Oxometalate and Phosphine Ligands Co-protected Silver Nanoclusters: $Ag_{28}(dppb)_6(MO_4)_4$ and $Ag_{32}(dppb)_{12}(MO_4)_4(NO_3)_4$

Guang-Xiong Duan,[a] Jun Han,[a] Bao-Zhu Yang,*[,b] Yun-Peng Xie,*[,a], Xing Lu*[,a]

[a]State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China.

[b]School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.

Experimental Section

All reagents employed are commercially available and used as received without further purification. ^{t}BuC≡CAg[S1] was prepared according to literature procedure. MALDI-TOF mass spectrometry was measured with a BIFLEX III spectrometer (Bruker Daltonics Inc., Germany). NMR spectra were recorded on a Bruker AV-II 400 MHz NMR spectrometer, locked on deuterated solvents and referenced to the solvent peak. The Vis-NIR experiments were carried out on a PE Lambda 750S UV-vis-NIR spectrophotometer. Fluorescent spectra were recorded on a FP-6500 fluorescence spectrometer, using 5 mm path length cuvettes. Crystal data of **1**, **2** were collected on a Bruker D8 Quest diffractometer with Mo-Kα radiation (λ= 0.71073Å). Crystal data of **3** was collected at 100 K using the radiation wavelength at 0.65250 Å with a MX300 detector at beamline BL17B of the Shanghai Synchrotron Radiation Facility (China). Multi-scan method was used for absorption corrections. The structures were solved with direct method and were refined with SHELXL-2014.[S2]

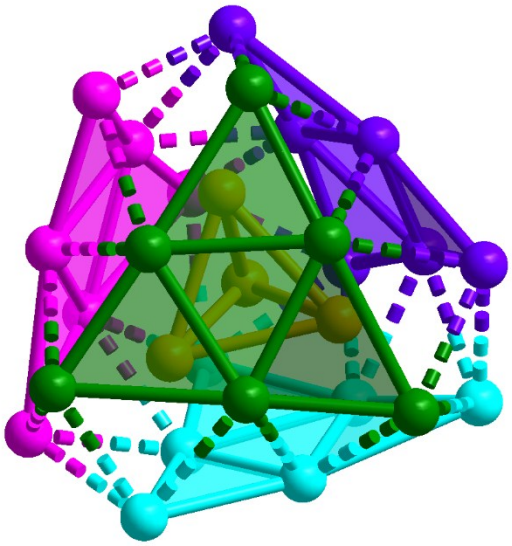

Figure S1: Detailed structure analysis of the $Ag_{28}(dppb)_6(MoO_4)_4$ cluster. An inner v_1 tetrahedral Ag_4 core capped on the four faces with four v_2 triangular Ag_6 facets. Dashed lines represent Ag…Ag interactions between neighboring Ag_6 facets. Color legend: Ag, purple, pink, green, sky blue and orange.

