Electronic Supplementary Information for

Novel Chloride-centered Ag_{18} Clusters Featuring Cuboctahedral Ag_{12} Skeleton

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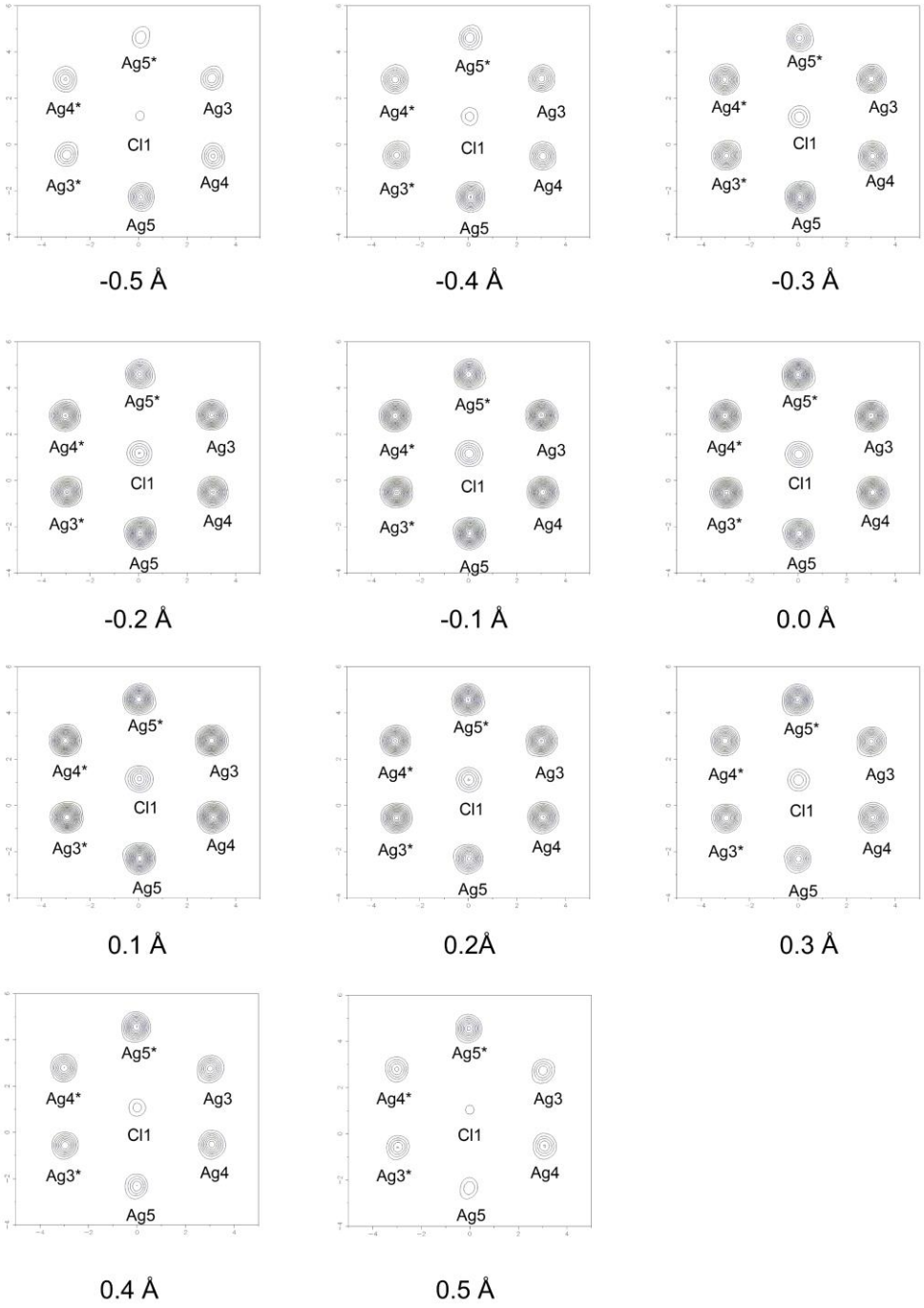

Figure S1. Fourier maps for one of the two independent clusters in **1**. The area depicted are the plane defined by the center chloride and six silver atoms. Each layer is sliced by 0.1 Å.

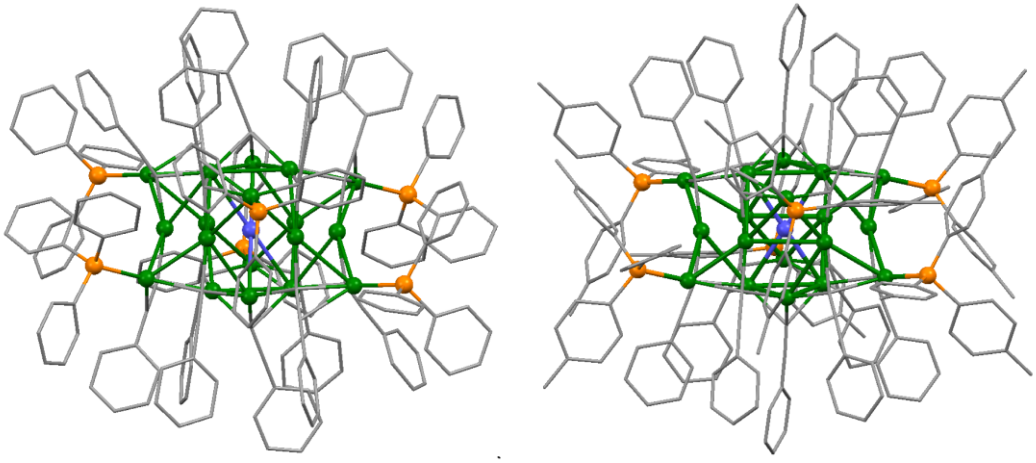

Figure S2. Molecular structures of **1** (left) and **2** (right). Color legend: green sphere, Ag; blue, Cl; orange, P; gray, C. All hydrogen atoms are omitted for clarity.

