Supporting Information

Ag(I)-mediated formation of a 2D cyano-bridged multinuclear silver(I) alkynyl network coupled with the C–C bond cleavage of acetonitrile

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1. Synthetic procedures

Materials and Measurements: In this paper, all reagents and solvents for synthesis were obtained from commercial sources and used without further purification, such as 3, 3-Dimethyl-1-butyne (Aladdin, >95%). All other reagents were of analytical grade and used as received. [AgC≡C^{t}Bu]$_n$, was synthesized according to the literature.[1] Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Luminescence was measured on an F-7000 FL Spectrophotometer.

Caution! *Owing to silver(I) alkynyls have the potential explosive nature, great care should be taken, handled with care and only small amounts should be used.*

[Ag$_{15}$(C≡C^{t}Bu)$_{10}$(CF$_3$COO)$_2$(CN)$_3$]$_n$ (1)

[AgC≡C^{t}Bu]$_n$ (0.0599 g, 0.3169 mmol) was dissolved in a solution of $AgCF_3COO$ (0.1046 g, 0.4736 mmol) in acetonitrile (12 mL) under ultrasonication. Then H_2O (1 mL) was added to the above resulting solution. The mixture was stirred for 3 h to give a gray suspension. The reaction mixture (pH ≈ 7.6) was transferred to a Teflon-lined stainless autoclave (25 mL) and kept at 85 ºC for 52 h. After cooling to room temperature, the solution (pH ≈ 5.9) was filtered and the filtrate evaporated slowly at room temperature in an Erlenmeyer flask. A few weeks later, we have successfully achieved compound **1**. They were deposited as colorless strip crystals. Yield: *ca.* 9% (based on Ag). Elemental analysis (%) calcd for $C_{67}H_{90}F_6O_4N_3Ag_{15}$: C, 29.44; H, 3.32; N, 1.54. Found: C, 29.01; H, 3.72; N, 1.37. IR (KBr): ν = 2098 cm^{-1} (s, C≡N); 2009 cm^{-1} (vs, C≡C); 1680 cm^{-1} (w, C=O).

2. Crystallographic studies

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at 293(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The structure of compound **1** was solved by direct methods and refined on F^2 by full-matrix least squares methods using the SHELXTL package.[2]

Crystal data for **1**: $C_{67}H_{90}F_6O_4N_3Ag_{15}$; monoclinic, space group $P2_1/c$, M = 2733.47, a = 14.6834(14) Å, b = 14.9015(14) Å, c = 20.0367(18) Å, α = 90 °, β = 107.3150(10) °, γ = 90 °, V = 4185.4(7) Å^3, Z = 2, 20654 reflns measured, 7327 unique reflections (R_{int}= 0.0511), R_1 = 0.0553, wR_2 = 0.1356, goodness-of-fit = 1.028 for 4486 observed reflections with $I > 2\sigma(I)$. CCDC-926486 (**1**) 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 for **1**. The C and N atoms of three cyanogroup (C33–N1, C34–N2 and C35–N3) were processed into two disordered parts in the ratio of 0.5:0.5.