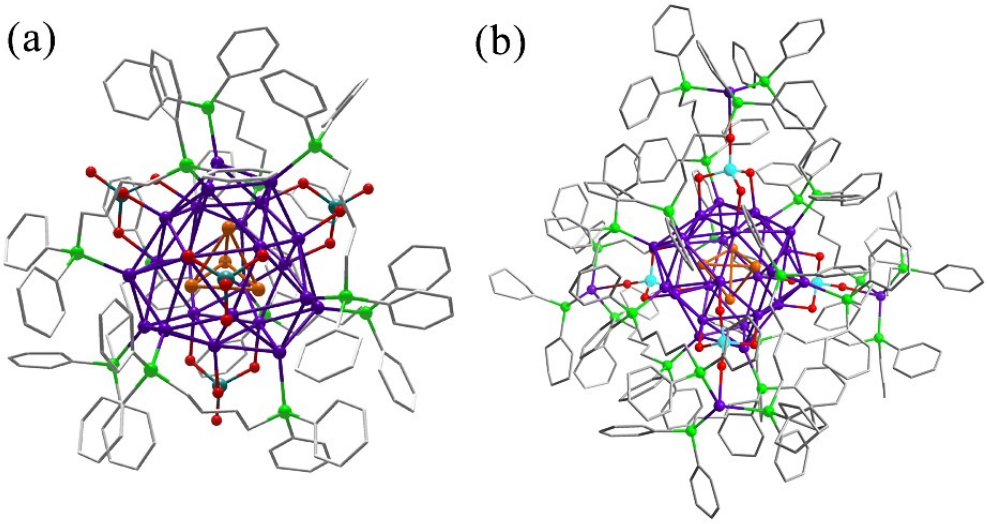

Figure S2: a) The structure of **2** established by X-ray crystallography. b) The structure of **3** established by X-ray crystallography. Color legend: Ag, purple，orange; P, green; Mo, blue; W cyan; O, red; C, grey.

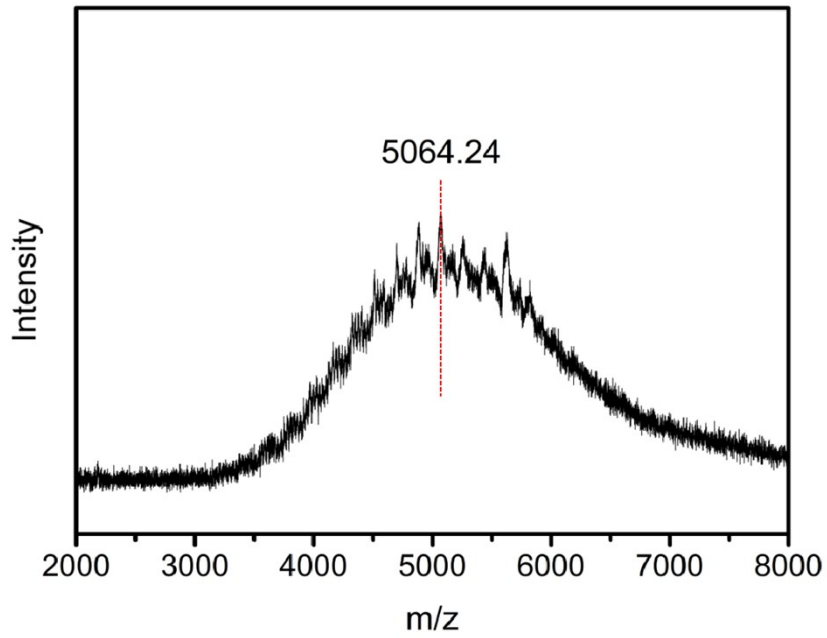

Figure S3: Positive MALDI-TOF-MS spectrum of $Ag_{28}(dppb)_6(MoO_4)_4$ cluster with DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]- malononitrile) matrix.