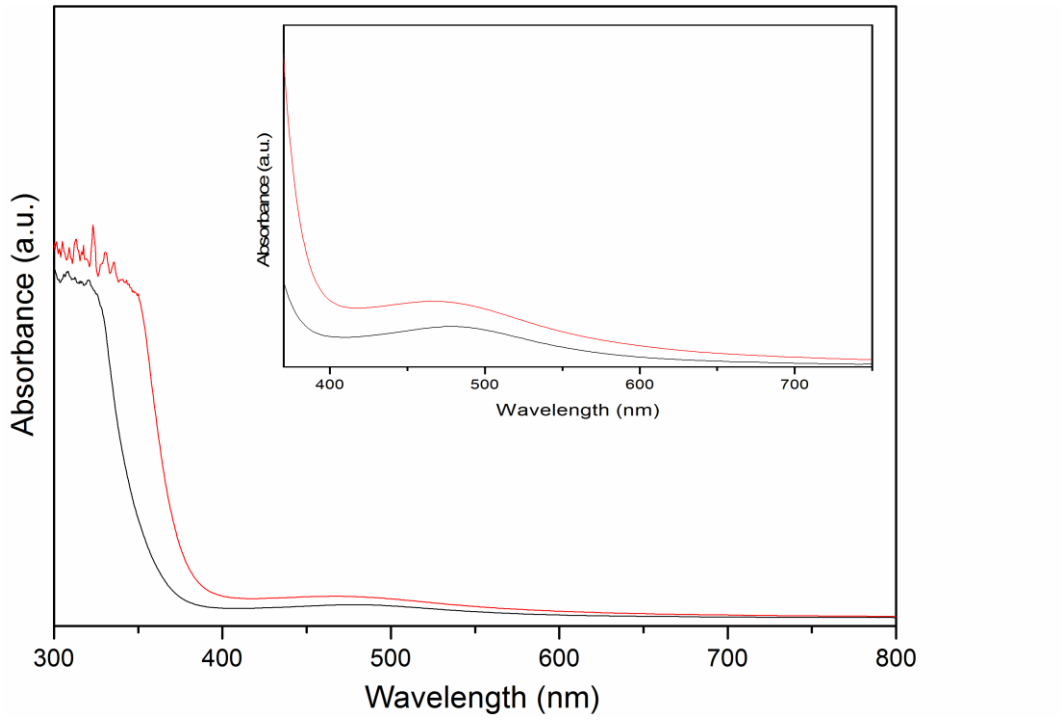

Figure S3. UV-vis spectra of concentrated solutions of **1** (black) and **2** (red) in CH_2Cl_2. Inset: Enlarged spectra of each cluster.

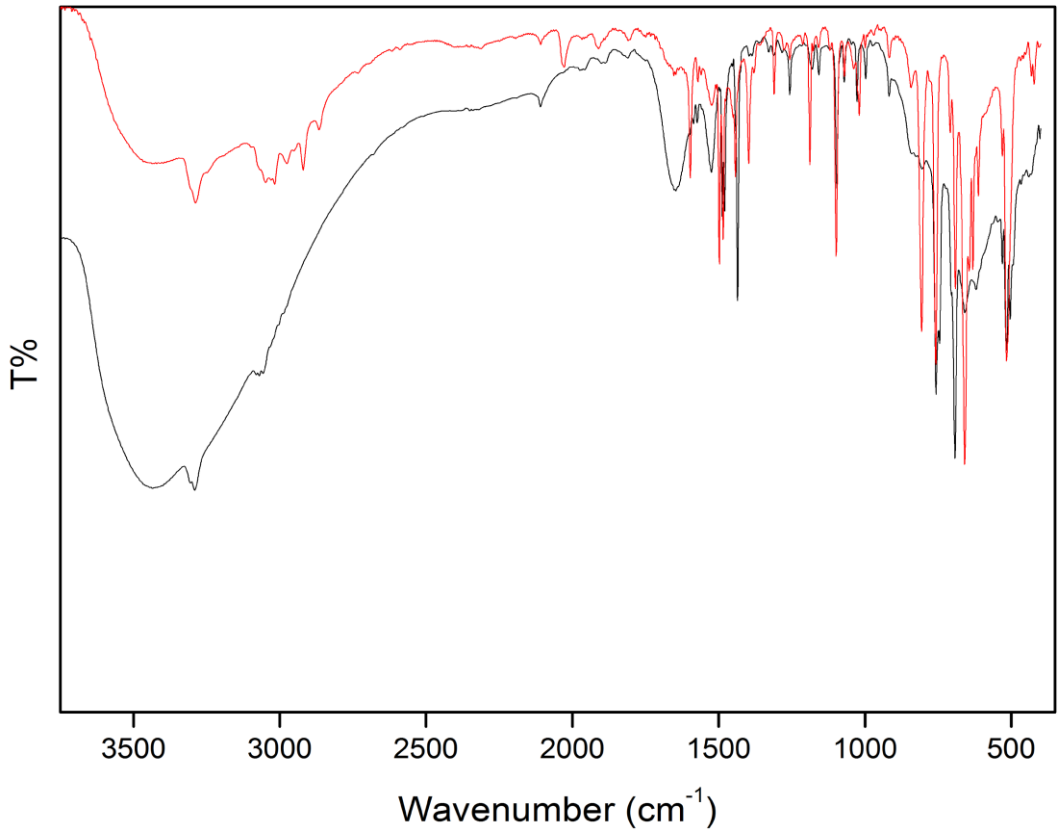

Figure S4. IR spectra of **1** (black) and **2** (red).

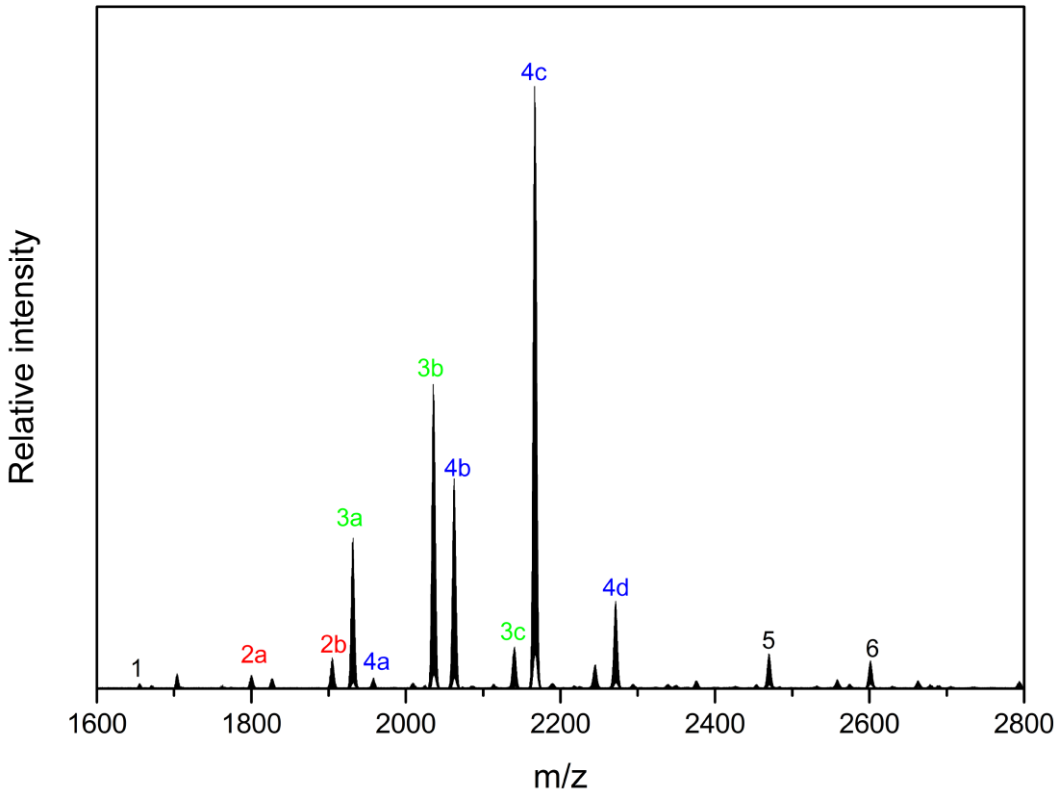

Figure S5. Cold-Spray Mass spectrum of **1** in CH_2Cl_2 ($PhC{\equiv}C^-$, denoted as PA).

