Thermochromic silver nanocluster exhibiting dual emission character

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Supplementary Information:

1. Experimental Section

Synthesis of naphthalen-2-yl-methanethiol. A mixture of 2-methyl-naphthalene (2.840 g, 0.020 mol), N-bromosuccinimide (3.920 g, 0.022 mol), and 2,2'-azobisisobutyronitrile (0.125 g) in CCl_4 (100 ml) was stirred and heated for 12 h at 80 °C. After filtering, the filtrate was washed with water and dried with anhydrous Mg_2SO_4. Upon concentration of the CCl_4 solution, 2-bromomethyl-naphthalene was obtained (yield, 92%). ^{1}H NMR ($CDCl_3$): δ 4.70 (s, 2H), 7.50–7.57 (m, 3H), 7.82–7.93 (m, 4H). IR data (KBr, cm^{-1}): 3060 w, 897 w, 823 s, 752 s.

0.770 g (3.470 mmol) of 2-bromomethyl-naphthalene, 0.400 g (5.300 mmol) of thiourea and 10 mL of acetone were placed in a previously oven-dried 50 mL round-bottomed flask. The reaction mixture was heated to reflux for 2 hours and then allowed to cool to room temperature. The solids formed were filtered off and dried under high vacuum. After dissolving the solid in 2 M NaOH (30 mL), the mixture was heated to reflux for 2 h. After acidification to pH = 2 with 2 M HCl, the product was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was washed with H_2O, dried over anhydrous Na_2SO_4 and concentrated in vacuum to afford of naphthalen-2-yl-methanethiol (yield, 62%). ^{1}H NMR ($CDCl_3$): δ 1.84 (t, 1H), 3.94 (d, 2H), 7.46–7.52 (m, 3H), 7.76–7.85 (m, 4H). Anal. Calcd for $C_{11}H_{10}S$: C 75.82, H 5.78, S 18.40 %, Found: C 75.44, H 6.08, S 18.48 %. IR data (KBr, cm^{-1}): 3050 w, 866 m, 823 m, 742 s.

Synthesis and crystallization of $Ag_{12}(SCH_2C_{10}H_7)_6(CF_3CO_2)_6(CH_3CN)_6$ (1). Naphthalen-2-yl-methanethiol (0.017 g, 0.100 mmol) and $AgCF_3CO_2$ (0.044 g, 0.200 mmol) were dissolved in 3 mL acetonitrile and 3 mL acetone with stirring and a clear solution was obtained. The clear solution was evaporated slowly in air at room temperature. The pale yellow crystals formed were filtered off, washed with diethyl ether and dried at room temperature. (yield: 68 % based on ligand). Anal. Calcd for $C_{90}H_{72}N_6O_{12}S_6F_{18}Ag_{12}$: C 33.17, H 2.23, N 2.58, O 5.89, S 5.90 %, Found: C 32.76, H 2.53, N 2.42, O 5.49, S 6.32 %. IR data (KBr, cm^{-1}): 3060 m, 3009 w, 2947 m, 2268 s, 1649 s, 1511 m, 1415 m, 1206 s, 1128 s, 823 s.

X-ray crystallographic determination of 1. Single-crystal X-ray analysis of the complex **1** was carried out on a Bruker SMART APEX CCD diffract meter[1] using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. The structure was solved by direct methods with *SHELXS-97*[2,3] and refined with the full-matrix least-squares technique using the *SHELXL-97*[4] program. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data, data collection parameters and details of the structure refinement are given in Table S1.

CCDC 1004246 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

1 SMART and SAINT, *Area Detector Control and Integration Software*, Siemens Analytical X-Ray Systems, Inc., Madison, WI, 1996.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 1990,**46**, 467.

