Supporting Information

Thiacalix[4]arene-protected alkynyl Ag_n (n =9, 18) nanoclusters: Syntheses, structural characterizations, photocurrent responses and fluorescence properties

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X-ray crystallography

Crystal data and structure refinements for **Ag_9** and **Ag_{18}** are listed in Table S1. Selected bond lengths, Ag···Ag interactions (Å) data and bond angles for **Ag_9** are listed in Table S2-Table S4. Selected bond lengths, Ag···Ag interactions (Å) data and bond angles for **Ag_{18}** are listed in Table S5-Table S7. Comparation of the average Ag···Ag interactions (Å) and the average bond distances (Å) of important bonds in **Ag_9** and **Ag_{18}** are listed in Table S8 and Table S9, respectively.

Table S1. Crystal data, data collection and structure refinement details for Ag_9 and Ag_{18}

	Ag_9	**Ag_{18}**
Formula	$C_{134}H_{180}Ag_{18}F_6Na_4O_{25}S_8Sb$	$C_{136}H_{176}Ag_{18}F_6O_{16}S_8$
Formula weight	4716.62	4378.90
Crystal system	Orthorhombic	Monoclinic
Space group	I mmm	C 2/m
a (Å)	15.2729(8)	22.163(2)
b (Å)	15.4945(8)	21.603(2)
c (Å)	39.339(2)	19.2809(18)
α (Å)	90	90
β (Å)	90	119.703(3)
γ (Å)	90	90
V (Å^3)	9309.4(8)	8018.5(14)
Z	2	2
Dc/g cm^{-3}	1.683	1.814
μ/mm^{-1}	2.144	2.306
F(000)	4614	4296
Reflection collected	15445	28325
Unique reflections	4495	7220
Parameters	318	641
R_{int}	0.0331	0.0841
GOF	1.111	1.046
R_1[a] [I>2σ(I)]	0.0687	0.0550
wR_2[b] (all data)	0.1849	0.1499

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) data for Ag_9

Bond	Bond length	Bond	Bond length
Ag(1)-C(15)	2.243(10)	Ag(2)-O(2)#1	2.395(9)
Ag(1)-O(2)	2.433(4)	Ag(2)-O(2)	2.395(9)
Ag(1)-O(1)	2.441(4)	Ag(3)-C(15)	2.129(11)
Ag(1)-S(1)	2.484(2)	Ag(3)-C(15)#2	2.129(11)
Ag(1)-C(16)	2.486(9)	Ag(3)-O(3)	2.41(3)
Ag(2)-O(1)#1	2.342(10)	Ag(4)-C(15)	2.171(13)
Ag(2)-O(1)	2.342(10)	Ag(4)-C(15)#3	2.171(13)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,z, #2 x,-y,z, #3 -x,y,z.

Table S3. Ag···Ag interactions (Å) data for Ag_9

Metal···metal contact	Distance	Metal···metal contact	Distance
Ag(1)-Ag(3)	3.1848(12)	Ag(3)-Ag(4)	2.8341(15)
Ag(1)-Ag(4)	3.2188(13)	Ag(3)-Ag(4)#1	2.8341(15)
Ag(1)-Ag(2)	3.2591(10)	Ag(4)-Ag(4)#1	3.331(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,z.

Table S4. Selected bond angle (°) data for Ag_9

Bond	Bond angle	Bond	Bond angle
C(15)-Ag(1)-O(2)	116.3(4)	O(1)#1-Ag(2)-O(1)	178.9(4)
C(15)-Ag(1)-O(1)	115.0(3)	O(1)#1-Ag(2)-O(2)#1	90.000(3)
O(2)-Ag(1)-O(1)	86.8(3)	O(1)-Ag(2)-O(2)#1	90.000(2)
C(15)-Ag(1)-S(1)	160.6(3)	O(1)#1-Ag(2)-O(2)	90.000(2)
O(2)-Ag(1)-S(1)	77.37(18)	O(1)-Ag(2)-O(2)	90.000(2)
O(1)-Ag(1)-S(1)	77.89(18)	O(2)#1-Ag(2)-O(2)	180.0(4)
C(15)-Ag(1)-C(16)	28.7(4)	C(15)-Ag(3)-C(15)#2	169.8(7)
O(2)-Ag(1)-C(16)	120.4(3)	C(15)-Ag(3)-O(3)	94.5(4)
O(1)-Ag(1)-C(16)	139.9(3)	C(15)#2-Ag(3)-O(3)	94.5(4)
S(1)-Ag(1)-C(16)	133.1(3)	C(15)-Ag(4)-C(15)#3	155.3(6)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,z, #2 x,-y,z, #3 -x,y,z.

Table S5. Selected bond distances (Å) data for Ag_{18}

Bond	Bond length	Bond	Bond length
Ag(1)-C(21)	2.224(12)	Ag(4)-O(2)	2.400(6)
Ag(1)-O(1)#1	2.447(5)	Ag(4)-C(28)	2.45(3)
Ag(1)-O(1)	2.447(5)	Ag(4)-O(1)#1	2.454(6)
Ag(1)-S(1)	2.501(3)	Ag(4)-S(2)	2.514(2)
Ag(1)-C(22)	2.508(18)	Ag(5)-C(27)	1.91(5)
Ag(1)-C(22)#1	2.508(18)	Ag(5)-C(33)	2.297(12)
Ag(2)-O(1)#1	2.367(6)	Ag(5)-C(34)#1	2.71(2)
Ag(2)-O(1)	2.367(6)	Ag(6)-C(27)	1.89(4)
Ag(2)-O(2)#1	2.415(6)	Ag(6)-C(21)	2.048(12)
Ag(2)-O(2)	2.415(6)	C(21)-Ag(6A)#1	2.345(11)
Ag(3)-C(33)	2.294(12)	C(21)-Ag(6A)	2.345(11)
Ag(3)-C(34)#1	2.330(18)	C(33)-Ag(5A)#1	2.059(10)
Ag(3)-C(34)	2.330(18)	C(33)-Ag(5A)	2.059(10)
Ag(3)-O(2)	2.397(6)	C(33)-Ag(6A)#3	2.566(11)
Ag(3)-O(2)#1	2.397(6)	C(33)-Ag(6A)#2	2.566(11)
Ag(3)-S(3)	2.506(3)	O(3)-Ag(6A)	2.33(2)
Ag(4)-C(27A)	2.24(3)	O(4)-Ag(5A)#2	2.361(17)
Ag(4)-C(27)	2.33(4)	C(27A)-Ag(5A)	2.22(3)
Ag(4)-C(28A)	2.36(3)	C(27A)-Ag(6A)	2.52(2)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z, #2 -x+1,y,-z+1, #3 -x+1,-y+1,-z+1.