3. Selected bond lengths (Å) and angles (º) for compound 1

Table S1. Selected bond lengths (Å) and angles (º) for compound **1**

Ag(1)-C(27)	2.076(10)	C(27)-Ag(3)#1	2.476(11)
Ag(1)-C(27)#1	2.076(10)	C(33)-C(34)#2	1.185(14)
Ag(1)-Ag(3)#1	2.9130(9)	C(34)-C(33)#3	1.185(14)
Ag(1)-Ag(3)	2.9130(9)	C(35)-C(35)#4	1.19(2)
Ag(1)-Ag(5)#1	2.9665(9)	C(27)-Ag(1)-Ag(3)#1	56.6(3)
Ag(1)-Ag(5)	2.9665(9)	C(27)#1-Ag(1)-Ag(3)#1	123.4(3)
Ag(1)-Ag(7)	3.0383(9)	C(27)-Ag(1)-Ag(3)	123.4(3)
Ag(1)-Ag(7)#1	3.0384(9)	C(27)#1-Ag(1)-Ag(3)	56.6(3)
Ag(1)-Ag(2)	3.2035(9)	Ag(3)#1-Ag(1)-Ag(3)	180
Ag(1)-Ag(2)#1	3.2035(9)	C(27)-Ag(1)-Ag(5)#1	53.4(3)
Ag(1)-Ag(4)#1	3.2450(9)	C(27)#1-Ag(1)-Ag(5)#1	126.6(3)
Ag(1)-Ag(4)	3.2450(9)	Ag(3)#1-Ag(1)-Ag(5)#1	66.63(3)
Ag(2)-C(15)#1	2.049(11)	Ag(3)-Ag(1)-Ag(5)#1	113.37(3)
Ag(2)-C(3)	2.069(12)	C(27)-Ag(1)-Ag(5)	126.6(3)
Ag(2)-Ag(3)#1	3.0632(12)	C(27)#1-Ag(1)-Ag(5)	53.4(3)
Ag(2)-Ag(7)	3.1384(12)	Ag(3)#1-Ag(1)-Ag(5)	113.37(3)
Ag(2)-Ag(8)	3.1609(14)	Ag(3)-Ag(1)-Ag(5)	66.63(3)
Ag(2)-Ag(4)#1	3.2020(12)	Ag(5)#1-Ag(1)-Ag(5)	180
Ag(2)-Ag(5)	3.2616(12)	C(27)-Ag(1)-Ag(7)	66.3(3)
Ag(3)-O(1)	2.305(8)	C(27)#1-Ag(1)-Ag(7)	113.7(3)
Ag(3)-C(9)	2.360(12)	Ag(3)#1-Ag(1)-Ag(7)	107.24(3)
Ag(3)-C(27)#1	2.476(11)	Ag(3)-Ag(1)-Ag(7)	72.76(3)
Ag(3)-C(15)	2.478(13)	Ag(5)#1-Ag(1)-Ag(7)	110.34(3)
Ag(3)-Ag(2)#1	3.0632(12)	Ag(5)-Ag(1)-Ag(7)	69.66(3)
Ag(3)-Ag(5)	3.2297(14)	C(27)-Ag(1)-Ag(7)#1	113.7(3)
Ag(3)-Ag(6)	3.2842(14)	C(27)#1-Ag(1)-Ag(7)#1	66.3(3)
Ag(3)-Ag(4)	3.2923(12)	Ag(3)#1-Ag(1)-Ag(7)#1	72.76(3)
Ag(4)-C(9)	2.057(12)	Ag(3)-Ag(1)-Ag(7)#1	107.24(3)
Ag(4)-C(21)	2.091(11)	Ag(5)#1-Ag(1)-Ag(7)#1	69.66(3)
Ag(4)-Ag(5)#1	3.0234(12)	Ag(5)-Ag(1)-Ag(7)#1	110.34(3)
Ag(4)-Ag(6)	3.0516(14)	Ag(7)-Ag(1)-Ag(7)#1	180
Ag(4)-Ag(8)#1	3.1016(14)	C(27)-Ag(1)-Ag(2)	69.0(3)
Ag(4)-Ag(2)#1	3.2020(12)	C(27)#1-Ag(1)-Ag(2)	111.0(3)
Ag(5)-C(3)	2.305(12)	Ag(3)#1-Ag(1)-Ag(2)	59.88(2)
Ag(5)-O(2)	2.332(8)	Ag(3)-Ag(1)-Ag(2)	120.12(2)
Ag(5)-C(27)#1	2.400(12)	Ag(5)#1-Ag(1)-Ag(2)	116.31(2)
Ag(5)-C(21)#1	2.633(12)	Ag(5)-Ag(1)-Ag(2)	63.69(2)
Ag(5)-Ag(4)#1	3.0234(12)	Ag(7)-Ag(1)-Ag(2)	60.30(2)
Ag(6)-C(34)	2.051(13)	Ag(7)#1-Ag(1)-Ag(2)	119.70(2)
Ag(6)-C(15)	2.270(12)	C(27)-Ag(1)-Ag(2)#1	111.0(3)
Ag(6)-C(16)	2.427(13)	C(27)#1-Ag(1)-Ag(2)#1	69.0(3)
Ag(6)-Ag(8)#1	3.1269(15)	Ag(3)#1-Ag(1)-Ag(2)#1	120.12(2)
Ag(7)-C(33)	2.252(12)	Ag(3)-Ag(1)-Ag(2)#1	59.88(2)
Ag(7)-C(3)	2.324(12)	Ag(5)#1-Ag(1)-Ag(2)#1	63.69(2)
Ag(7)-C(9)	2.434(13)	Ag(5)-Ag(1)-Ag(2)#1	116.31(2)
Ag(8)-C(35)	2.082(11)	Ag(7)-Ag(1)-Ag(2)#1	119.70(2)
Ag(8)-C(21)#1	2.142(13)	Ag(7)#1-Ag(1)-Ag(2)#1	60.30(2)
Ag(8)-Ag(4)#1	3.1016(14)	Ag(2)-Ag(1)-Ag(2)#1	180
Ag(8)-Ag(6)#1	3.1269(15)	C(27)-Ag(1)-Ag(4)#1	115.1(3)
C(15)-Ag(2)#1	2.049(11)	C(27)#1-Ag(1)-Ag(4)#1	64.9(3)
C(21)-Ag(8)#1	2.142(13)	Ag(3)#1-Ag(1)-Ag(4)#1	64.38(2)
C(21)-Ag(5)#1	2.633(12)	Ag(3)-Ag(1)-Ag(4)#1	115.62(2)
C(27)-Ag(5)#1	2.400(12)	Ag(5)#1-Ag(1)-Ag(4)#1	121.95(2)