3 G. M. Sheldrick, *SHELXS-97*, *Program for solution of crystalstructures*, University of Göttingen, Germany, 1997.

4 G. M. Sheldrick, *SHELXL-97*, *Program for Crystal Structures Refinement*, University of Göttingen, Germany, 1997.

2. Supplementary Figures

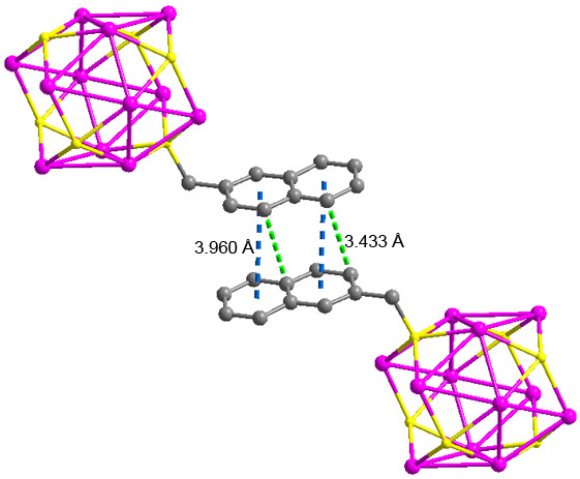


Fig. S1 π···π stacking interaction for compound **1** between adjacent naphthyl ligands with distance of centroid-to-centroid (3.960 Å) and closest C···C (3.433 Å).

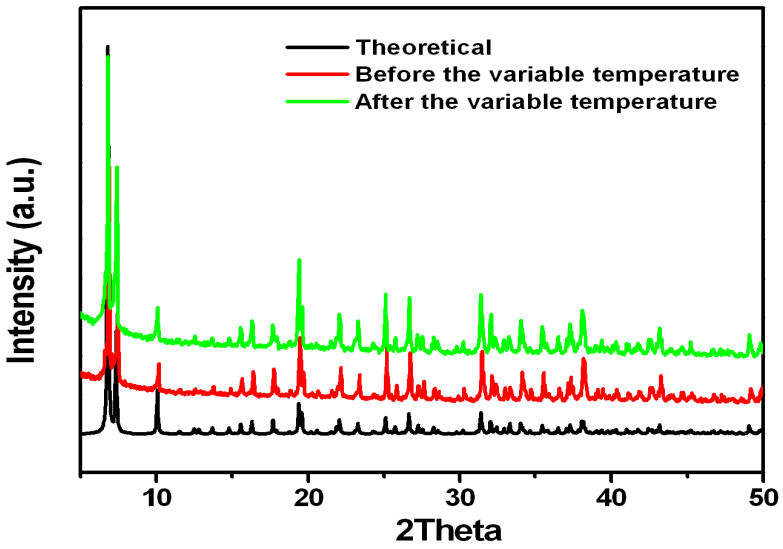


Fig. S2 The PXRD pattern of compound **1** at room temperature and after the variable temperature, respectively.

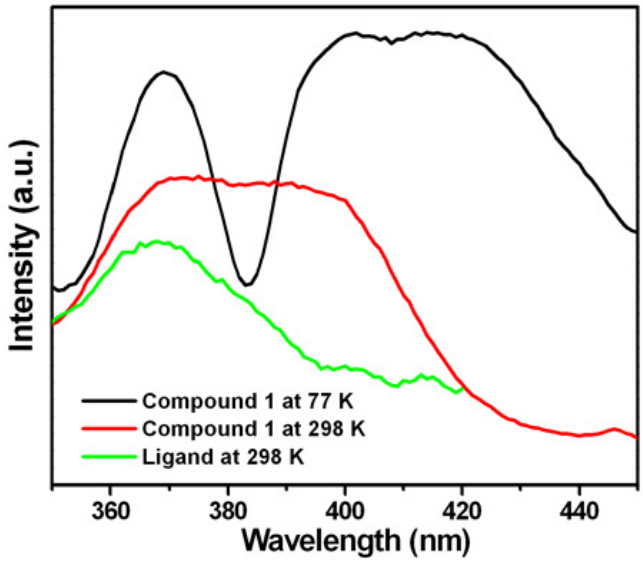


Fig. S3 The excitation spectra of compound **1** for λ_{em} = 660 nm at room temperature and λ_{em} = 690 nm at 77 K, and the excitation spetrum of ligand for λ_{em} = 468 nm at room temperature.