Table S6. Ag···Ag interactions (Å) data for Ag_{18}

Metal···metal contact	Distance	Metal···metal contact	Distance
Ag(1)-Ag(6)#1	3.1187(17)	Ag(4)-Ag(5)	3.222(5)
Ag(1)-Ag(6)	3.1187(17)	Ag(4)-Ag(5A)	3.323(4)
Ag(1)-Ag(2)	3.2534(14)	Ag(5)-Ag(6)	2.441(3)
Ag(2)-Ag(3)	3.2266(15)	Ag(5)-Ag(5)#1	2.758(10)
Ag(2)-Ag(4)	3.2784(9)	Ag(5)-Ag(5)#2	2.938(9)
Ag(2)-Ag(4)#1	3.2785(9)	Ag(6)-Ag(6)#1	2.286(3)
Ag(3)-Ag(5A)#1	3.043(4)	Ag(5A)-Ag(6A)#2	2.932(4)
Ag(3)-Ag(5A)	3.043(4)	Ag(5A)-Ag(5A)#1	3.103(9)
Ag(3)-Ag(5)#1	3.219(4)	Ag(5A)-Ag(5A)#2	3.209(8)
Ag(3)-Ag(5)	3.219(4)	Ag(6A)-Ag(6A)#1	2.823(4)
Ag(4)-Ag(6)	3.1013(16)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z, #2 -x+1,y,-z+1.

Table S7. Selected bond angle (°) data for Ag_{18}

Bond	Bond angle	Bond	Bond angle
C(21)-Ag(1)-O(1)#1	113.2(3)	C(33)-Ag(3)-S(3)	151.2(4)
C(21)-Ag(1)-O(1)	113.2(3)	C(34)#1-Ag(3)-S(3)	124.5(5)
O(1)#1-Ag(1)-O(1)	87.2(3)	C(34)-Ag(3)-S(3)	124.5(5)
C(21)-Ag(1)-S(1)	164.7(4)	O(2)-Ag(3)-S(3)	78.40(14)
O(1)#1-Ag(1)-S(1)	77.31(13)	O(2)#1-Ag(3)-S(3)	78.40(14)
O(1)-Ag(1)-S(1)	77.31(14)	C(27A)-Ag(4)-C(28A)	29.8(10)
C(21)-Ag(1)-C(22)	29.6(5)	C(27A)-Ag(4)-O(2)	113.8(8)
O(1)#1-Ag(1)-C(22)	138.5(5)	C(27)-Ag(4)-O(2)	112.3(12)
O(1)-Ag(1)-C(22)	119.5(5)	C(28A)-Ag(4)-O(2)	141.9(7)
S(1)-Ag(1)-C(22)	135.9(5)	C(27)-Ag(4)-C(28)	33.5(12)
C(21)-Ag(1)-C(22)#1	29.6(5)	O(2)-Ag(4)-C(28)	132.1(7)
O(1)#1-Ag(1)-C(22)#1	119.5(5)	C(27)-Ag(4)-O(1)#1	109.9(11)
O(1)-Ag(1)-C(22)#1	138.5(5)	O(2)-Ag(4)-O(1)#1	87.9(2)
S(1)-Ag(1)-C(22)#1	135.9(5)	C(28)-Ag(4)-O(1)#1	128.2(7)
C(22)-Ag(1)-C(22)#1	21.4(10)	C(27A)-Ag(4)-S(2)	161.7(6)
O(1)#1-Ag(2)-O(1)	91.0(3)	C(27)-Ag(4)-S(2)	167.4(11)
O(1)#1-Ag(2)-O(2)#1	175.71(19)	C(28A)-Ag(4)-S(2)	134.4(8)
O(1)-Ag(2)-O(2)#1	89.61(19)	O(2)-Ag(4)-S(2)	77.97(14)
O(1)#1-Ag(2)-O(2)	89.61(19)	C(28)-Ag(4)-S(2)	134.1(7)
O(1)-Ag(2)-O(2)	175.71(19)	O(1)#1-Ag(4)-S(2)	76.70(13)
O(2)#1-Ag(2)-O(2)	89.5(3)	C(27)-Ag(5)-C(33)	170.4(14)
C(33)-Ag(3)-C(34)#1	32.9(5)	C(27)-Ag(5)-C(34)#1	142.2(14)
C(33)-Ag(3)-C(34)	32.9(5)	C(33)-Ag(5)-C(34)#1	28.8(5)
C(34)#1-Ag(3)-C(34)	48.7(11)	C(27)-Ag(6)-C(21)	156.9(15)
C(33)-Ag(3)-O(2)	120.1(2)	C(33)-Ag(5A)-C(27A)	169.0(7)
C(34)#1-Ag(3)-O(2)	107.7(6)	C(33)-Ag(5A)-O(4)#2	95.9(5)
C(34)-Ag(3)-O(2)	152.7(5)	O(3)-Ag(6A)-C(21)	112.0(7)
C(33)-Ag(3)-O(2)#1	120.1(2)	O(3)-Ag(6A)-C(27A)	113.1(10)
C(34)#1-Ag(3)-O(2)#1	152.7(5)	C(21)-Ag(6A)-C(27A)	115.9(6)
C(34)-Ag(3)-O(2)#1	107.7(6)	C(21)-Ag(6A)-C(33)#3	106.6(3)
O(2)-Ag(3)-O(2)#1	90.4(3)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z, #2 -x+1,y,-z+1, #3 -x+1,-y+1,-z+1.

Table S8. Comparation of the average Ag···Ag interactions (Å) in Ag_9 and Ag_{18}

	Ag_5@TC4A	**Ag_4@(^{t}BuC≡C)$_4$**	Between **Ag_5@TC4A** and **Ag_4@(^{t}BuC≡C)$_4$**	Between **Ag_9** and **Ag_9**
Ag_9	3.259 Å	3.000 Å	3.202 Å	6.500 Å
Ag_{18}	3.259 Å	2.648 Å	3.156 Å	3.083 Å

Table S9. Comparation of the average bond distances (Å) of important bonds in Ag_9 and Ag_{18}

	The Ag-S bond in **Ag_5@TC4A**	The Ag-O bond in **Ag_5@TC4A**	The Ag-C bond in **Ag_4@(^{t}BuC≡C)$_4$**	The Ag-O bond attached to CH_3OH/CF_3COO^-
Ag_9	2.484 Å	2.391 Å	2.222 Å	2.410 Å (CH_3OH)
Ag_{18}	2.507 Å	2.411 Å	2.309 Å	2.346 Å (CF_3COO^-)