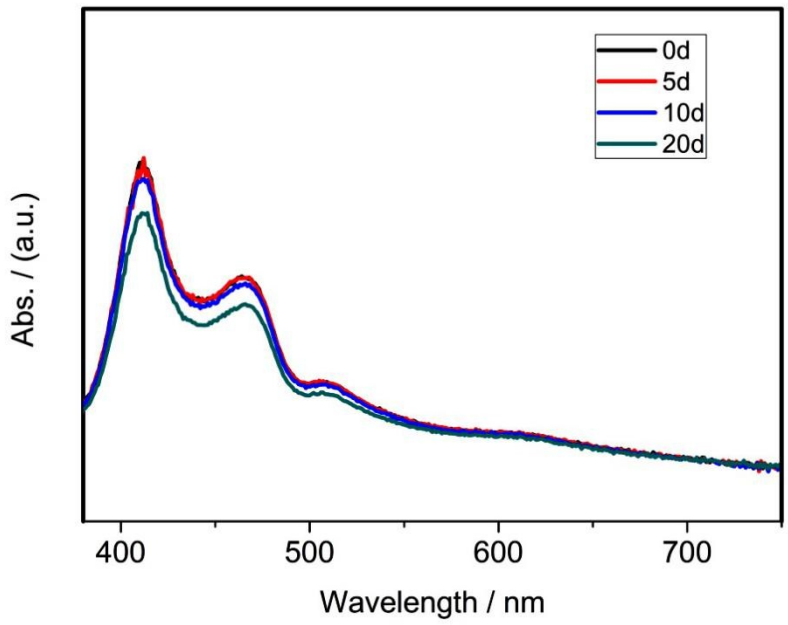

Figure S4: UV-vis absorption spectra of $Ag_{28}(dppb)_6(MoO_4)_4$ in CH_3OH solution in the dark at various days.

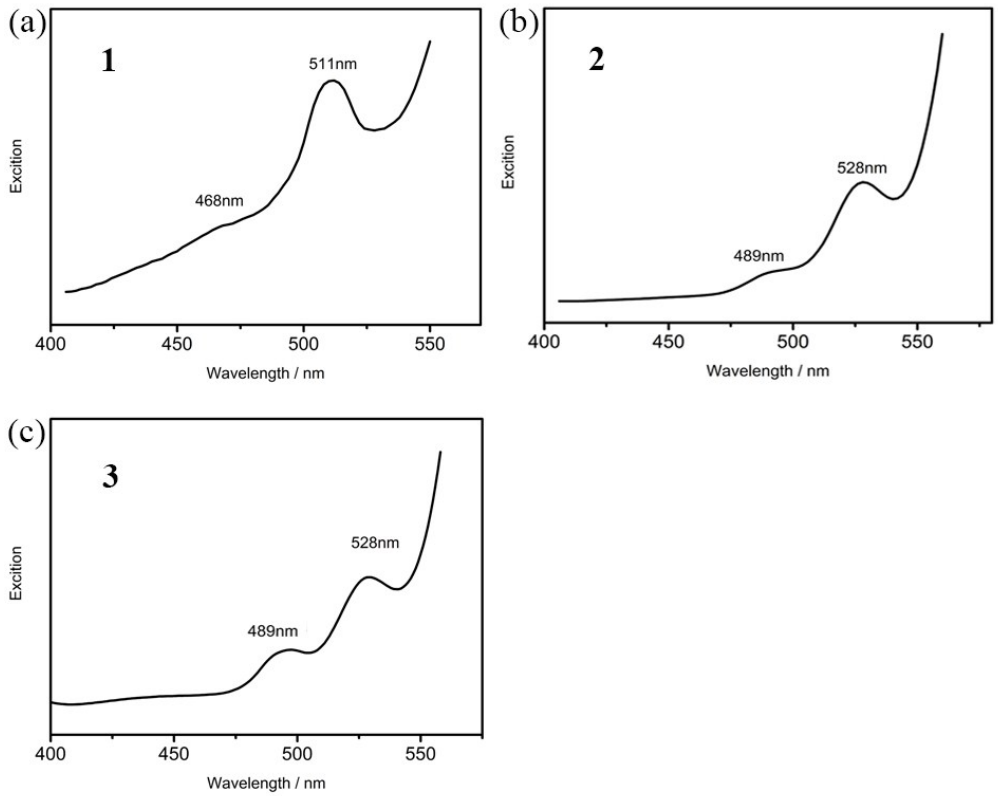

Figure S5: Excition spectra of complexes **1-3** in CH_3OH solution at room temperature.