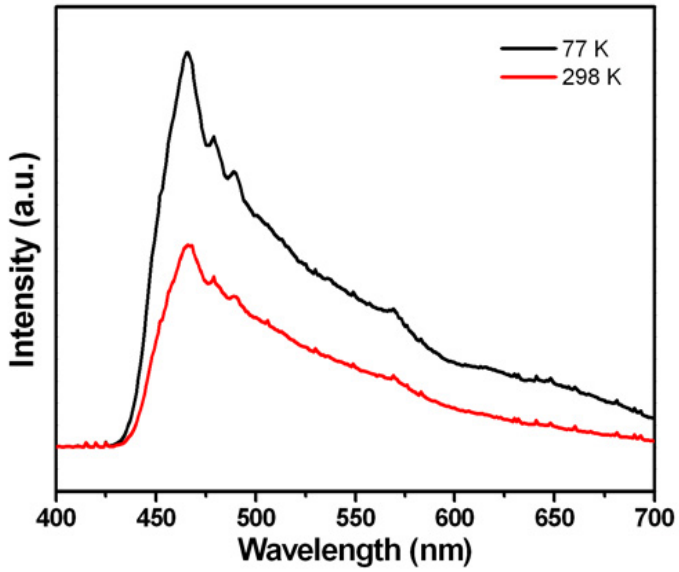


Fig. S4 The emission spectra of ligand $C_{10}H_7CH_2SH$ for λ_{ex} = 370 nm at room temperature and 77 K.

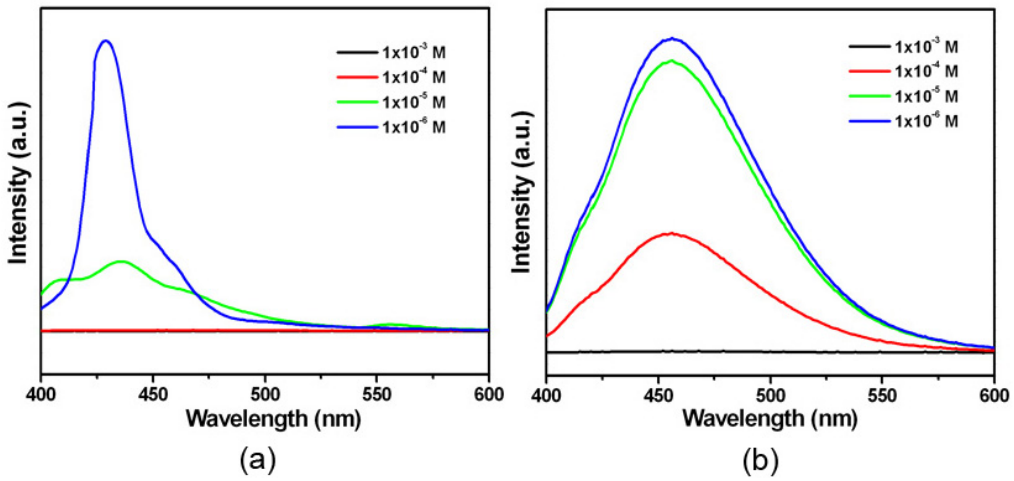
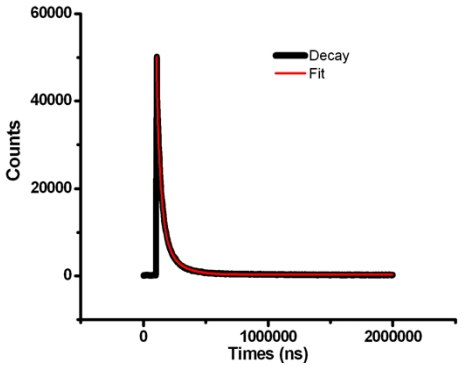
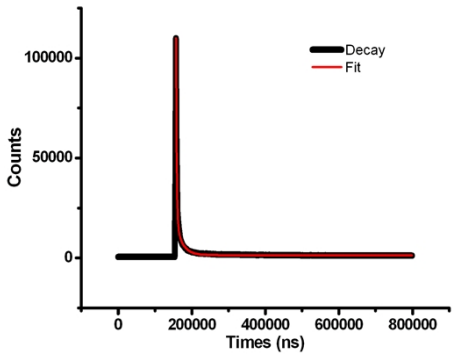


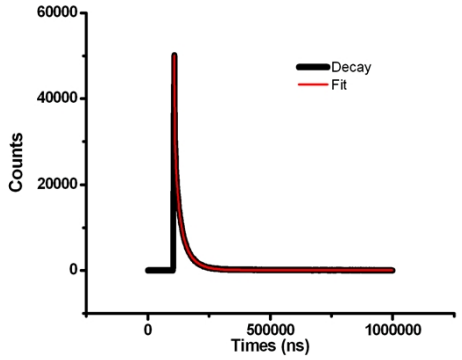
Fig. S5 The emission spectra of compound **1** in $CHCl_3$ (a) and THF (b) in different concentrations at room temperature under 370 nm excitation.