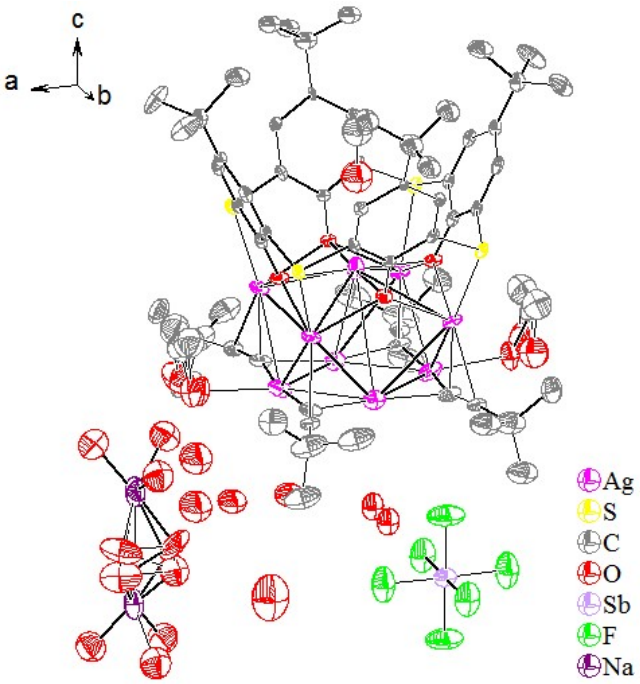

Fig. S1 30% Ellipsoid representations of **Ag_9** containing all disordered atoms. All the hydrogen atoms have been omitted.

As shown in Fig. S2, although Sb1 is still highly over-assigned, both of the charge conservation and the rationality of crystal data refinement have been taken into consideration, the assignment of atom Sb1 is reasonable.

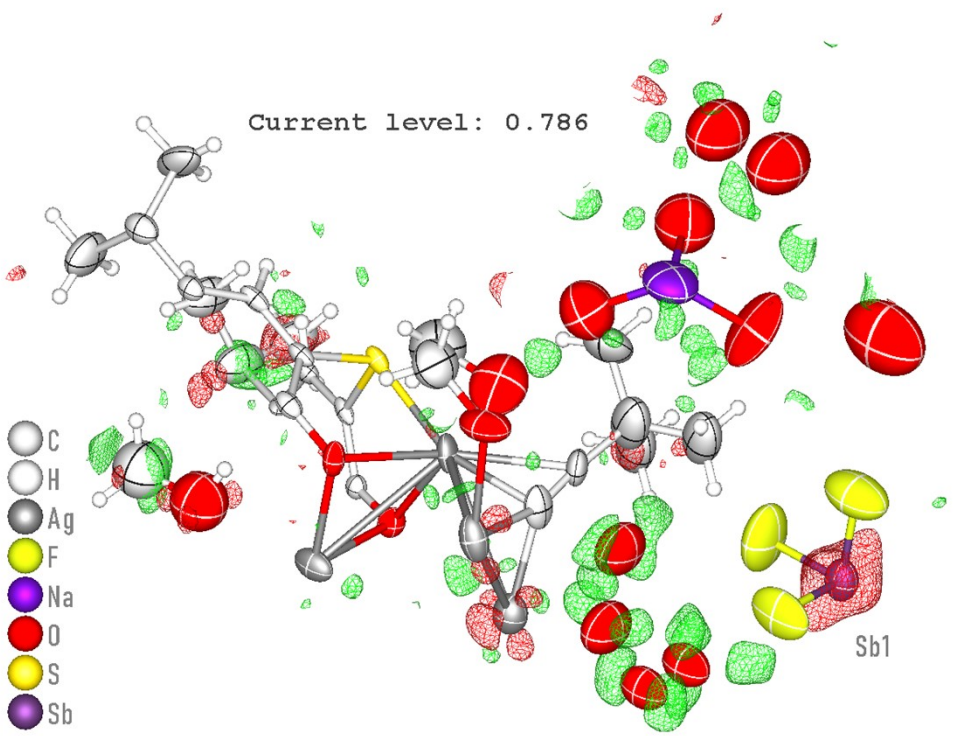

Fig. S2 The residual density plot of **Ag_9**.

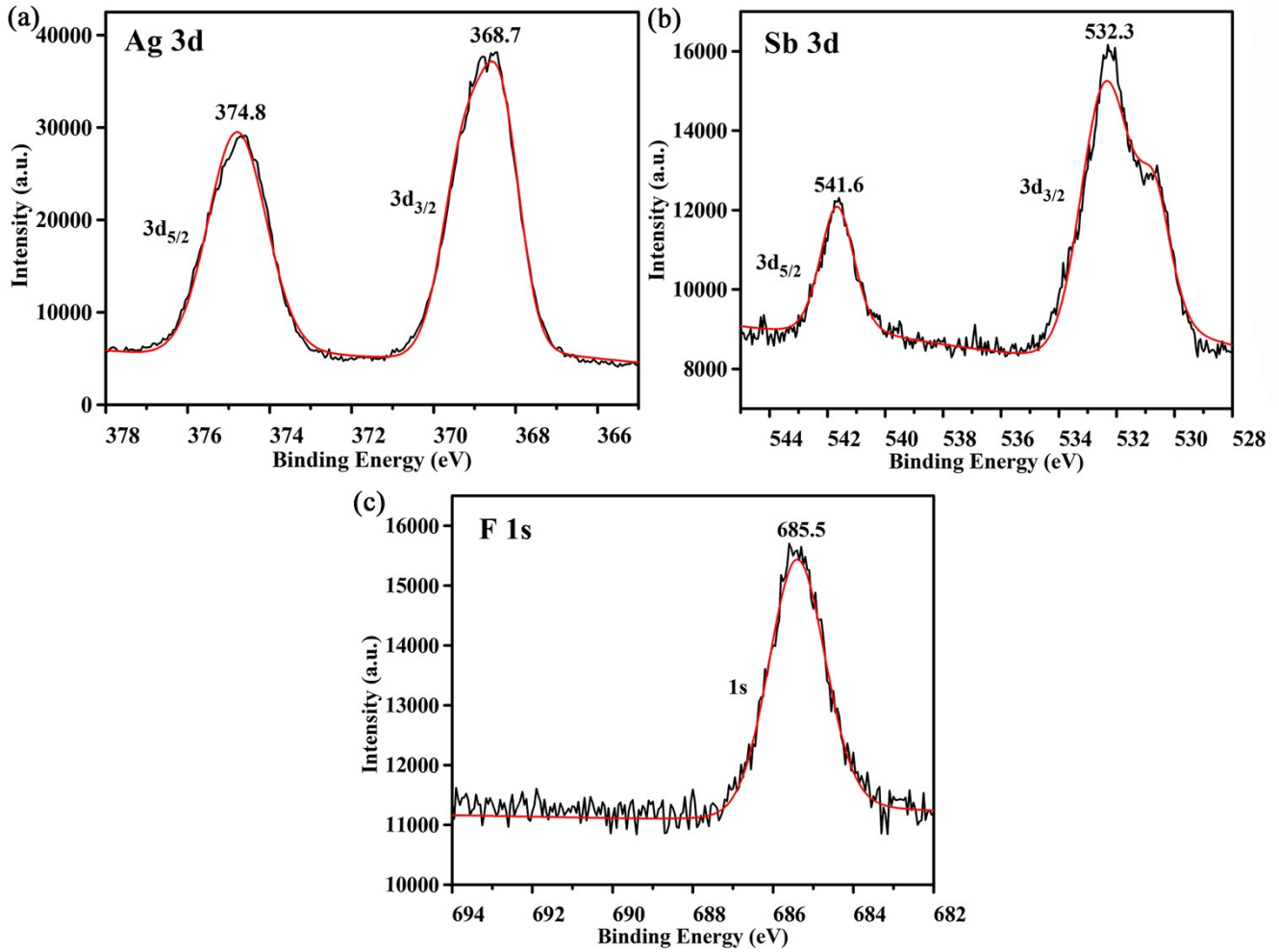

Fig. S3 (a) XPS peak of Ag 3d in **Ag$_9$**. (b) XPS peak of Sb 3d in **Ag$_9$**. (c) XPS peak of F 1s in **Ag$_9$**.

