a**, 1974470 for **Ag12b** and 1974488 for **Ag12c**, respectively.

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Table S1 Crystal data collection and structure refinement parameters for **Ag12a-c**.

Compound	**Ag12a**	**Ag12b**	**Ag12c**
Empirical formula	$C_{90}H_{100}Ag_{12}F_{36}N_{12}O_{26}S_6$	$C_{84}H_{92}Ag_{12}F_{36}N_8O_{26}S_6$	$C_{82}H_{84}Ag_{12}F_{36}N_8O_{24}S_6$
Formula weight	3936.61	3800.45	3736.37
Temperature/K	190	190	190
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*C*2/*c*	*P*2_1/*c*
a/Å	20.9281(12)	30.2957(17)	13.8315(8)
b/Å	22.1548(12)	20.8495(10)	29.7018(15)
c/Å	28.9986(12)	22.4448(12)	16.2995(9)
α/°	90	90	90
β/°	90	114.615(2)	94.930(2)
γ/°	90	90	90
Volume/ $Å^3$	13445.4(13)	12888.9(12)	6671.4(12)
Z	4	4	2
ρ_{calc}/g·cm^{-3}	1.945	1.959	1.860
μ/mm^{-1}	1.914	1.992	1.922
F(000)	7664	7376	3616
θ range for data collection	2.264 to 28.347	2.192 to 27.521	2.306 to 27.569
Reflection collected	414509	123394	166651
Independent reflection	16752 [R_{int} = 0.0885]	14827 [R_{int} = 0.0625]	15365 [R_{int} = 0.0799]
Data/restraints/parameters	16752/216/946	14827/155/948	15365/270/878
Goodness-of-fit on F^2	1.064	1.019	1.045
Final *R* indexes [$I>2\sigma(I)$]	$R_1 = 0.0484$, $wR_2 = 0.1009$	$R_1 = 0.0394$, $wR_2 = 0.0869$	$R_1 = 0.0809$, $wR_2 = 0.2077$
Final *R* indexes [all data]	$R_1 = 0.0756$, $wR_2 = 0.1142$	$R_1 = 0.0608$, $wR_2 = 0.0959$	$R_1 = 0.1273$, $wR_2 = 0.2451$
Largest diff. peak/hole/e·$Å^{-3}$	1.540/-1.108	0.974/-1.204	1.541/-1.395

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. GOF $= \{\sum w[(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is total number of parameters refined.

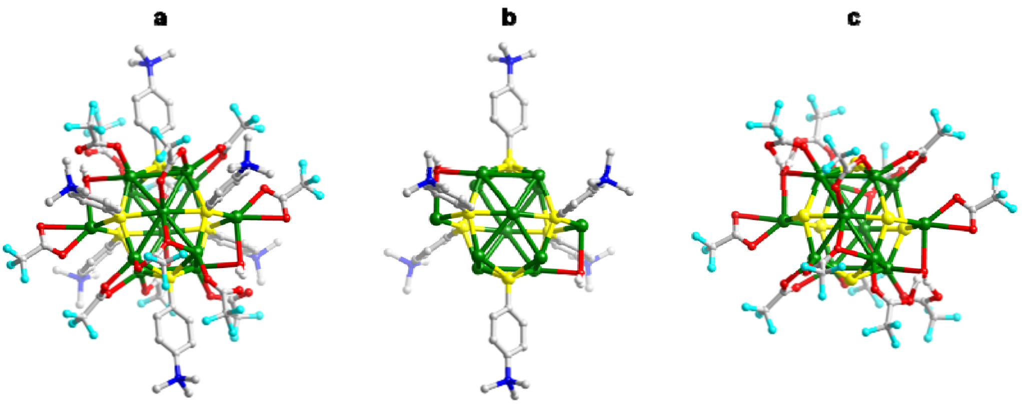

Fig. S1 (a) Ball-stick representation of the crystal structure of **Ag12a**; (b) View of the Ag12 kernel coordinated by Tab ligands in **Ag12a**; (c) View of the Ag12 kernel coordinated by trifluoroacetate anions in **Ag12a**. Free solvents and H atoms are omitted for clarity. Color codes: Ag, green; S, yellow; O, red; F, sky blue; C, gray; N, blue.