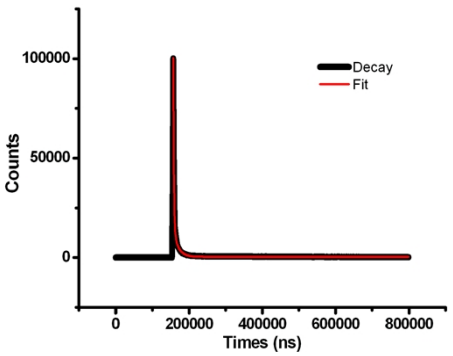
(a) 77 K Ex = 370 nm Em = 690 nm



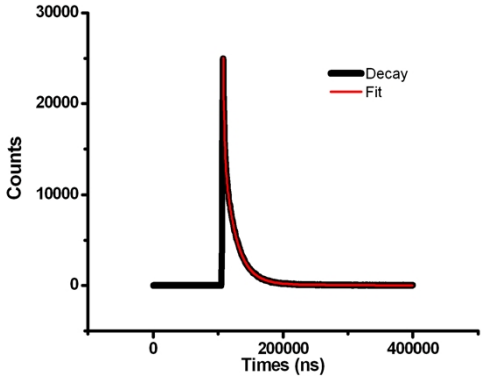
(b) 77 K Ex = 370 nm Em = 570 nm



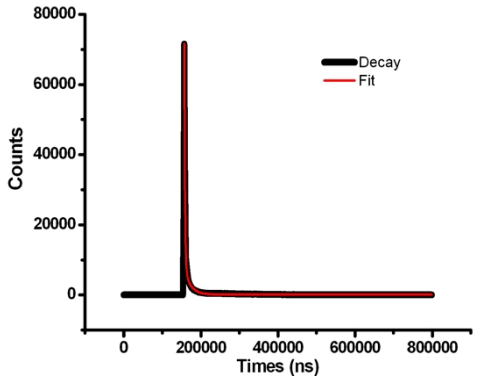
(c) 143 K Ex = 370 nm Em = 686 nm



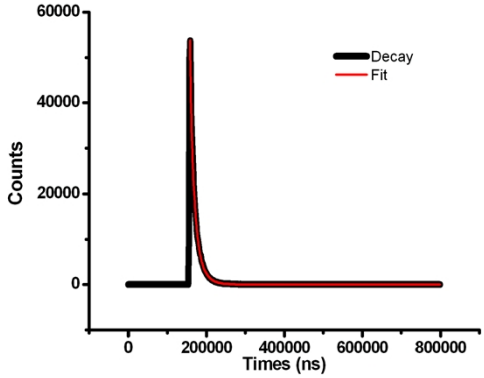
(d) 143 K Ex = 370 nm Em = 570 nm



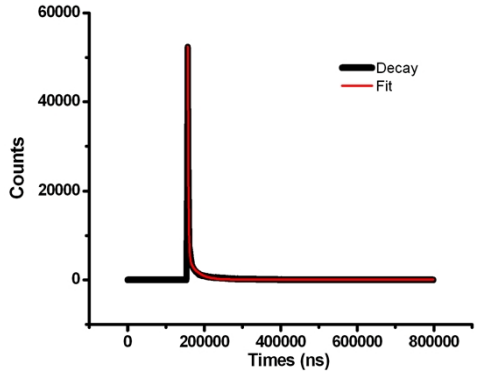
(e) 193 K Ex = 370 nm Em = 674 nm



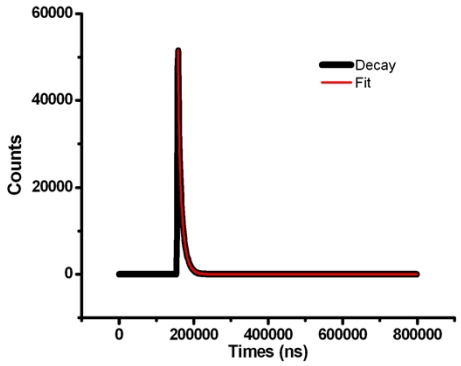
(f) 193 K Ex = 370 nm Em = 570nm



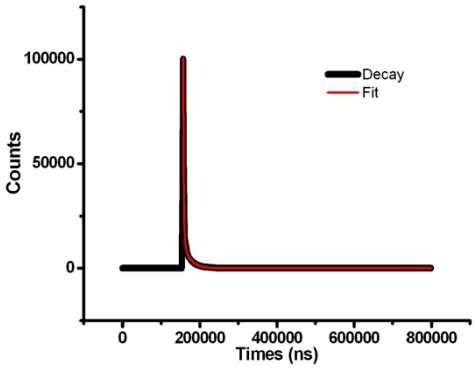
(g) 243 K Ex = 370 nm Em = 667 nm



(h) 243 K Ex = 370 nm Em = 570nm



(i) 298 K Ex = 370 nm Em = 660 nm



(j) 298 K Ex = 370 nm Em = 570 nm

Fig. S6 Selected luminescence decay of **1** monitored at corresponding excitation/emission maxima under various temperatures.