(Peak assignments see below Table S1)

Table S1. The assigned formulae of species in Figure S5.

Species	Peak assignment	Obs.	Calc.	Δm/z
1	$[Ag_{18}(PA)_{14}(PPh_3)_6Cl]^{3+}$	1655.44	1655.45	-0.01
2a	$[Ag_{16}(PA)_{13}(PPh_3)_2Cl]^{2+}$	1800.59	1800.07	0.52
2b	$[Ag_{17}(PA)_{14}(PPh_3)_2Cl]^{2+}$	1904.56	1904.04	0.52
3a	$[Ag_{16}(PA)_{13}(PPh_3)_3Cl]^{2+}$	1931.63	1931.12	0.51
4a	$[Ag_{15}(PA)_{12}(PPh_3)_4Cl]^{2+}$	1957.70	1957.19	0.51
3b	$[Ag_{17}(PA)_{14}(PPh_3)_3Cl]^{2+}$	2035.59	2035.09	0.5
4b	$[Ag_{16}(PA)_{13}(PPh_3)_4Cl]^{2+}$	2062.17	2062.16	0.01
3c	$[Ag_{18}(PA)_{15}(PPh_3)_3Cl]^{2+}$	2140.07	2140.06	0.01
4c	$[Ag_{17}(PA)_{14}(PPh_3)_4Cl]^{2+}$	2166.15	2166.13	0.02
4d	$[Ag_{18}(PA)_{15}(PPh_3)_4Cl]^{2+}$	2271.12	2271.61	-0.49
5	$[Ag_{18}(PA)_{14}(PPh_3)_5ClSbF_6]^{2+}$	2469.58	2469.58	0
6	$[Ag_{18}(PA)_{14}(PPh_3)_6ClSbF_6]^{2+}$	2600.14	2600.63	-0.49

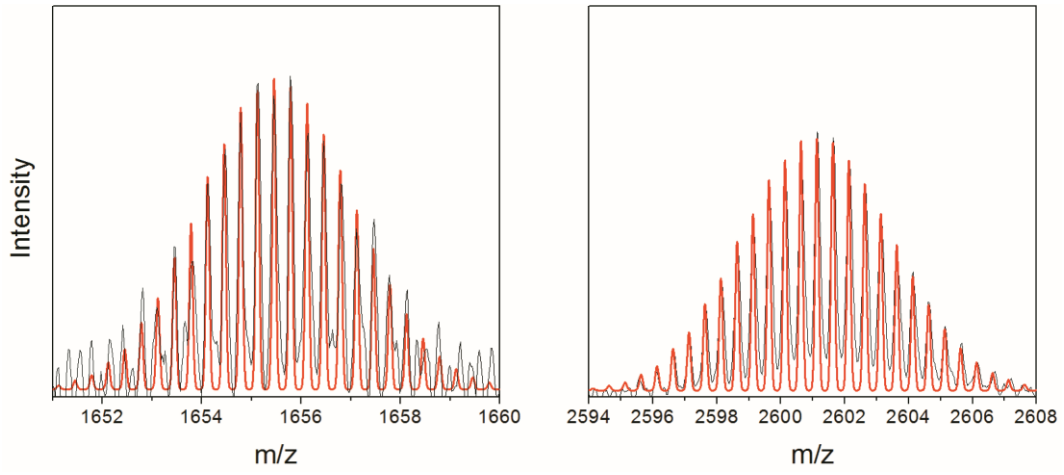

Figure S6. Enlarged portion of the spectrum showing the measured (black) and simulated (red) isotopic distribution patterns of the species $[Ag_{18}(PA)_{14}(PPh_3)_6Cl]^{3+}$ (left) and $[Ag_{18}(PA)_{14}(PPh_3)_6ClSbF_6]^{2+}$(right).

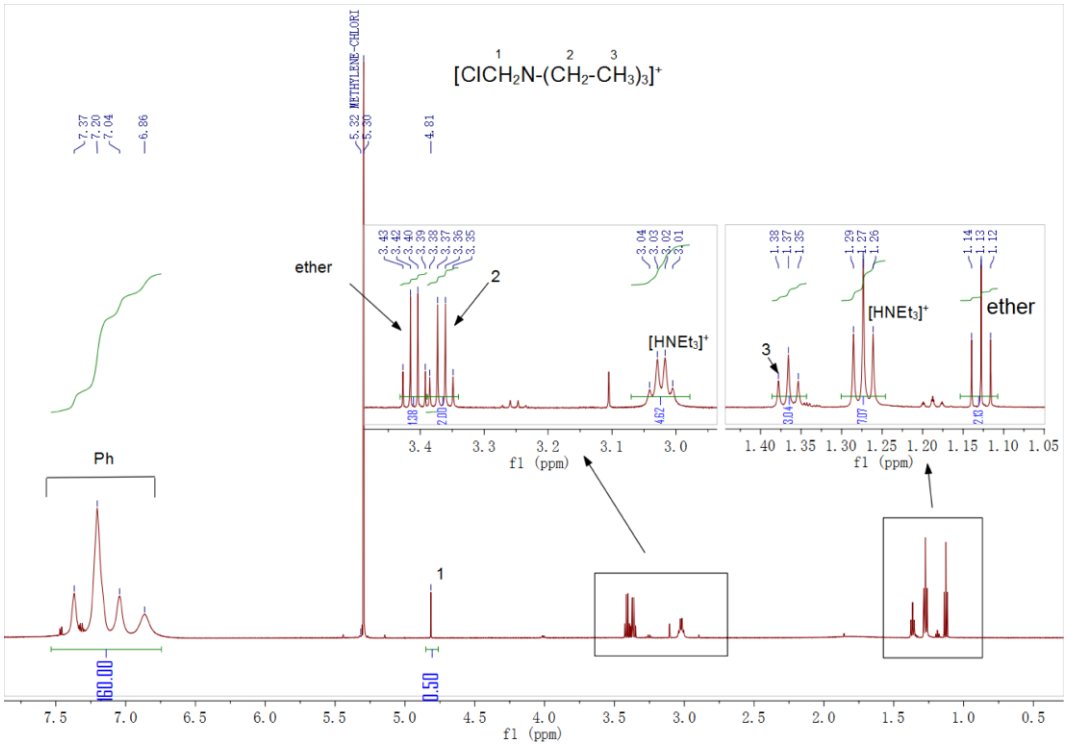

Figure S7. ^{1}H NMR of **1** in CD_2Cl_2 ($[ClCH_2N\text{-}(CH_2CH_3)_3]^+$（ref. 1） and $[HNEt_3]^+$ (ref.2)).