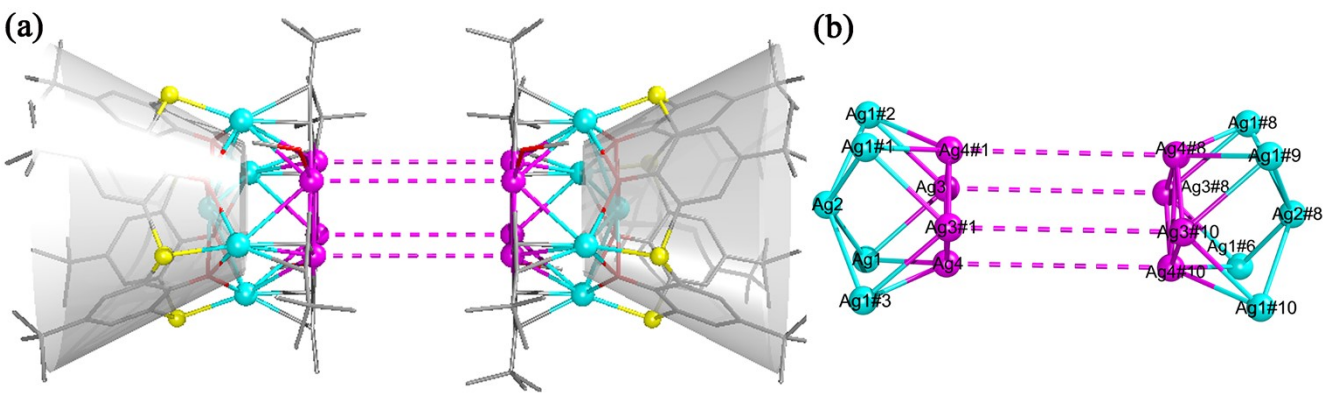

Fig. S4 (a) Side view of two $[Ag_9(TC4A)(^tBuC{\equiv}C)_4(CH_3OH)_2]^+$ cationic cluster in **Ag$_9$** and the grey cone representation of the $TC4A^{4-}$ ligand, and the Ag···Ag distances between the two Ag_9 cores drawn in dotted lines. (b) The two Ag_9 cores in **Ag$_9$**, and the Ag···Ag distances between the two Ag_9 cores drawn in dotted lines. Color code: Ag, turquoise, pink; O, red; S, yellow; C, gray-50%.

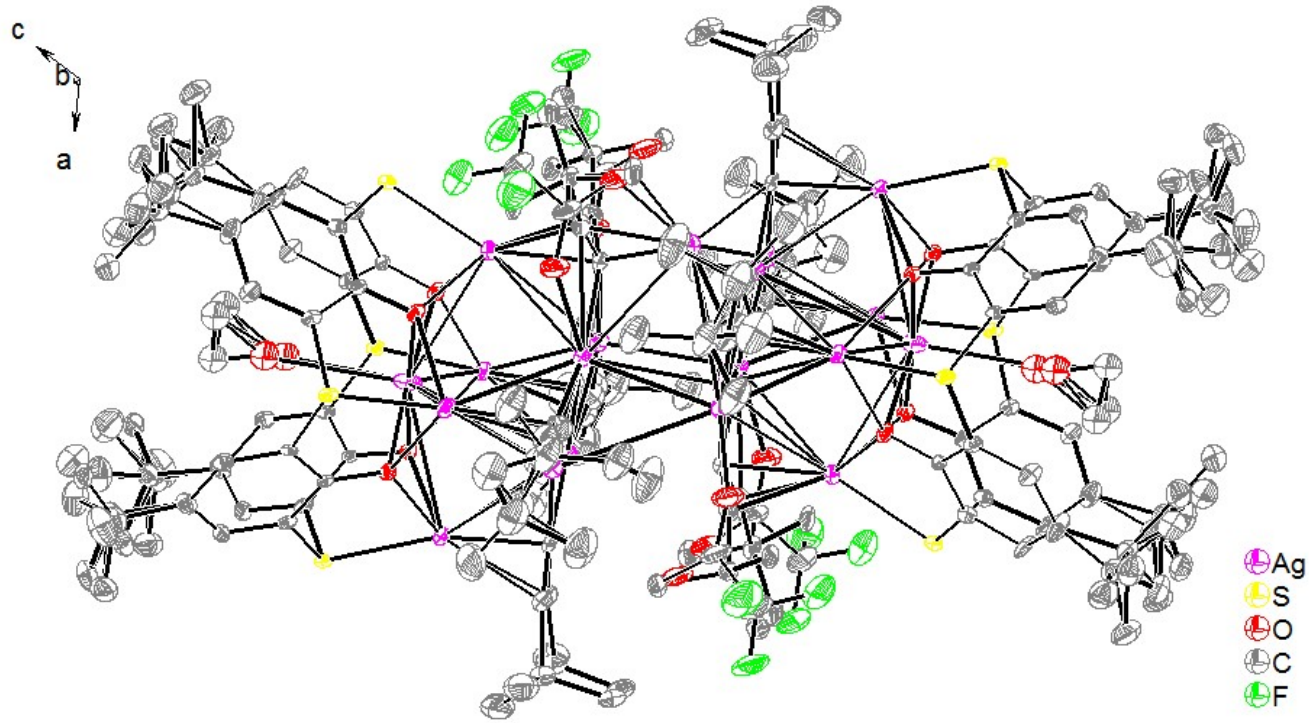

Fig. S5 30% Ellipsoid representations of **Ag_{18}** containing all disordered atoms. All the hydrogen atoms have been omitted.