Ag(5)-Ag(1)-Ag(4)#1	58.05(2)
Ag(7)-Ag(1)-Ag(4)#1	112.28(3)
Ag(7)#1-Ag(1)-Ag(4)#1	67.72(3)
Ag(2)-Ag(1)-Ag(4)#1	59.54(2)
Ag(2)#1-Ag(1)-Ag(4)#1	120.46(2)
C(27)-Ag(1)-Ag(4)	64.9(3)
C(27)#1-Ag(1)-Ag(4)	115.1(3)
Ag(3)#1-Ag(1)-Ag(4)	115.62(2)
Ag(3)-Ag(1)-Ag(4)	64.38(2)
Ag(5)#1-Ag(1)-Ag(4)	58.05(2)
Ag(5)-Ag(1)-Ag(4)	121.95(2)
Ag(7)-Ag(1)-Ag(4)	67.72(3)
Ag(7)#1-Ag(1)-Ag(4)	112.28(3)
Ag(2)-Ag(1)-Ag(4)	120.46(2)
Ag(2)#1-Ag(1)-Ag(4)	59.54(2)
Ag(4)#1-Ag(1)-Ag(4)	180
C(15)#1-Ag(2)-Ag(3)#1	53.6(4)
C(3)-Ag(2)-Ag(3)#1	138.6(3)
C(15)#1-Ag(2)-Ag(7)	139.5(4)
C(3)-Ag(2)-Ag(7)	47.8(3)
Ag(3)#1-Ag(2)-Ag(7)	101.19(4)
C(15)#1-Ag(2)-Ag(8)	87.2(4)
C(3)-Ag(2)-Ag(8)	87.0(3)
Ag(3)#1-Ag(2)-Ag(8)	109.66(3)
Ag(7)-Ag(2)-Ag(8)	133.30(4)
C(15)#1-Ag(2)-Ag(4)#1	87.1(3)
C(3)-Ag(2)-Ag(4)#1	98.9(3)
Ag(3)#1-Ag(2)-Ag(4)#1	63.36(3)
Ag(7)-Ag(2)-Ag(4)#1	110.79(3)
Ag(8)-Ag(2)-Ag(4)#1	58.34(3)
C(15)#1-Ag(2)-Ag(1)	109.0(4)
C(3)-Ag(2)-Ag(1)	83.3(3)
Ag(3)#1-Ag(2)-Ag(1)	55.34(2)
Ag(7)-Ag(2)-Ag(1)	57.24(2)
Ag(8)-Ag(2)-Ag(1)	115.70(3)
Ag(4)#1-Ag(2)-Ag(1)	60.87(2)
C(15)#1-Ag(2)-Ag(5)	142.9(3)
C(3)-Ag(2)-Ag(5)	44.6(3)
Ag(3)#1-Ag(2)-Ag(5)	101.89(3)
Ag(7)-Ag(2)-Ag(5)	64.78(3)
Ag(8)-Ag(2)-Ag(5)	74.98(3)
Ag(4)#1-Ag(2)-Ag(5)	55.77(3)
Ag(1)-Ag(2)-Ag(5)	54.62(2)
O(1)-Ag(3)-Ag(1)	134.5(2)
C(9)-Ag(3)-Ag(1)	81.6(3)
C(27)#1-Ag(3)-Ag(1)	44.4(2)
C(15)-Ag(3)-Ag(1)	106.5(3)
O(1)-Ag(3)-Ag(2)#1	141.3(3)
C(9)-Ag(3)-Ag(2)#1	98.5(3)
C(27)#1-Ag(3)-Ag(2)#1	67.9(3)
C(15)-Ag(3)-Ag(2)#1	41.8(3)
Ag(1)-Ag(3)-Ag(2)#1	64.77(2)
O(1)-Ag(3)-Ag(5)	77.2(2)
C(9)-Ag(3)-Ag(5)	103.9(3)
C(27)#1-Ag(3)-Ag(5)	47.5(3)
C(15)-Ag(3)-Ag(5)	144.3(3)
Ag(1)-Ag(3)-Ag(5)	57.48(2)
Ag(2)#1-Ag(3)-Ag(5)	112.82(3)
O(1)-Ag(3)-Ag(6)	111.4(2)
C(9)-Ag(3)-Ag(6)	64.2(3)
C(27)#1-Ag(3)-Ag(6)	134.7(3)
C(15)-Ag(3)-Ag(6)	43.7(3)
Ag(1)-Ag(3)-Ag(6)	113.98(3)
Ag(2)#1-Ag(3)-Ag(6)	66.83(3)
Ag(5)-Ag(3)-Ag(6)	167.29(4)
O(1)-Ag(3)-Ag(4)	152.8(2)
C(9)-Ag(3)-Ag(4)	38.4(3)
C(27)#1-Ag(3)-Ag(4)	102.7(3)
C(15)-Ag(3)-Ag(4)	78.7(3)
Ag(1)-Ag(3)-Ag(4)	62.71(2)
Ag(2)#1-Ag(3)-Ag(4)	60.38(3)
Ag(5)-Ag(3)-Ag(4)	112.82(3)
Ag(6)-Ag(3)-Ag(4)	55.29(3)
C(9)-Ag(4)-Ag(5)#1	134.1(3)
C(21)-Ag(4)-Ag(5)#1	58.7(3)
C(9)-Ag(4)-Ag(6)	71.8(4)
C(21)-Ag(4)-Ag(6)	102.4(4)
Ag(5)#1-Ag(4)-Ag(6)	127.88(4)
C(9)-Ag(4)-Ag(8)#1	132.8(4)
C(21)-Ag(4)-Ag(8)#1	43.5(3)
Ag(5)#1-Ag(4)-Ag(8)#1	79.32(3)
Ag(6)-Ag(4)-Ag(8)#1	61.08(3)
C(9)-Ag(4)-Ag(2)#1	101.4(3)
C(21)-Ag(4)-Ag(2)#1	86.6(3)
Ag(5)#1-Ag(4)-Ag(2)#1	63.11(3)
Ag(6)-Ag(4)-Ag(2)#1	68.03(3)
Ag(8)#1-Ag(4)-Ag(2)#1	60.17(3)
C(9)-Ag(4)-Ag(1)	78.2(3)
C(21)-Ag(4)-Ag(1)	114.7(3)
Ag(5)#1-Ag(4)-Ag(1)	56.36(2)
Ag(6)-Ag(4)-Ag(1)	111.34(3)
Ag(8)#1-Ag(4)-Ag(1)	116.20(3)
Ag(2)#1-Ag(4)-Ag(1)	59.59(2)
C(9)-Ag(4)-Ag(3)	45.4(3)
C(21)-Ag(4)-Ag(3)	142.6(3)
Ag(5)#1-Ag(4)-Ag(3)	102.06(3)
Ag(6)-Ag(4)-Ag(3)	62.22(3)
Ag(8)#1-Ag(4)-Ag(3)	105.42(4)
Ag(2)#1-Ag(4)-Ag(3)	56.27(3)
Ag(1)-Ag(4)-Ag(3)	52.92(2)
C(3)-Ag(5)-Ag(1)	85.3(3)
O(2)-Ag(5)-Ag(1)	133.1(2)
C(27)#1-Ag(5)-Ag(1)	44.0(2)
C(21)#1-Ag(5)-Ag(1)	108.0(2)
C(3)-Ag(5)-Ag(4)#1	98.8(3)
O(2)-Ag(5)-Ag(4)#1	138.0(3)
C(27)#1-Ag(5)-Ag(4)#1	66.5(3)
C(21)#1-Ag(5)-Ag(4)#1	42.7(2)
Ag(1)-Ag(5)-Ag(4)#1	65.60(2)
C(3)-Ag(5)-Ag(3)	105.7(3)
O(2)-Ag(5)-Ag(3)	77.9(2)
C(27)#1-Ag(5)-Ag(3)	49.5(3)
C(21)#1-Ag(5)-Ag(3)	149.1(3)
Ag(1)-Ag(5)-Ag(3)	55.89(2)
Ag(4)#1-Ag(5)-Ag(3)	112.96(4)
C(3)-Ag(5)-Ag(2)	39.1(3)