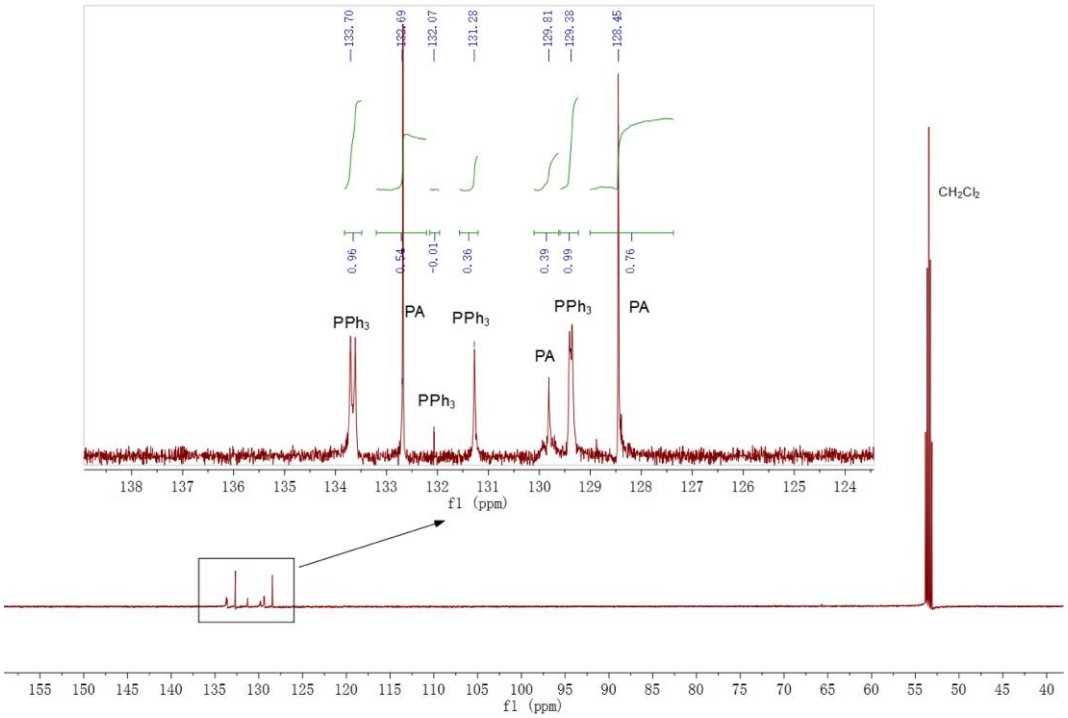

Figure S8. ^{13}C NMR of **1** in CD_2Cl_2 (PA (ref.3) and PPh_3 (ref.4)).

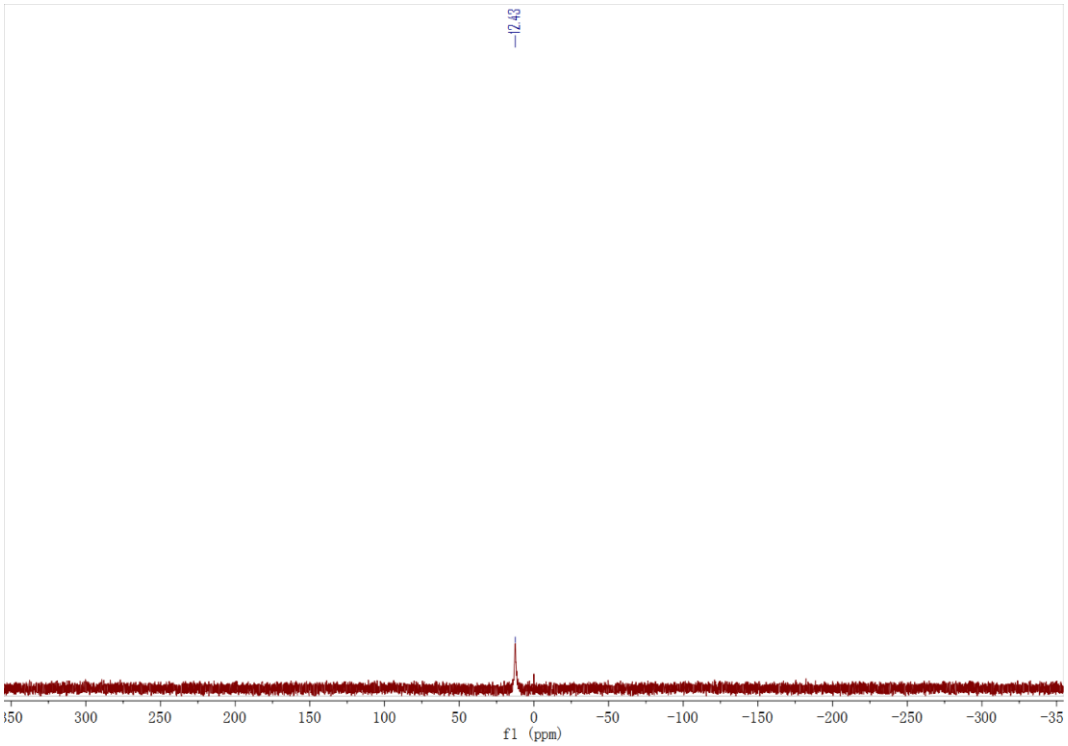

Figure S9. ^{31}P NMR of **1** in CD_2Cl_2.