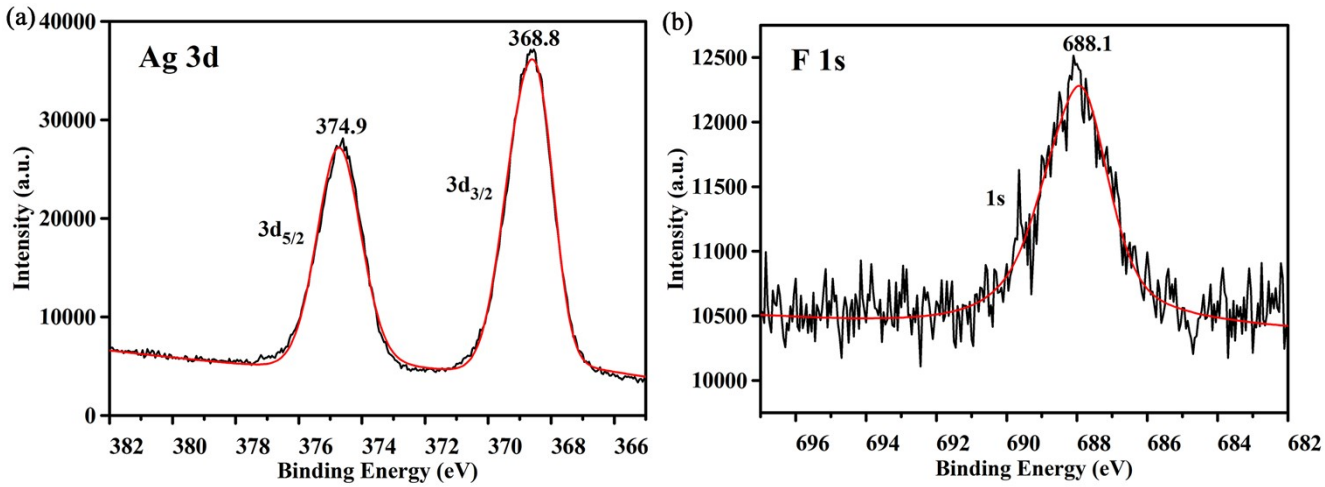

Fig. S6 (a) XPS peak of Ag 3d in **Ag_{18}**. (b) XPS peak of F 1s in **Ag_{18}**.

^{1}H NMR

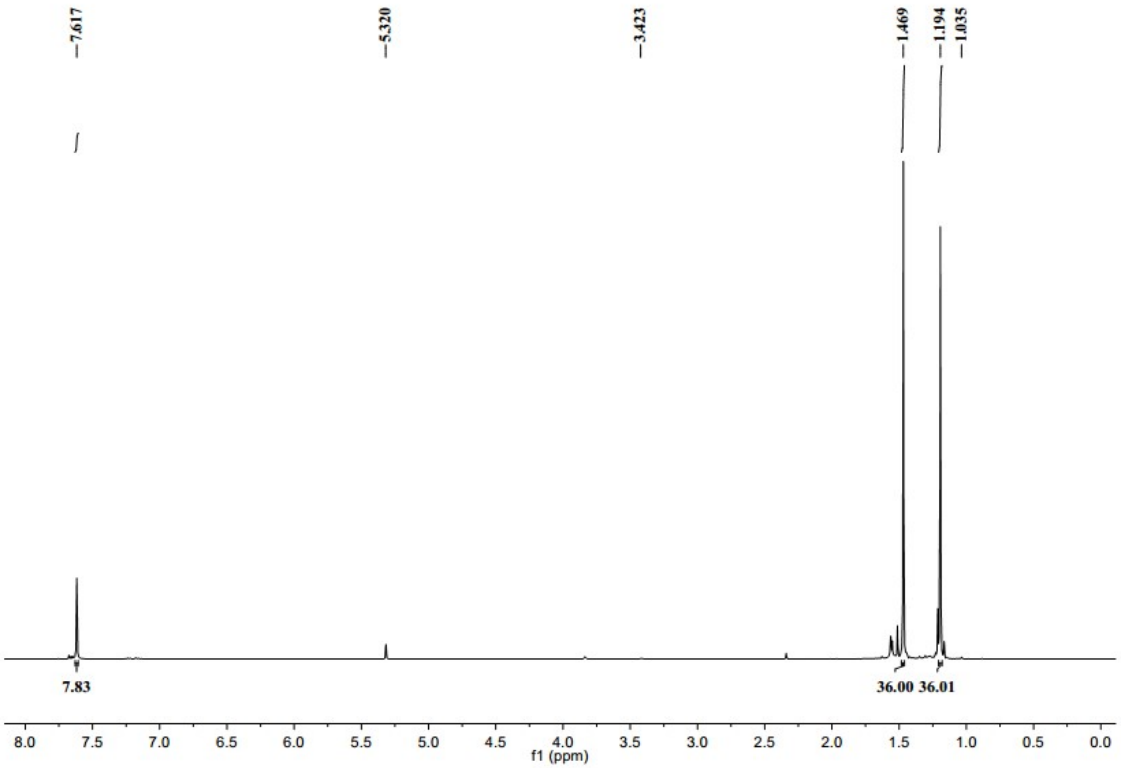

Fig. S7 ^{1}H NMR of **Ag_9**.

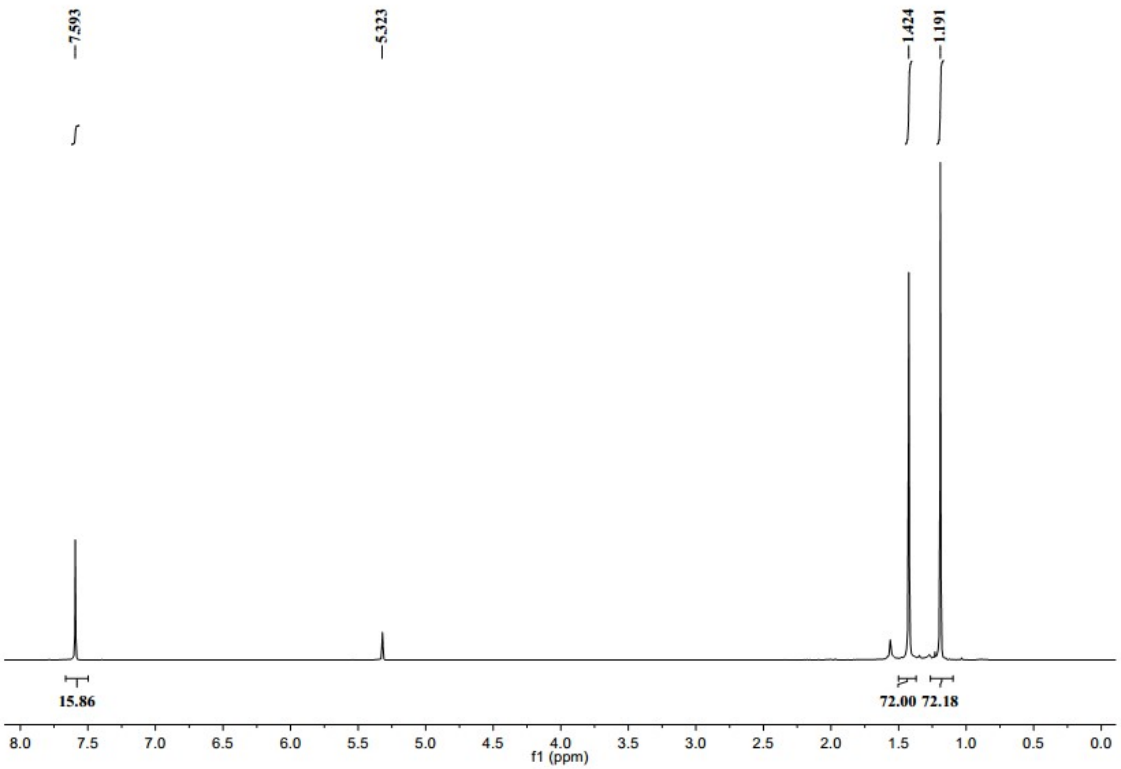

Fig. S8 ^{1}H NMR of **Ag_{18}**.