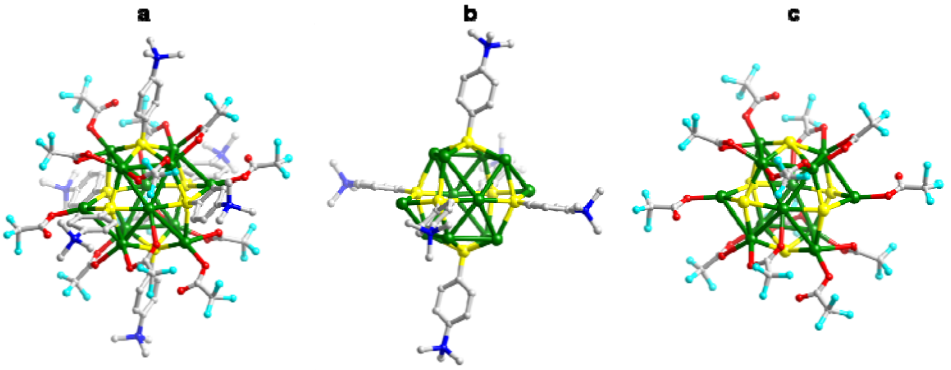

Fig. S2 (a) Ball-stick representation of the crystal structure of **Ag12b**; (b) View of the Ag12 kernel coordinated by Tab ligands in **Ag12b**; (c) View of the Ag12 kernel coordinated by trifluoroacetate anions in **Ag12b**. Free solvents and H atoms are omitted for clarity. Color codes: Ag, green; S, yellow; O, red; F, sky blue; C, gray; N, blue.

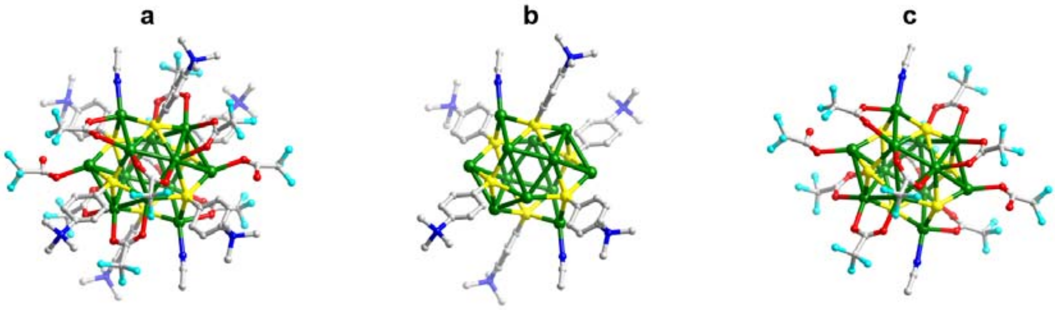

Fig. S3 (a) Ball-stick representation of the crystal structure of **Ag12c**; (b) View of the Ag12 kernel coordinated by Tab ligands in **Ag12c**; (c) View of the Ag12 kernel coordinated by trifluoroacetate anions in **Ag12c**. Free solvents and H atoms are omitted for clarity. Color codes: Ag, green; S, yellow; O, red; F, sky blue; C, gray; N, blue.