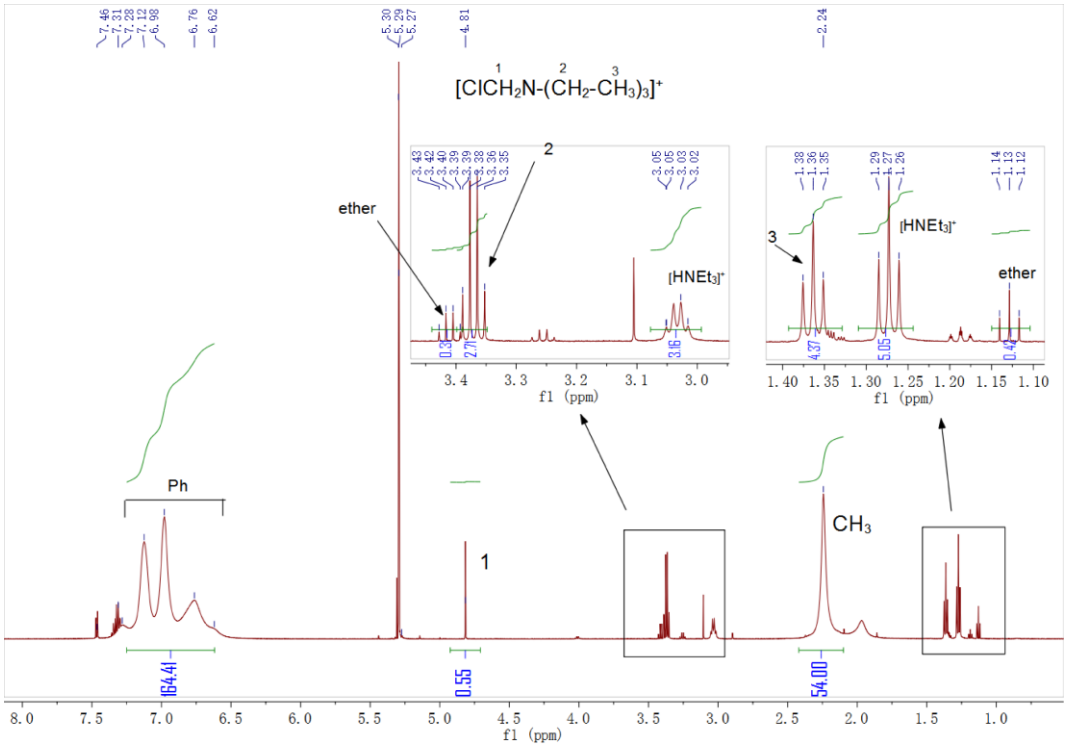

Figure S10. ^{1}H NMR of **2** in CD_2Cl_2.

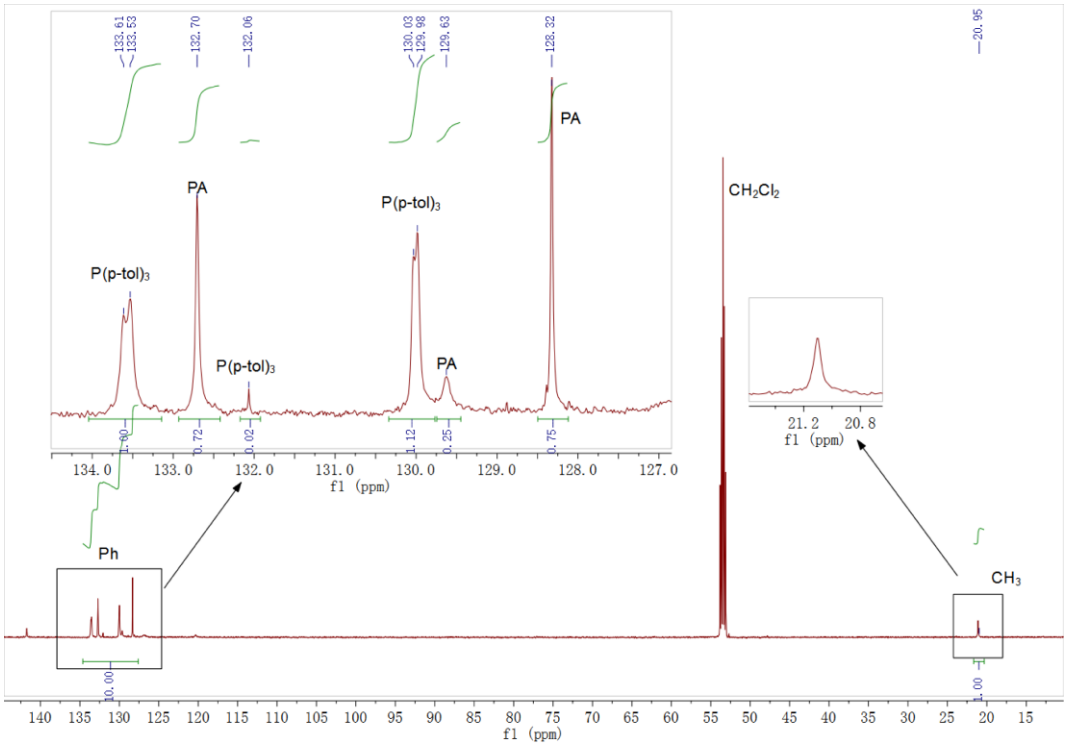

Figure S11. ^{13}C NMR of **2** in CD_2Cl_2 ($P(p\text{-}Tol)_3$ (ref.5)).

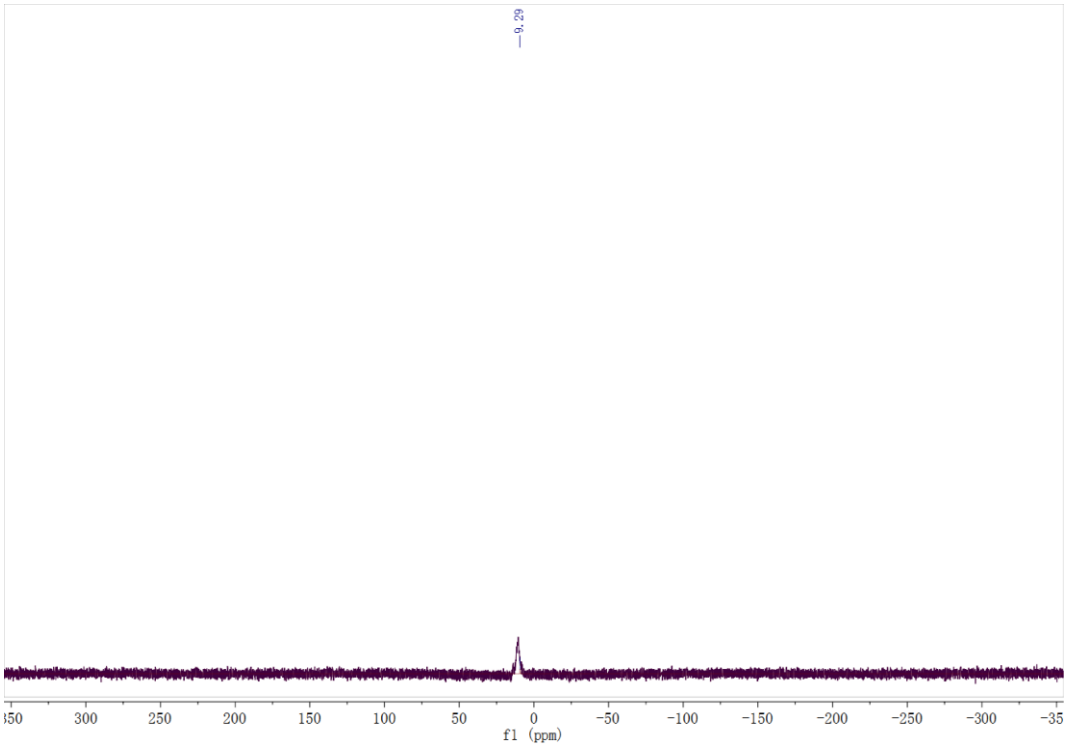

Figure S12. ^{31}P NMR of **2** in CD_2Cl_2.