MALDI-TOF mass spectrometry

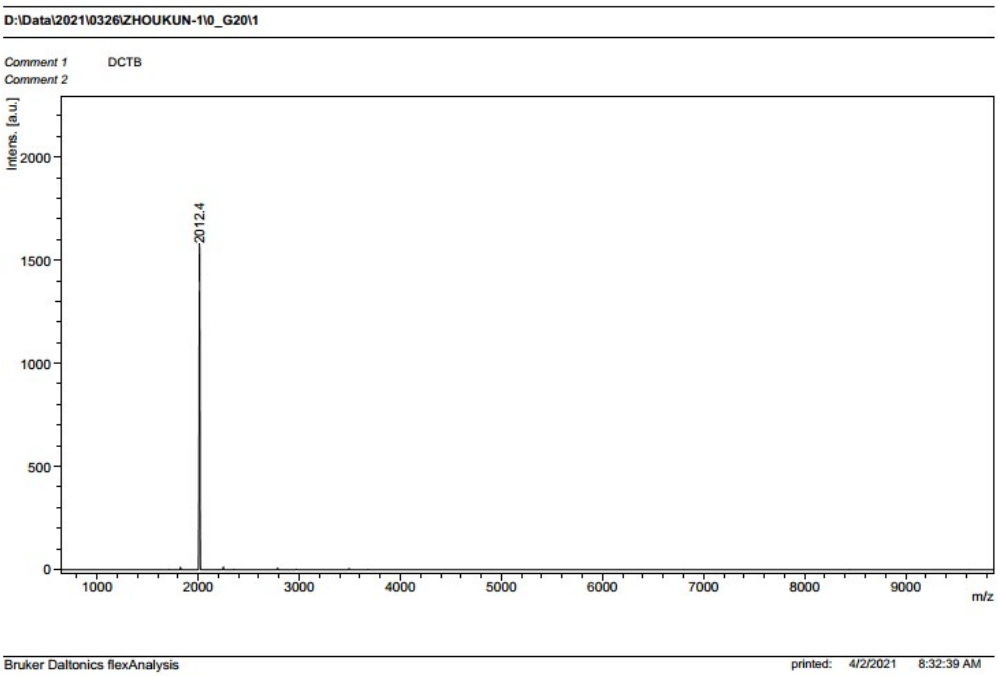

Fig. S9 The full range file of MALDI-TOF MS of the $[Ag_9(TC4A)(^tBuC{\equiv}C)_4]^+$ cluster in $\mathbf{Ag_9}$.

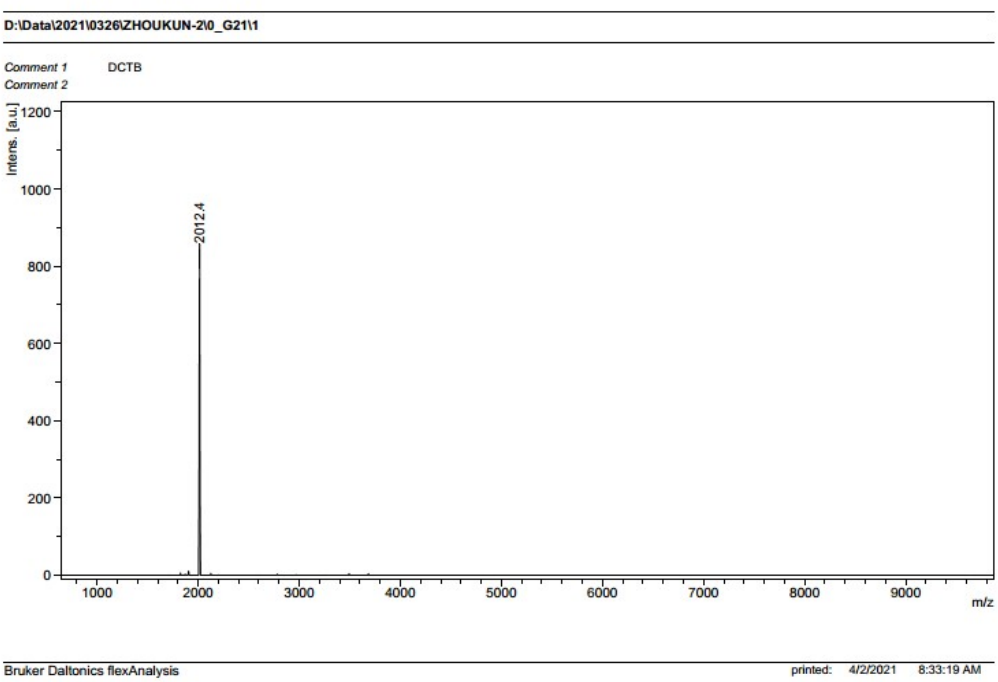

Fig. S10 The full range file of MALDI-TOF MS of the $[Ag_9(TC4A)(^tBuC{\equiv}C)_4]_2^{2+}$ cluster in $\mathbf{Ag_{18}}$.

PXRD Measurements

The experimental powder X-ray diffraction patterns of the two compounds are in accordance with the simulated ones from the single crystal X-ray data, confirming the phase purity of the samples.