O(2)-Ag(5)-Ag(2)	156.4(2)
C(27)#1-Ag(5)-Ag(2)	100.8(3)
C(21)#1-Ag(5)-Ag(2)	77.4(2)
Ag(1)-Ag(5)-Ag(2)	61.70(2)
Ag(4)#1-Ag(5)-Ag(2)	61.12(3)
Ag(3)-Ag(5)-Ag(2)	109.53(3)
C(34)-Ag(6)-Ag(4)	104.2(3)
C(15)-Ag(6)-Ag(4)	87.2(3)
C(16)-Ag(6)-Ag(4)	116.9(3)
C(34)-Ag(6)-Ag(8)#1	100.6(3)
C(15)-Ag(6)-Ag(8)#1	84.4(3)
C(16)-Ag(6)-Ag(8)#1	107.2(3)
Ag(4)-Ag(6)-Ag(8)#1	60.25(3)
C(34)-Ag(6)-Ag(3)	137.4(4)
C(15)-Ag(6)-Ag(3)	48.9(3)
C(16)-Ag(6)-Ag(3)	63.5(3)
Ag(4)-Ag(6)-Ag(3)	62.49(3)
Ag(8)#1-Ag(6)-Ag(3)	105.03(4)
C(33)-Ag(7)-Ag(1)	158.1(3)
C(3)-Ag(7)-Ag(1)	83.3(3)
C(9)-Ag(7)-Ag(1)	77.8(3)
C(33)-Ag(7)-Ag(2)	107.7(3)
C(3)-Ag(7)-Ag(2)	41.2(3)
C(9)-Ag(7)-Ag(2)	140.3(3)
Ag(1)-Ag(7)-Ag(2)	62.46(2)
C(35)-Ag(8)-Ag(4)#1	144.1(3)
C(21)#1-Ag(8)-Ag(4)#1	42.2(3)
C(35)-Ag(8)-Ag(6)#1	86.0(3)
C(21)#1-Ag(8)-Ag(6)#1	98.9(3)
Ag(4)#1-Ag(8)-Ag(6)#1	58.67(3)
C(35)-Ag(8)-Ag(2)	101.0(3)
C(21)#1-Ag(8)-Ag(2)	86.8(3)
Ag(4)#1-Ag(8)-Ag(2)	61.49(3)
Ag(6)#1-Ag(8)-Ag(2)	67.66(3)
C(34)#2-C(33)-Ag(7)	167.3(11)
C(33)#3-C(34)-Ag(6)	177.0(11)
C(35)#4-C(35)-Ag(8)	174.8(15)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z; #2 -x, y-1/2, -z+1/2; #3 -x, y+1/2, -z+1/2; #4 -x, -y-1, -z.