Table S2. Crystal data and structure refinement of **1** and **2**.

Name	**1**	**2**
Empirical formula	$C_{227}H_{177}NF_{24}P_6Ag_{18}Sb_4Cl_2$	$C_{238}H_{196}F_{18}P_6ClAg_{18}Sb_3$
Formula weight	6060.07	5926.12
Temperature/K	173.15	173.15
Crystal system, Space group	Triclinic, P-1	Triclinic, P-1
a/Å	17.652(3)	18.465(2)
b/Å	18.127(3)	19.820(2)
c/Å	35.796(7)	20.121(3)
α/°	77.262(2)	117.4530(10)
β/°	81.309(2)	116.6710(10)
γ/°	84.350(2)	92.003(2)
Volume/Å^3	11019(3)	5561.0(12)
Z	2	1
F(000)	5872.0	2892.0
Crystal size/mm^3	0.28 × 0.23 × 0.18	0.3 × 0.21 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKa (λ = 0.71073)
2θ range for data collection/°	3.396 to 55.062	3.96 to 54.816
Index ranges	-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -46 ≤ l ≤ 35	-23 ≤ h ≤ 14, -25 ≤ k ≤ 24, -24 ≤ l ≤ 26
Reflections collected	62262	30384
Independent reflections	48056 [R_{int} = 0.0243, R_{sigma} = 0.0843]	23488 [R_{int} = 0.0189, R_{sigma} = 0.0538]
Data/restraints/parameters	48056/378/2483	23488/137/1280
Goodness-of-fit on F^2	1.019	1.020
Final R indexes [I>=2σ (I)]	R1 = 0.0838, wR2 = 0.2026	R1 = 0.0524, wR2 = 0.1210
Final R indexes [all data]	R1 = 0.1705, wR2 = 0.2445	R1 = 0.0999, wR2 = 0.1549
Largest diff. peak/hole / e Å^{-3}	1.71/-1.44	1.75/-1.01

Table S3. Selected bond lengths for **1**.

Atom	Atom	Bond length(Å)	Atom	Atom	Bond length(Å)
Ag1	C1	2.230(15)	Ag10	C111	2.285(13)
Ag1	C9	2.352(11)	Ag10	C119	2.304(14)
Ag1	C17	2.377(14)	Ag10	C127	2.378(14)
Ag1	Ag2	2.9440(14)	Ag10	Ag13	2.9371(15)
Ag1	Ag3	3.0563(15)	Ag10	Ag12	3.0392(15)
Ag1	Ag5	3.1912(16)	Ag10	Ag11	3.0927(15)
Ag1	Ag4	3.3227(15)	Ag10	Ag14	3.3595(17)
Ag2	C1	2.210(15)	Ag11	C111	2.200(14)
Ag2	C33	2.329(12)	Ag11	C135	2.358(12)
Ag2	C25	2.373(13)	Ag11	C143	2.362(12)
Ag2	Ag3	3.1119(14)	Ag11	Ag12	2.9476(15)
Ag2	Ag4	3.2166(16)	Ag11	Ag15	3.1668(15)
Ag2	Ag6	3.2444(16)	Ag11	Ag13	3.3011(15)
Ag3	C49	2.287(12)	Ag12	C111	2.270(13)
Ag3	C1	2.321(13)	Ag12	C151	2.358(13)
Ag3	C41	2.339(13)	Ag12	C159	2.409(11)
Ag3	Ag6	3.0852(15)	Ag12	C160	2.671(14)
Ag3	Ag5	3.1697(16)	Ag12	Ag14	3.0740(16)
Ag4	C9	2.044(16)	Ag13	C143	2.082(14)
Ag4	C33	2.109(15)	Ag13	C119	2.099(16)
Ag4	Ag8	2.9853(16)	Ag13	Ag18	2.9416(16)
Ag4	Ag9	3.1081(16)	Ag13	Ag17	3.1096(16)
Ag4	Ag6	3.2804(16)	Ag13	Ag15	3.3246(15)
Ag5	C41	2.068(16)	Ag14	C127	2.049(18)
Ag5	C17	2.088(16)	Ag14	C151	2.094(15)
Ag5	Ag7	2.9672(15)	Ag14	Ag17	2.9119(15)
Ag5	Ag8	3.0217(14)	Ag14	Ag16	3.0262(15)

Ag6	C25	2.068(15)	Ag14	Ag15	3.3137(15)
Ag6	C49	2.101(15)	Ag15	C159	2.057(15)
Ag6	Ag9	2.9705(15)	Ag15	C135	2.067(13)
Ag6	Ag7	3.0452(16)	Ag15	Ag16	2.9893(15)
Ag7	C17	2.383(13)	Ag15	Ag18	3.0279(15)
Ag7	C25	2.386(13)	Ag16	C127	2.326(16)
Ag7	P1	2.406(4)	Ag16	C135	2.394(11)
Ag7	C26	2.630(13)	Ag16	P4	2.405(4)
Ag8	C41	2.350(12)	Ag17	C151	2.390(13）
Ag8	P2	2.393(3)	Ag17	P5	2.405(3)
Ag8	C33	2.407(12)	Ag17	C143	2.448(12)
Ag8	C42	2.661(13)	Ag17	C144	2.678(12)
Ag9	C49	2.347(14)	Ag18	C119	2.307(15)
Ag9	C9	2.384(12)	Ag18	P6	2.414(4)
Ag9	P3	2.407(3)	Ag18	C159	2.426(12)
Ag9	C10	2.697(14)	P1	C69	1.791(13)

Table S4. Selected bond lengths for **2**.

Atom	Atom	Bond length (Å)	Atom	Atom	Bond length (Å)
Ag1	C1	2.273(8)	Ag4	Ag7	2.9856(9)
Ag1	C33	2.334(7)	Ag4	Ag8	3.0390(9)
Ag1	C17	2.401(7)	Ag5	C33	2.059(8)
Ag1	Ag3	2.9476(8)	Ag5	C25	2.059(8)
Ag1	Ag2	3.0530(9)	Ag5	Ag8	2.9450(9)
Ag1	Ag5	3.2160(9)	Ag5	Ag9	3.0867(9)
Ag1	Ag4	3.2573(10)	Ag5	Ag6	3.2175(9)
Ag2	C1	2.269(8)	Ag6	C41	2.084(8)
Ag2	C9	2.351(7)	Ag6	C49	2.092(9)
Ag2	C49	2.379(7)	Ag6	Ag7	2.9842(9)
Ag2	C50	2.646(7)	Ag6	Ag9	3.0389(9)
Ag2	Ag3	2.9060(8)	Ag7	C17	2.294(7)
Ag2	Ag4	3.1324(9)	Ag7	P1	2.4046(19)
Ag3	C1	2.235(7)	Ag7	C41	2.490(7)
Ag3	C41	2.319(7)	Ag8	C25	2.337(7)
Ag3	C25	2.391(7)	Ag8	C9	2.389(7)
Ag3	Ag6	3.1876(9)	Ag8	P2	2.4035(19)
Ag3	Ag5	3.2710(9)	Ag9	C33	2.336(7)
Ag4	C17	2.082(9)	Ag9	C49	2.367(7)
Ag4	C9	2.095(9)	Ag9	P3	2.409(2)

Table S5. Selected bond angles for **1**.