3. Supplementary Tables for structural parameters

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{90}H_{72}N_6O_{12}S_6F_{18}Ag_{12}$
Formula weight	3258.34
Crystal size, mm^3	0.20 × 0.18 × 0.16
Crystal system	hexagonal

Space group	*R*-3
a, Å	23.9571(6)
b, Å	23.9571(6)
c, Å	16.5415(8)
α, deg	90
β, deg	90
γ, deg	120
Volume, Å^3	8221.9(5)
Z	3
Temperature, K	293(2)
Density (calcd.), g cm^{-3}	1.974
Absorption coeff., mm^{-1}	2.292
F(000), e	4716
Theta range for data collection	3.15 to 25.00°
Index ranges	-18<=h<=27, -18<=k<=27, -19<=l<=11
Completeness to theta = 25.00°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7105 and 0.6571
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3212/0/218
Wavelength	0.71073 Å
Reflections collected/independent/R_{int}	5037[*R*(int) = 0.0184]
Final *R*1/*wR*2[*I*≥2*σ*(*I*)]	0.0449 / 0.1453
Final *R*1/*wR*2 (all data)	0.0619 / 0.1569
Goodness of fit (GOF)	1.052
Final diff. peaks(max/min), e Å^{-3}	2.241/–0.717

Table S2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	9090(1)	10508(1)	-14(1)	48(1)
Ag(2)	8952(1)	9858(1)	-1700(1)	63(1)
C(1)	8155(3)	9749(4)	1645(4)	50(2)
C(2)	7885(3)	9252(3)	2304(4)	48(2)

C(3)	7483(4)	8592(4)	2109(5)	59(2)
C(4)	7230(4)	8135(4)	2709(7)	78(3)
C(5)	7368(4)	8294(4)	3505(5)	66(2)
C(6)	7114(6)	7817(6)	4074(8)	97(4)
C(7)	7273(8)	7983(8)	4865(11)	136(7)
C(8)	7689(9)	8621(9)	5113(7)	133(6)
C(9)	7942(6)	9115(6)	4529(6)	102(4)
C(10)	7770(4)	8953(5)	3716(5)	68(2)
C(11)	8014(4)	9418(4)	3106(5)	59(2)
C(12)	9517(4)	11942(3)	534(4)	49(2)
C(13)	9409(4)	12503(4)	756(6)	66(2)
C(14)	7593(5)	9284(4)	-2807(5)	65(2)
C(15)	6989(4)	9107(5)	-3182(6)	84(3)
F(1)	9845(3)	12922(2)	1276(3)	87(2)
F(2)	8850(3)	12304(3)	1130(5)	137(3)
F(3)	9414(4)	12829(3)	145(4)	143(3)
N(1)	8069(4)	9435(3)	-2518(4)	70(2)
O(1)	9039(3)	11437(3)	391(4)	80(2)
O(2)	10094(3)	12110(3)	484(4)	75(2)
S(1)	8903(1)	9828(1)	1236(1)	41(1)

Table S3 Bond lengths [Å] and angles [°] for **1**.

Bond lengths (Å)