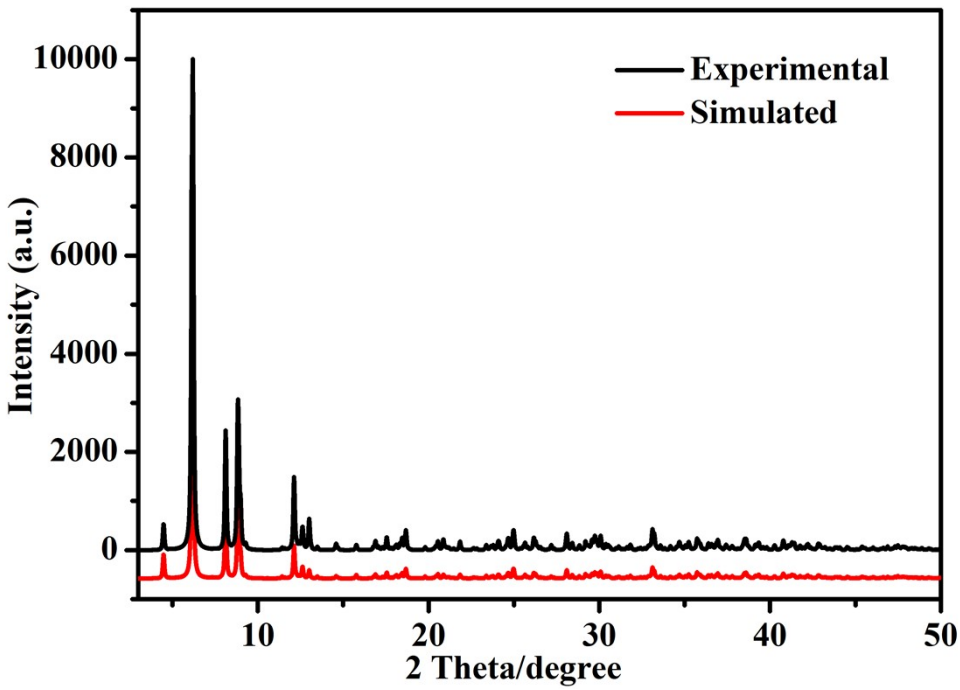

Fig. S11 PXRD of **Ag_9**.

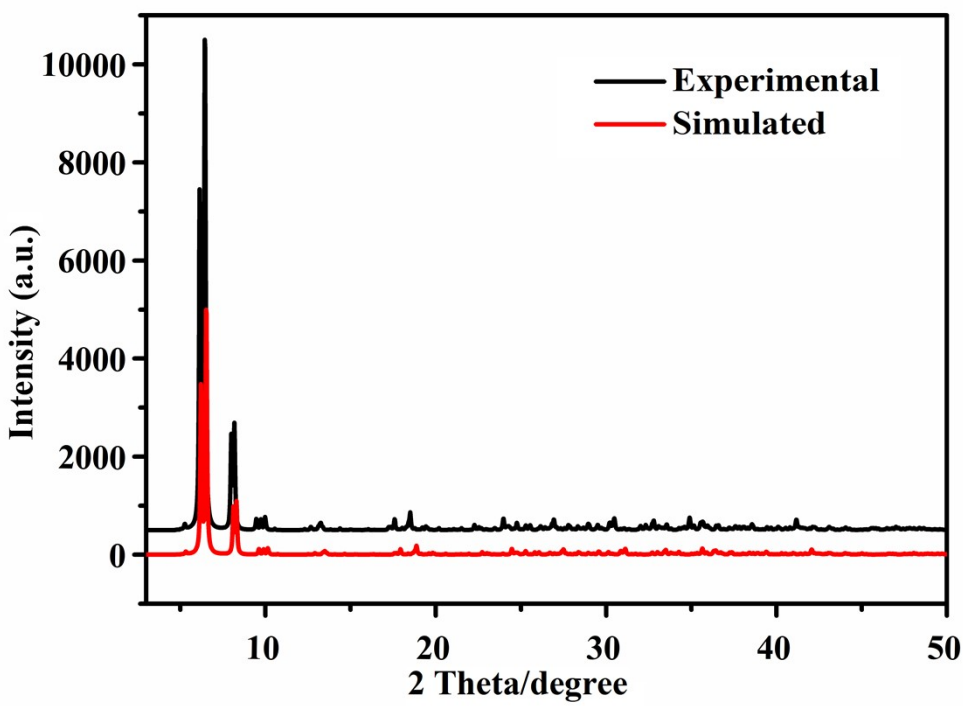

Fig. S12 PXRD of **Ag_{18}**.

FT-IR Spectra

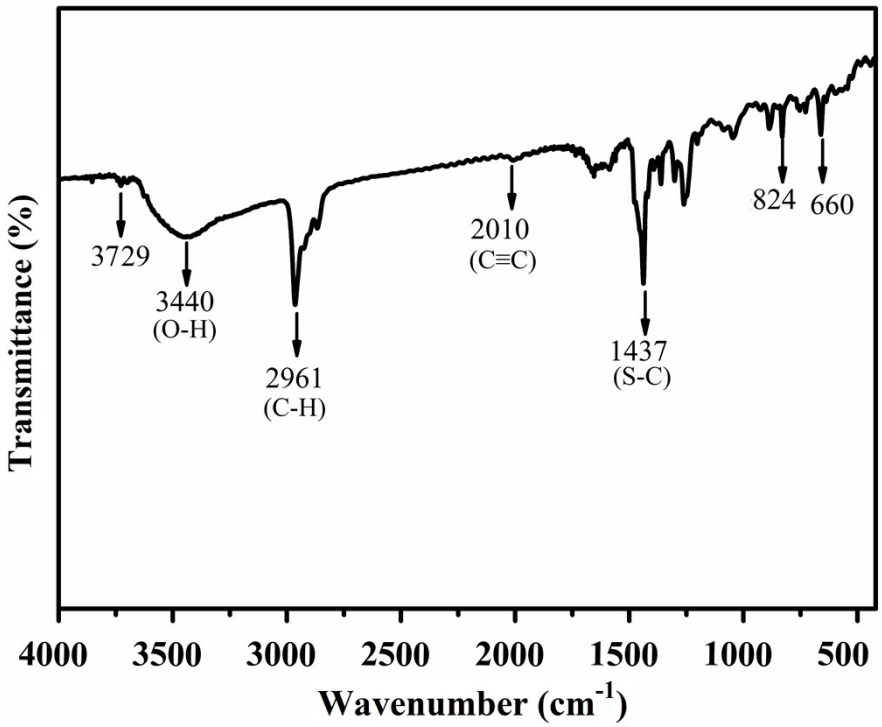

Fig. S13 FT-IR spectrum of **Ag_9**.