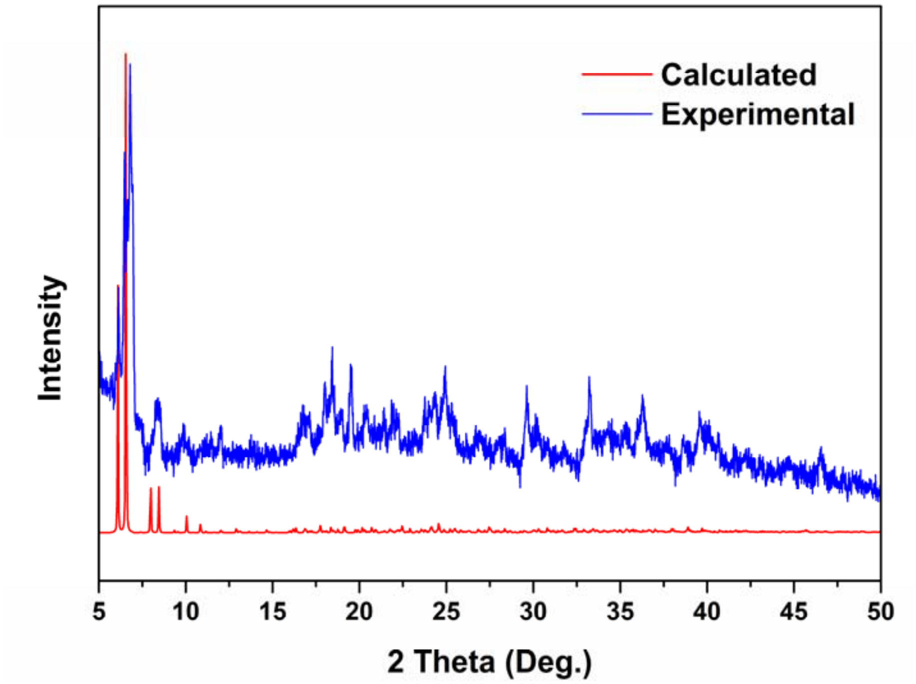

Fig. S4 PXRD patterns of **Ag12a**: simulated from single crystal data (red line) and single-phase polycrystalline sample (blue line).

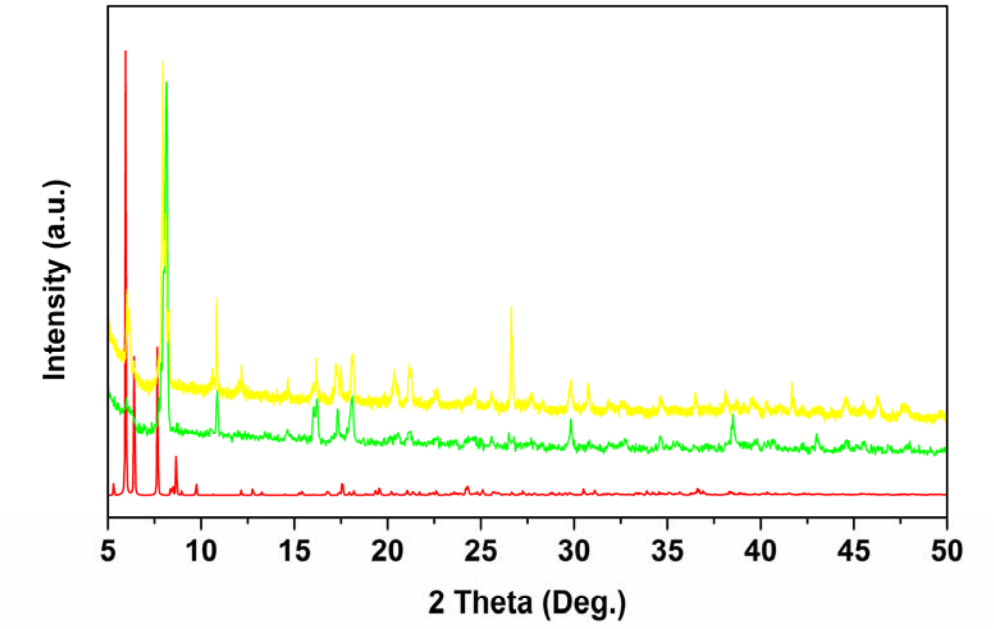

Fig. S5 PXRD patterns of **Ag12b**: (a) simulated from single crystal data (red line); (b) sample obtained from recrystallization of **Ag12a** in DMF (green line); (c) sample derived from recrystallization of **Ag12c** in DMF (yellow line).