Ag(1)–O(1)	2.386(5)	C(5)–C(10)	1.422(13)
Ag(1)–O(2)#1	2.446(5)	C(6)–C(7)	1.37(2)
Ag(1)–S(1)	2.5289(17)	C(7)–C(8)	1.41(2)
Ag(1)–S(1)#2	2.5384(17)	C(8)–C(9)	1.409(17)
Ag(1)–Ag(1)#1	2.9814(6)	C(9)–C(10)	1.404(13)
Ag(1)–Ag(1)#2	2.9814(6)	C(10)–C(11)	1.397(11)
Ag(1)–Ag(2)	3.1300(9)	C(12)–O(1)	1.203(8)
Ag(1)–Ag(2)#2	3.2513(9)	C(12)–O(2)	1.234(9)
Ag(2)–N(1)	2.277(7)	C(12)–C(13)	1.536(10)
Ag(2)–S(1)#2	2.4827(17)	C(13)–F(3)	1.274(10)
Ag(2)–S(1)#1	2.5673(17)	C(13)–F(2)	1.328(10)
Ag(2)–Ag(1)#1	3.2513(9)	C(13)–F(1)	1.338(9)
C(1)–C(2)	1.502(10)	C(14)–N(1)	1.116(10)
C(1)–S(1)	1.834(6)	C(14)–C(15)	1.432(12)
C(2)–C(11)	1.375(10)	O(2)–Ag(1)#2	2.446(5)
C(2)–C(3)	1.418(10)	S(1)–Ag(2)#1	2.4827(17)
C(3)–C(4)	1.373(13)	S(1)–Ag(1)#1	2.5384(17)
C(4)–C(5)	1.365(13)	S(1)–Ag(2)#2	2.5673(17)
C(5)–C(6)	1.365(12)		

Bond Angles (°)			
O(1)–Ag(1)–O(2)#1	85.2(2)	C(11)–C(2)–C(3)	118.1(7)
O(1)–Ag(1) –S(1)	107.27(18)	C(11)–C(2)–C(1)	121.8(7)
O(2)#1–Ag(1)–S(1)	101.03(14)	C(3)–C(2)-C(1)	120.1(7)
O(1)–Ag(1)–S(1)#2	101.93(16)	C(4)–C(3)–C(2)	120.5(8)
O(2)#1–Ag(1)–S(1)#2	107.83(15)	C(3)–C(4)–C(5)	121.8(8)
S(1)–Ag(1)–S(1)#2	140.24(7)	C(6)–C(5)–C(4)	119.2(10)
O(1)–Ag(1)–Ag(1)#1	151.25(14)	C(6)–C(5)–C(10)	122.1(10)
O(2)#1–Ag(1)–Ag(1)#1	78.48(14)	C(4)–C(5)–C(10)	118.7(8)
S(1)–Ag(1)–Ag(1)#1	54.11(4)	C(7)–C(6)–C(5)	118.3(12)
S(1)#2–Ag(1)–Ag(1)#1	105.53(4)	C(6)–C(7)–C(8)	122.7(12)
O(1)–Ag(1)–Ag(1)#2	83.41(13)	C(9)–C(8)–C(7)	119.1(12)
O(2)#1–Ag(1)–Ag(1)#2	155.31(13)	C(8)–C(9)–C(10)	118.8(12)
S(1)–Ag(1)–Ag(1)#2	103.25(4)	C(11)–C(10)–C(9)	121.5(9)
S(1)#2–Ag(1)–Ag(1)#2	53.81(4)	C(11)–C(10)–C(5)	119.4(8)
Ag(1)#1–Ag(1)–Ag(1)#2	119.978(1)	C(9)–C(10)–C(5)	119.0(9)
O(1)–Ag(1)–Ag(2)	132.21(18)	C(2)–C(11)–C(10)	121.5(8)
O(2)#1–Ag(1)–Ag(2)	71.99(16)	O(1)–C(12)–O(2)	131.7(7)
S(1)–Ag(1)–Ag(2)	117.84(4)	O(1)–C(12)–C(13)	115.6(7)
S(1)#2–Ag(1)–Ag(2)	50.65(4)	O(2)–C(12)–C(13)	112.5(7)
Ag(1)#1–Ag(1)–Ag(2)	64.23(2)	F(3)–C(13)–F(2)	106.8(8)
Ag(1)#2–Ag(1)–Ag(2)	100.12(2)	F(3)–C(13)–F(1)	106.6(7)
O(1)–Ag(1)–Ag(2)#2	76.56(17)	F(2)–C(13)–F(1)	103.7(7)
O(2)#1–Ag(1)–Ag(2)#2	137.37(16)	F(3)–C(13)–C(12)	113.2(7)
S(1)–Ag(1)–Ag(2)#2	50.88(4)	F(2)–C(13)–C(12)	112.3(7)