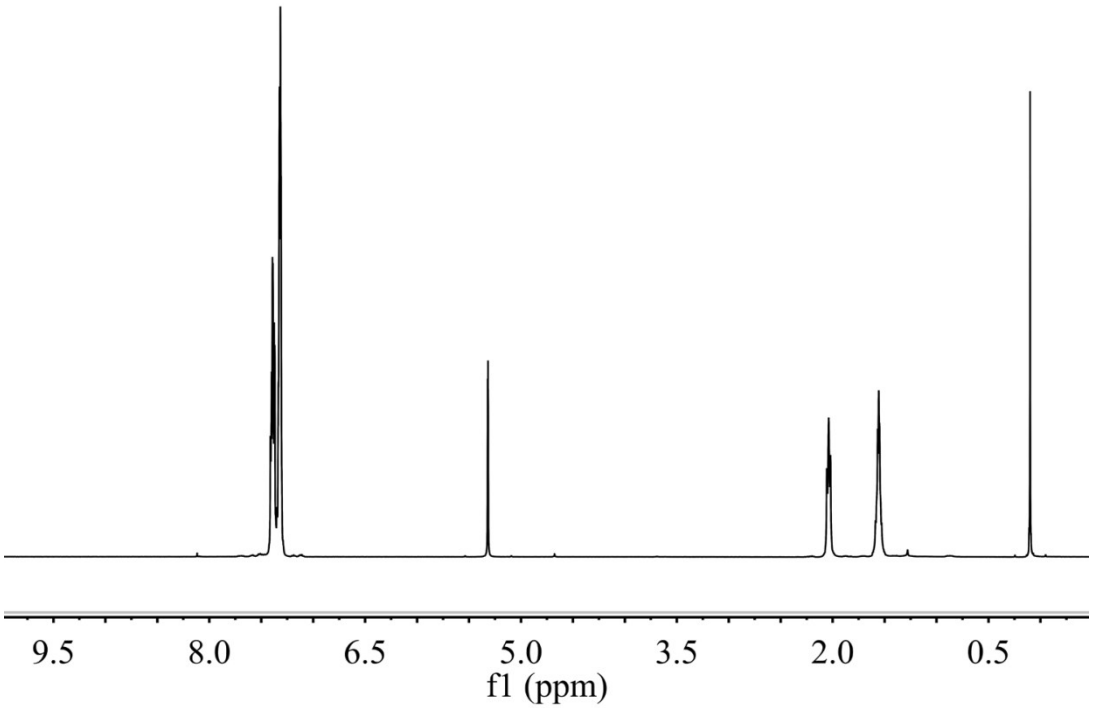

Figure S6: ^{1}H NMR spectrum of $Ag_{28}(dppb)_6(MoO_4)_4$ in CD_2Cl_2.

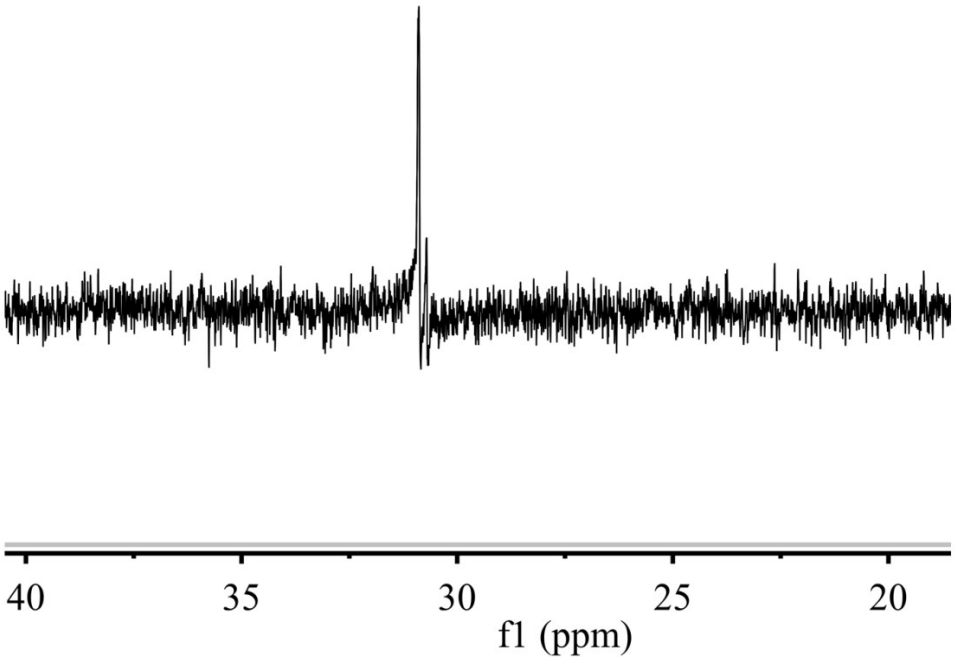

Figure S7: ^{31}P NMR spectrum of $Ag_{28}(dppb)_6(MoO_4)_4$ in CD_2Cl_2.