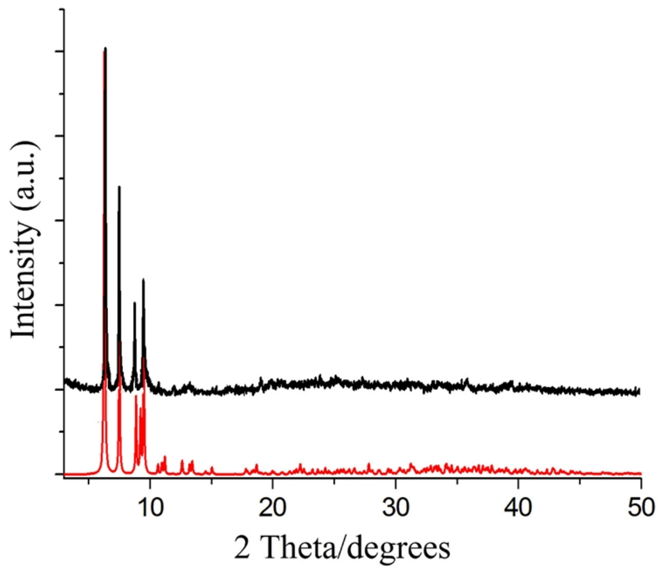

Fig. S1 Experimental (black trace) and simulated (red trace) X-ray powder diffraction patterns of **1**.

Reference:

1 (*a*) L. Zhao, C.-Q. Wan, J. Han, X.-D. Chen and T. C. W. Mak, *Chem. –Eur. J.*, 2008, **14**, 10437; (*b*) Z.-G. Jiang, K. Shi, Y.-M. Lin and Q.-M. Wang, *Chem. Commun.*, 2014, **50**, 2353.

2 (*a*) G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.