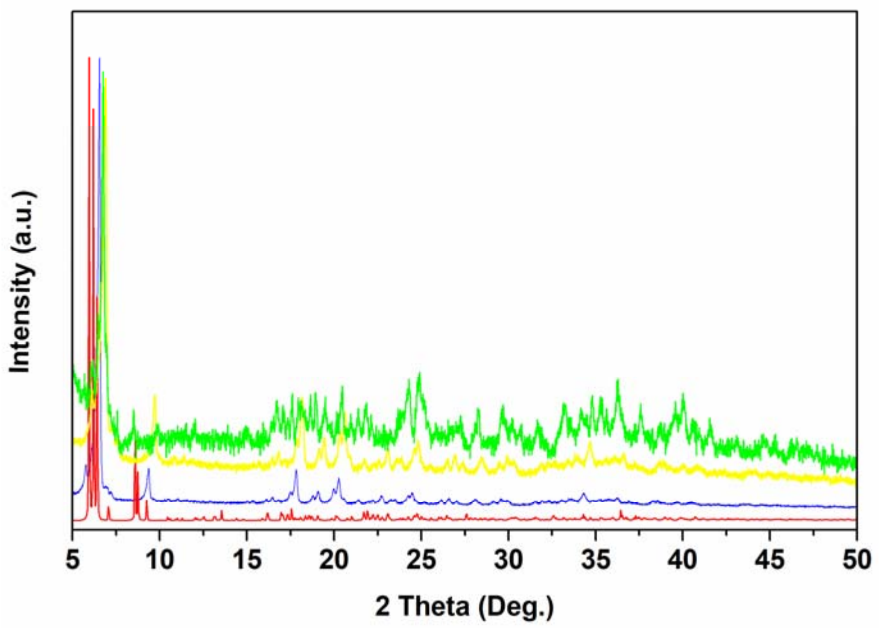

Fig. S6 PXRD patterns of **Ag12c**: (a) simulated from single crystal data (red line); (b) single-phase polycrystalline sample (blue line); (c) sample obtained from recrystallization of **Ag12a** in CH_3CN (yellow line); (d) sample derived from recrystallization of **Ag12b** in CH_3CN (green line).

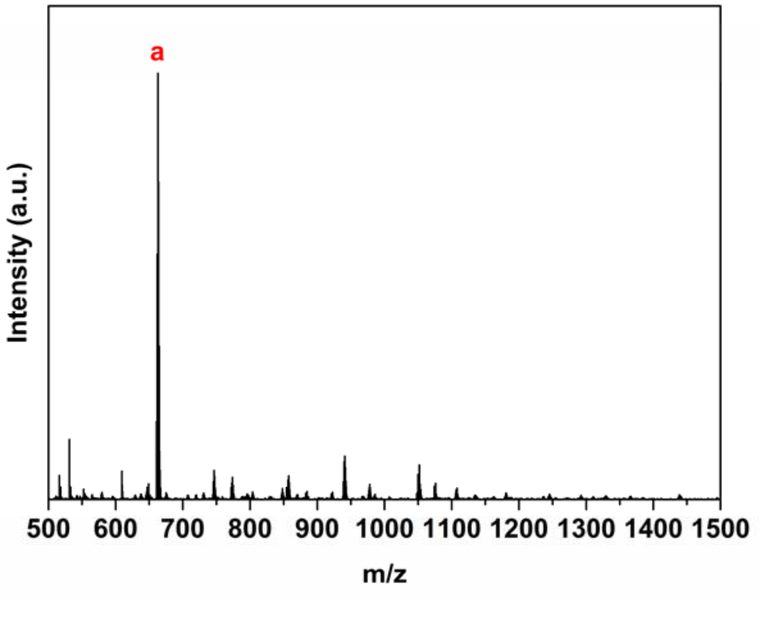

Fig. S7 ESI mass spectrum of the solution of **Ag12c** (obtained from dissolving **Ag12a** in CH_3CN) in the positive mode.