Atom	Atom	Atom	Angle(°)	Atom	Atom	Atom	Angle(°)
C1	Ag1	C9	123.2(5)	C1	Ag1	C17	126.5(5)
C9	Ag1	C17	102.9(5)	C1	Ag1	Ag2	48.2(4)
C9	Ag1	Ag2	154.2(3)	C17	Ag1	Ag2	98.9(3)
C1	Ag1	Ag3	49.1(3)	C9	Ag1	Ag3	93.4(3)
C17	Ag1	Ag3	158.9(4)	Ag2	Ag1	Ag3	62.45(3)
C1	Ag1	Ag5	143.1(4)	C9	Ag1	Ag5	92.1(4)
C17	Ag1	Ag5	40.9(4)	Ag2	Ag1	Ag5	95.42(4)
Ag3	Ag1	Ag5	126.42(4)	C1	Ag1	Ag4	138.3(3)
C9	Ag1	Ag4	37.5(4)	C17	Ag1	Ag4	94.6(3)
Ag2	Ag1	Ag4	127.37(4)	Ag3	Ag1	Ag4	90.19(4)
Ag5	Ag1	Ag4	64.41(3)	C1	Ag2	C33	124.8(5)
C1	Ag2	C25	128.5(5)	C33	Ag2	C25	99.7(4)
C1	Ag2	Ag1	48.8(4)	C33	Ag2	Ag1	157.9(3)
C25	Ag2	Ag1	97.9(3)	C1	Ag2	Ag3	48.1(3)
C33	Ag2	Ag3	98.9(3)	C25	Ag2	Ag3	154.8(3)
Ag1	Ag2	Ag3	60.54(3)	C1	Ag2	Ag4	140.0(3)
C33	Ag2	Ag4	40.9(4)	C25	Ag2	Ag4	90.1(3)
Ag1	Ag2	Ag4	126.13(4)	Ag3	Ag2	Ag4	92.86(4)
C1	Ag2	Ag6	142.3(4)	C33	Ag2	Ag6	91.3(4)
C25	Ag2	Ag6	39.5(4)	Ag1	Ag2	Ag6	93.83(4)
Ag3	Ag2	Ag6	123.36(4)	Ag4	Ag2	Ag6	61.02(4)
C49	Ag3	C1	124.9(5)	C49	Ag3	C41	104.8(5)
C1	Ag3	C41	120.8(5)	C49	Ag3	Ag1	101.5(4)
C1	Ag3	Ag1	46.6(4)	C41	Ag3	Ag1	151.7(3)
C49	Ag3	Ag6	42.9(4)	C1	Ag3	Ag6	139.4(4)
C41	Ag3	Ag6	98.3(4)	Ag1	Ag3	Ag6	93.79(4)
C49	Ag3	Ag2	158.0(4)	C1	Ag3	Ag2	45.2(4)

C41	Ag3	Ag2	95.7(3)	Ag1	Ag3	Ag2	57.01(3)
Ag6	Ag3	Ag2	127.00(5)	C49	Ag3	Ag5	96.8(4)
C1	Ag3	Ag5	137.8(4)	C41	Ag3	Ag5	40.7(4)
Ag1	Ag3	Ag5	125.77(5)	Ag6	Ag3	Ag5	67.25(3)
Ag2	Ag3	Ag5	93.63(4)	C9	Ag4	C33	170.1(5)
C9	Ag4	Ag8	124.3(4)	C33	Ag4	Ag8	53.1(3)
C9	Ag4	Ag9	50.1(3)	C33	Ag4	Ag9	127.8(3)
Ag8	Ag4	Ag9	157.93(5)	C9	Ag4	Ag2	143.0(4)
C33	Ag4	Ag2	46.3(3)	Ag8	Ag4	Ag2	82.59(4)
Ag9	Ag4	Ag2	113.94(4)	C9	Ag4	Ag6	90.9(4)
C33	Ag4	Ag6	94.5(3)	Ag8	Ag4	Ag6	142.39(5)
Ag9	Ag4	Ag6	55.34(3)	Ag2	Ag4	Ag6	59.90(3)
C9	Ag4	Ag1	44.5(3)	C33	Ag4	Ag1	144.3(3)
Ag8	Ag4	Ag1	109.47(4)	Ag9	Ag4	Ag1	80.82(4)
Ag2	Ag4	Ag1	106.44(4)	Ag6	Ag4	Ag1	85.54(4)
C41	Ag5	C17	165.4(6)	P1	Ag7	C26	121.9(3)
C41	Ag5	Ag7	122.7(4)	C17	Ag7	Ag5	44.3(4)
C17	Ag5	Ag7	52.8(3)	C25	Ag7	Ag5	98.2(3)
C41	Ag5	Ag8	50.9(3)	P1	Ag7	Ag5	115.87(9)
C17	Ag5	Ag8	126.2(4)	C26	Ag7	Ag5	119.1(3)
Ag7	Ag5	Ag8	156.28(5)	C17	Ag7	Ag6	99.4(4)
C41	Ag5	Ag3	47.5(4)	C25	Ag7	Ag6	42.6(4)
C17	Ag5	Ag3	145.0(4)	P1	Ag7	Ag6	114.23(10)
Ag7	Ag5	Ag3	108.23(4)	C26	Ag7	Ag6	70.2(3)
Ag8	Ag5	Ag3	83.50(4)	Ag5	Ag7	Ag6	70.36(4)
C41	Ag5	Ag1	145.5(4)	C41	Ag8	P2	135.8(4)
C17	Ag5	Ag1	48.1(4)	C41	Ag8	C33	102.3(4)
Ag7	Ag5	Ag1	84.60(4)	P2	Ag8	C33	121.8(3)
Ag8	Ag5	Ag1	112.09(4)	C41	Ag8	C42	27.7(4)