S(1)#2–Ag(1)–Ag(2)#2	113.46(4)	F(1)–C(13)–C(12)	113.6(7)
Ag(1)#1–Ag(1)–Ag(2)#2	99.80(2)	N(1)–C(14)–C(15)	178.5(9)
Ag(1)#2–Ag(1)–Ag(2)#2	60.10(2)	C(14)–N(1)–Ag(2)	165.7(8)
Ag(2)–Ag(1)–Ag(2)#2	145.73(3)	C(12)–O(1)–Ag(1)	121.6(5)
N(1)–Ag(2)–S(1)#2	139.53(17)	C(12)–O(2)–Ag(1)#2	124.6(5)
N(1)–Ag(2)–S(1)#1	106.02(17)	C(1)–S(1)–Ag(2)#1	112.5(2)
S(1)#2–Ag(2)–S(1)#1	114.25(7)	C(1)–S(1)–Ag(1)	102.6(2)
N(1)–Ag(2)–Ag(1)	126.5(2)	Ag(2)#1–S(1)–Ag(1)	138.50(7)
S(1)#2–Ag(2)–Ag(1)	52.24(4)	C(1)–S(1)–Ag(1)#1	106.4(3)
S(1)#1–Ag(2)–Ag(1)	98.42(4)	Ag(2)#1–S(1)–Ag(1)#1	77.11(5)
N(1)–Ag(2)–Ag(1)#1	109.67(19)	Ag(1)–S(1)–Ag(1)#1	72.08(5)
S(1)#2–Ag(2)–Ag(1)#1	99.45(4)	C(1)–S(1)–Ag(2)#2	109.1(3)
S(1)#1–Ag(2)–Ag(1)#1	49.84(4)	Ag(2)#1–S(1)–Ag(2)#2	108.08(7)
Ag(1)–Ag(2)–Ag(1)#1	55.669(14)	Ag(1)–S(1)–Ag(2)#2	79.28(5)
C(2)–C(1)–S(1)	111.2(5)	Ag(1)#1–S(1)–Ag(2)#2	138.25(7)

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

Table S4 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
Ag(1)	44(1)	36(1)	58(1)	5(1)	7(1)	15(1)
Ag(2)	60(1)	46(1)	76(1)	-4(1)	-15(1)	21(1)
C(1)	50(4)	60(5)	55(4)	4(4)	13(3)	38(4)
C(2)	46(4)	50(4)	56(4)	-6(3)	11(3)	30(3)
C(3)	46(4)	53(5)	78(5)	-14(4)	14(4)	24(4)
C(4)	54(5)	47(5)	128(8)	-10(5)	27(5)	22(4)
C(5)	71(5)	58(5)	80(6)	13(5)	35(5)	41(4)
C(6)	99(8)	89(8)	127(9)	46(7)	66(8)	66(7)
C(7)	151(13)	140(13)	180(15)	97(12)	109(12)	120(12)
C(8)	237(18)	173(14)	66(7)	27(9)	49(9)	160(15)
C(9)	140(11)	123(10)	68(6)	-3(6)	16(6)	85(9)
C(10)	74(6)	86(6)	59(5)	15(5)	31(4)	51(5)

C(11)	57(5)	54(4)	65(5)	-5(4)	11(4)	27(4)
C(12)	52(4)	52(4)	51(4)	0(3)	3(3)	33(4)
C(13)	52(5)	57(5)	95(6)	-11(5)	-7(5)	32(4)
C(14)	66(6)	46(4)	78(6)	3(4)	-15(5)	24(4)
C(15)	62(6)	79(6)	98(7)	3(5)	-26(5)	26(5)
F(1)	98(4)	65(3)	100(4)	-35(3)	-25(3)	41(3)
F(2)	76(4)	95(5)	246(9)	-58(5)	22(5)	47(4)
F(3)	252(10)	125(6)	123(5)	-18(4)	-71(6)	148(7)
N(1)	67(5)	56(4)	90(5)	-3(4)	-25(4)	32(4)
O(1)	48(3)	44(3)	144(6)	-29(3)	3(3)	21(3)
O(2)	52(3)	73(4)	107(5)	-28(3)	-11(3)	37(3)
S(1)	38(1)	35(1)	48(1)	2(1)	8(1)	19(1)

Table S5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1A)	8240	10162	1857	60
H(1B)	7840	9627	1214	60
H(3)	7389	8467	1571	71
H(4)	6958	7706	2569	93
H(6)	6839	7391	3926	116
H(7)	7099	7661	5255	163
H(8)	7796	8716	5656	160
H(9)	8217	9541	4680	122

H(11)	8271	9850	3245	71
H(15A)	6787	9312	-2904	125
H(15B)	6713	8648	-3157	125
H(15C)	7059	9243	-3737	125