Noted: The major peak at m/z = 662.96 is assignable to the corresponding cationic species $[Ag_4(Tab)_4(TFA)_2]^{2+}$ (a).

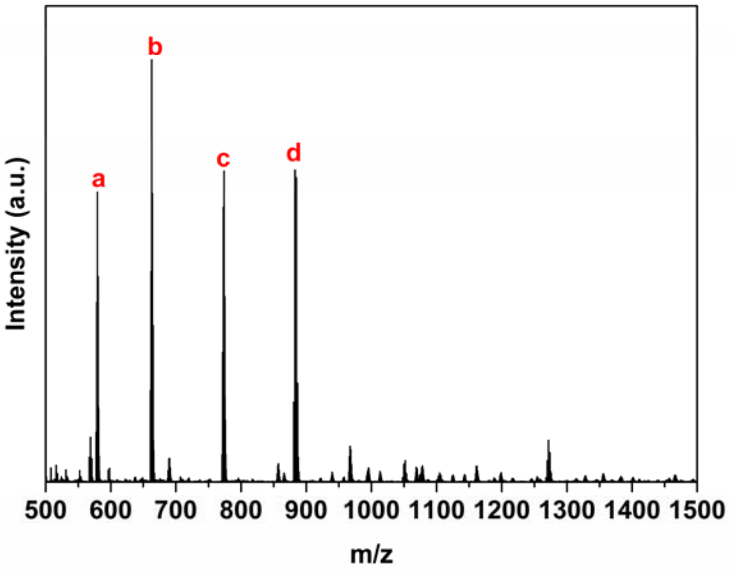

Fig. S8 ESI mass spectrum of the solution of **Ag12b** (obtained from dissolving **Ag12a** in DMF and CH_3OH) in the positive mode.

Noted: The peaks at m/z = 579.41, 652.46, 773.89 and 883.84 are assignable to the corresponding cationic species $[Ag_4(Tab)_3(TFA)_2]^{2+}$ (a), $[Ag_4(Tab)_3(TFA)_2(DMF)_2]^{2+}$ (b), $[Ag_5(Tab)_4(TFA)_3]^{2+}$ (c) and $[Ag_6(Tab)_4(TFA)_4]^{2+}$ (d).

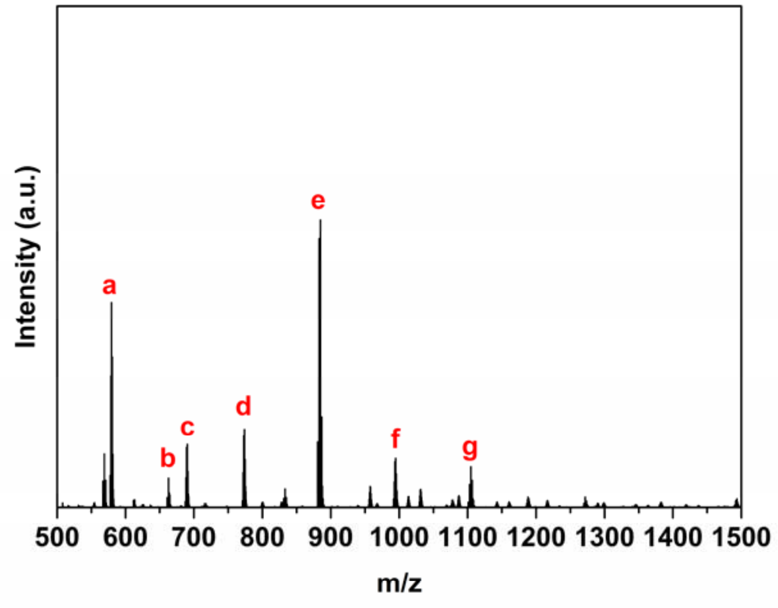

Fig. S9 ESI mass spectrum of the solution of **Ag12a** (dissolved in H_2O, CH_3CN and DMF) in the positive mode.