Ag3	Ag5	Ag1	107.49(4)	P2	Ag8	C42	123.6(3)
C25	Ag6	C49	161.8(5)	C33	Ag8	C42	106.3(4)
C25	Ag6	Ag9	128.9(3)	C41	Ag8	Ag4	99.7(4)
C49	Ag6	Ag9	51.7(4)	P2	Ag8	Ag4	112.76(10)
C25	Ag6	Ag7	51.4(4)	C33	Ag8	Ag4	44.5(4)
C49	Ag6	Ag7	118.2(4)	C42	Ag8	Ag4	122.2(3)
Ag9	Ag6	Ag7	153.12(5)	C41	Ag8	Ag5	43.1(4)
C25	Ag6	Ag3	144.8(3)	P2	Ag8	Ag5	121.65(9)
C49	Ag6	Ag3	47.8(3)	C33	Ag8	Ag5	100.9(3)
Ag9	Ag6	Ag3	82.87(4)	C42	Ag8	Ag5	70.1(3)
Ag7	Ag6	Ag3	108.44(4)	Ag4	Ag8	Ag5	70.65(4)
C25	Ag6	Ag2	46.9(3)	C49	Ag9	C9	101.3(4)
C49	Ag6	Ag2	151.3(3)	C49	Ag9	P3	132.5(3)
Ag9	Ag6	Ag2	117.07(5)	C9	Ag9	P3	126.3(3)
Ag7	Ag6	Ag2	82.92(4)	C49	Ag9	C10	106.8(4)
Ag3	Ag6	Ag2	109.35(4)	C9	Ag9	C10	27.6(4)
C25	Ag6	Ag4	94.1(4)	P3	Ag9	C10	115.5(3)
C49	Ag6	Ag4	99.4(4)	C49	Ag9	Ag6	44.6(4)
Ag9	Ag6	Ag4	59.39(4)	C9	Ag9	Ag6	92.6(3)
Ag7	Ag6	Ag4	141.61(5)	P3	Ag9	Ag6	123.15(11)
Ag3	Ag6	Ag4	90.48(4)	C10	Ag9	Ag6	115.9(3)
Ag2	Ag6	Ag4	59.07(3)	C49	Ag9	Ag4	98.9(4)
C17	Ag7	C25	99.5(5)	C9	Ag9	Ag4	41.1(4)
C17	Ag7	P1	131.5(4)	P3	Ag9	Ag4	115.85(10)
C25	Ag7	P1	129.0(3)	C10	Ag9	Ag4	68.0(4)
C17	Ag7	C26	101.3(5)	P1	Ag7	C26	121.9(3)
C25	Ag7	C26	27.8(4)	C17	Ag7	Ag5	44.3(4)

Table S6. Selected bond angles for **2**.

Atom	Atom	Atom	Angle（°）	Atom	Atom	Atom	Angle (°)
C1	Ag1	C33	123.4(3)	C41	Ag3	C25	98.1(3)
C1	Ag1	C17	123.4(3)	C1	Ag3	Ag2	50.34(19)
C33	Ag1	C17	105.4(3)	C41	Ag3	Ag2	160.08(19)
C1	Ag1	Ag3	48.61(18)	C25	Ag3	Ag2	94.23(17)
C33	Ag1	Ag3	156.43(18)	C1	Ag3	Ag1	49.7(2)
C17	Ag1	Ag3	94.79(18)	C41	Ag3	Ag1	100.88(18)
C1	Ag1	Ag2	47.72(19)	C25	Ag3	Ag1	153.42(18)
C33	Ag1	Ag2	99.68(18)	Ag2	Ag3	Ag1	62.87(2)
C17	Ag1	Ag2	150.77(19)	C1	Ag3	Ag6	143.2(2)
Ag3	Ag1	Ag2	57.90(2)	C41	Ag3	Ag6	40.8(2)
C1	Ag1	Ag5	139.70(19)	C25	Ag3	Ag6	88.28(19)
C33	Ag1	Ag5	39.7(2)	Ag2	Ag3	Ag6	124.62(3)
C17	Ag1	Ag5	95.9(2)	Ag1	Ag3	Ag6	94.00(3)
Ag3	Ag1	Ag5	127.41(3)	C1	Ag3	Ag5	139.88(19)
Ag2	Ag1	Ag5	93.85(2)	C41	Ag3	Ag5	89.9(2)
C1	Ag1	Ag4	142.99(19)	C25	Ag3	Ag5	38.9(2)
C33	Ag1	Ag4	92.82(19)	Ag2	Ag3	Ag5	89.91(2)
C17	Ag1	Ag4	39.7(2)	Ag1	Ag3	Ag5	122.48(3)
Ag3	Ag1	Ag4	95.20(3)	Ag6	Ag3	Ag5	59.741(19)
Ag2	Ag1	Ag4	125.44(3)	C17	Ag4	C9	165.7(3)
Ag5	Ag1	Ag4	64.30(2)	C17	Ag4	Ag7	50.0(2)
C1	Ag2	C9	128.8(3)	C9	Ag4	Ag7	126.14(19)
C1	Ag2	C49	120.6(3)	C17	Ag4	Ag8	125.0(2)
C9	Ag2	C49	101.5(2)	C9	Ag4	Ag8	51.56(19)
C1	Ag2	C50	108.9(3)	Ag7	Ag4	Ag8	156.55(3)
C9	Ag2	C50	95.2(2)	C17	Ag4	Ag2	144.5(2)
C49	Ag2	C50	27.1(3)	C9	Ag4	Ag2	48.6(2)

C1	Ag2	Ag3	49.31(18)	Ag7	Ag4	Ag2	113.28(2)
C9	Ag2	Ag3	102.35(17)	Ag8	Ag4	Ag2	82.75(2)
C49	Ag2	Ag3	152.82(19)	C17	Ag4	Ag1	47.4(2)
C50	Ag2	Ag3	157.94(17)	C9	Ag4	Ag1	144.9(2)
C1	Ag2	Ag1	47.8(2)	Ag7	Ag4	Ag1	84.34(2)
C9	Ag2	Ag1	159.47(19)	Ag8	Ag4	Ag1	107.97(2)
C49	Ag2	Ag1	94.86(18)	Ag2	Ag4	Ag1	107.22(2)
C50	Ag2	Ag1	104.99(17)	C33	Ag5	C25	164.0(3)
Ag3	Ag2	Ag1	59.23(2)	C33	Ag5	Ag8	120.7(2)
C1	Ag2	Ag4	148.74(19)	C25	Ag5	Ag8	52.1(2)
C9	Ag2	Ag4	42.0(2)	C33	Ag5	Ag9	49.18(19)
C49	Ag2	Ag4	89.24(19)	C25	Ag5	Ag9	128.9(2)
C50	Ag2	Ag4	102.08(18)	Ag8	Ag5	Ag9	152.71(3)
Ag3	Ag2	Ag4	99.92(2)	C33	Ag5	Ag1	46.40(19)
Ag1	Ag2	Ag4	127.05(3)	C25	Ag5	Ag1	146.7(2)
C1	Ag3	C41	129.0(3)	Ag8	Ag5	Ag1	111.48(3)
C1	Ag3	C25	126.4(3)	Ag9	Ag5	Ag1	79.92(2)

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