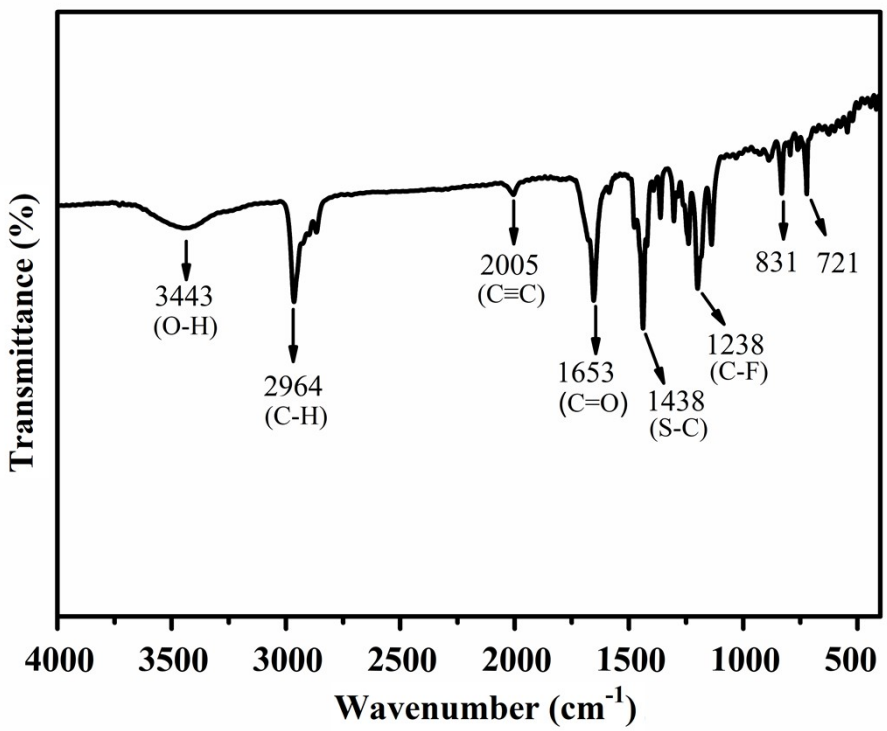

Fig. S14 FT-IR spectrum of **Ag_{18}**.

TG-DSC Analyses

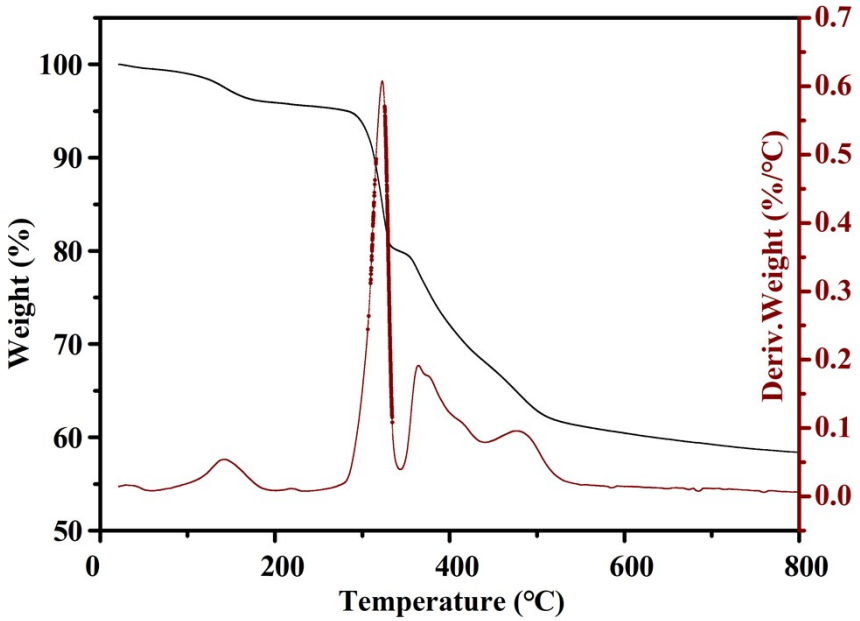

Fig. S15 TG curves of **Ag_9**.

As shown in Fig. S16, the weight loss of **Ag_{18}** from room temperature to 220 °C could be attributed to the loss of CH_3OH molecules attached to the crystal surface. From 220 °C to 290 °C, there is a sharp drop in weight due to the shed of tert-butyl acetylene ligands and CF_3COO^- ligands. After 290 °C, the weight decreased sharply, which can be attributed to the decomposition of thiacalix[4]arene ligands and the collapse of the skeleton of **Ag_{18}**.

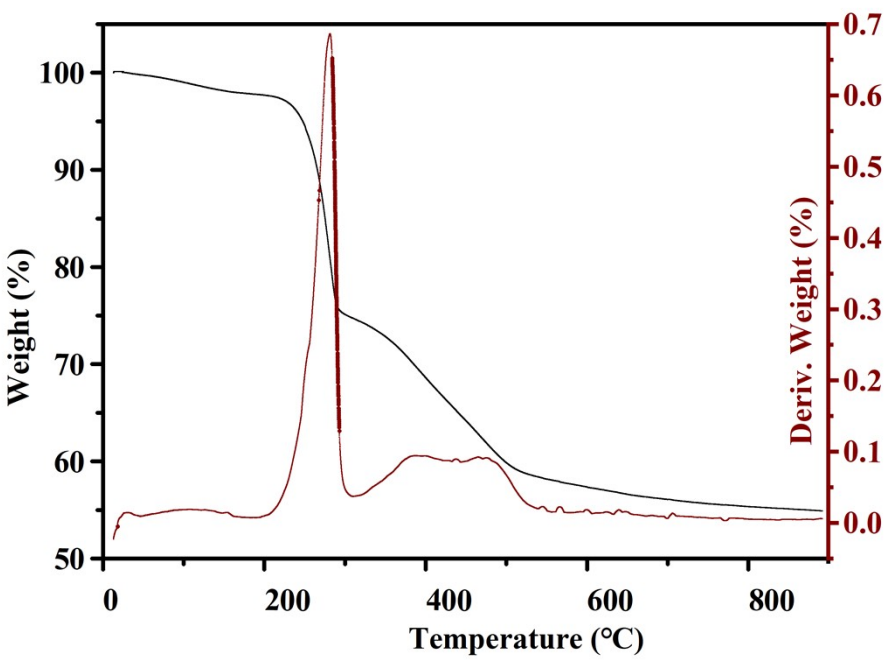

Fig. S16 TG curves of **Ag_{18}**.

Photocurrent measurement

The photocurrent test was carried out on a CHI660E electrochemistry workstation[1,2] and in a typical three-electrode system. The crystals (10 mg) of **Ag_9** and **Ag_{18}** were dispersed in 1 mL trichloromethane, the mixture was sonicated for about 30 min. Then a 20 μL solution was transferred by pipetting gun dropped on the cleaned FTO glass, which apply three to five times in the same way after evaporation under ambient atmosphere. Then a conductive layer of 0.8 × 1 cm^2 compounds made of AB glue were transferred into a drying oven and kept at 80 °C for 10 h. The coated film was obtained. The prepared FTO glass film was used as working electrode, platinum wire as the counter electrode, Ag/AgCl as the reference electrode and keeping the bias voltage at 0.6 V, and a 0.2 M Na_2SO_4 aqueous solution was used as the electrolyte.

Reference:

1.Z. Wang, H.-F. Su, Y.-W. Gong, Q.-P. Qu, Y.-F. Bi , C.-H. Tung, D. Sun and L.-S. Zheng, *Nat. Commun.*, 2020, **11**, 308.

2.P.-P. Zhang, J. Peng, H.-J. Pang, J.-Q. Sha, M. Zhu, D.-D. Wang and M.-G. Liu, *CrystEngComm*, 2011, **13**, 3832–3841.