Noted: The peaks at m/z = 579.41, 652.46, 662.96, 773.89, 883.84, 993.78 and 1105.23 are assignable to the corresponding cationic species $[Ag_4(Tab)_3(TFA)_2]^{2+}$ (a), $[Ag_4(Tab)_3(TFA)_2(DMF)_2]^{2+}$ (b), $[Ag_4(Tab)_4(TFA)_2]^{2+}$ (c), $[Ag_5(Tab)_4(TFA)_3]^{2+}$ (d), $[Ag_6(Tab)_4(TFA)_4]^{2+}$ (e), $[Ag_7(Tab)_4(TFA)_5]^{2+}$ (f) and $[Ag_8(Tab)_4(TFA)_6]^{2+}$ (g).

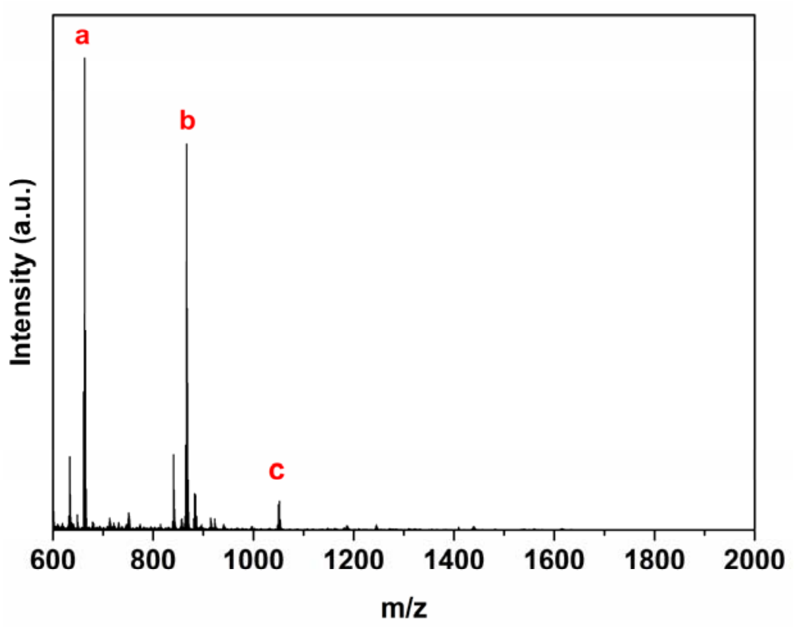

Fig. S10 ESI mass spectrum of the solution of **Ag12b** (obtained from dissolving Ag**12c** in DMF) in the positive mode.

Noted: The peaks at *m*/*z* = 662.96, 873.35 and 1041.95 are assignable to the corresponding cationic species $[Ag_4(Tab)_4(TFA)_2]^{2+}$ (a), $[Ag_6(Tab)_4(TFA)_3(DMF)_2]^{2+}$ (b) and $[Ag_8(Tab)_3(TFA)_6(CH_3CN)]^{2+}$ (c).

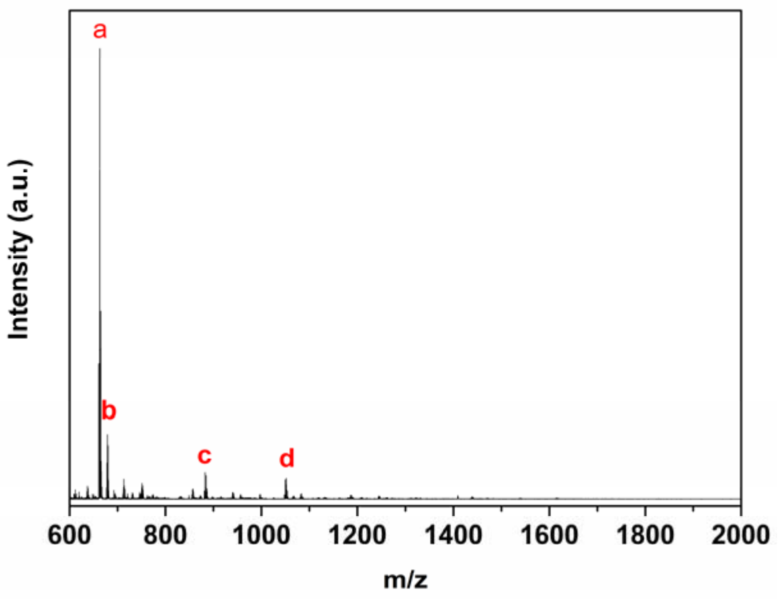

Fig. S11 ESI mass spectrum of the solution of **Ag12c** (obtained from dissolving **Ag12b** in CH_3CN) in the positive mode.

Noted: The peaks at *m*/*z* = 662.96, 683.46, 883.84 and 1041.95 are assignable to the corresponding cationic species $[Ag_4(Tab)_4(TFA)_2]^{2+}$ (a); $[Ag_4(Tab)_4(TFA)_2(CH_3CN)]^{2+}$ (b), $[Ag_6(Tab)_4(TFA)_4]^{2+}$ (c) and $[Ag_8(Tab)_3(TFA)_6(CH_3CN)]^{2+}$ (d).

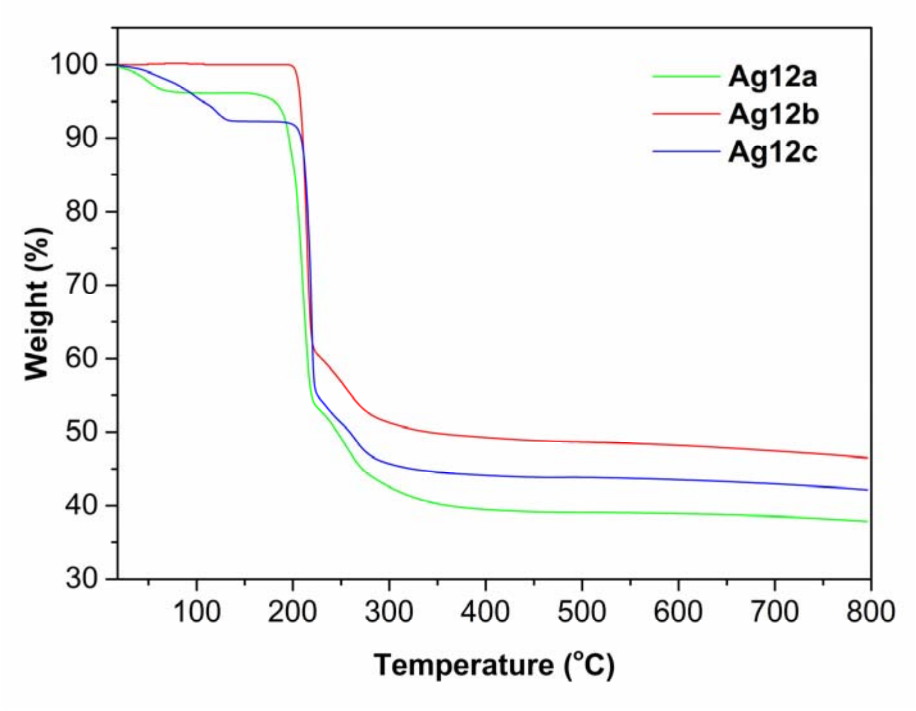

Fig. S12 The TGA plots of **Ag12a**, **Ag12b** and **Ag12c**.

Noted: The isolated silver nanoclusters can stabilize up to 215 °C before their decomposition.