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

Empirical formula	C173 H189 Ag28 Mo4 O21 P12
Formula weight	6379.99
Crystal system	Monoclinic
Space group	*C2/c*
a	57.470(5)Å
b	33.556(3)Å
c	39.361(7)Å
α	90°
β	122.9670(10)°
γ	90°
Volume	63684(14)Å^3
Z	8
ρ_{calc}	1.331Mg/m^{-3}
Absorption coefficient	1.922 mm-1
F(000)	24472
Crystal size	0.32 x 0.24 x 0.16 mm^3
Crystal color and habit	black block
Theta range for data collection	2.829 to 24.786
Index ranges	-67<=h<=67, -39<=k<=39, -45<=l<=46
Reflections collected	180080
Independent reflections	53842 [R(int) = 0.0734]
Observed reflections (I > 2sigma(I))	27271
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.1177, wR2 = 0.3143
R indices (all data)	R1 = 0.1798, wR2 = 0.3572
Largest diff. peak and hole	4.797 and -2.601 eÅ^{-3}
CCDC number	1909219

Table 2. Crystal data and structure refinement for **2**

Empirical formula	C168 H170 Ag28 O17 P12 W4
Formula weight	6588.43
Crystal system	Monoclinic
Space group	*C2/c*
a	57.246(3)Å
b	33.4588(16)Å
c	38.553(4)Å
α	90°
β	120.8820(10)°
γ	90°
Volume	63375(8)Å^3
Z	8
ρ_{calc}	1.381Mg/m^{-3}
Absorption coefficient	3.036 mm^{-1}
F(000)	24848
Crystal size	0.240 x 0.200 x 0.160 mm^3
Crystal color and habit	black block
Theta range for data collection	1.088 to 24.711
Index ranges	-67<=h<=67, -39<=k<=39, -45<=l<=45
Reflections collected	366423
Independent reflections	53734 [R(int) = 0.0674]
Observed reflections (I > 2sigma(I))	37228
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.1214, wR2 = 0.3161
R indices (all data)	R1 = 0.1762, wR2 = 0.3674
Largest diff. peak and hole	3.546 and -2.354 eÅ^{-3}
CCDC number	1909220

Table 3. Crystal data and structure refinement for **3**

Empirical formula	C337 H339 Ag32 Mo4 P24 O26 N3
Formula weight	9425.97
Crystal system	Monoclinic
Space group	*C2*
a	41.161(3)Å
b	24.6172(13)Å
c	40.061(2)Å
α	90°
β	103.141(2)°
γ	90°
Volume	39529(4)Å^3
Z	4
ρ_{calc}	1.584Mg/m^{-3}
Absorption coefficient	1.42 mm^{-1}
F(000)	18488
Crystal size	0.320 x 0.240 x 0.160 mm^3
Crystal color and habit	black block
Theta range for data collection	0.971 to 25.382
Index ranges	-49<=h<=49, -29<=k<=29, -48<=l<=48
Reflections collected	259222
Independent reflections	72440 [R(int) = 0.0659]
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.1802
R indices (all data)	R1 = 0.0819, wR2 = 0.1938
Largest diff. peak and hole	3.140 and -2.177 eÅ^{-3}
CCDC number	1909221

Ag-Ag bond list of **1**					
Ag1-Ag2	2.949(2)	Ag1-Ag3	2.951(2)	Ag1-Ag15	2.820(2)
Ag1-Ag16	2.952(2)	Ag1-Ag17	2.830(2)	Ag1-Ag23	2.689(2)
Ag1-Ag26	2.981(2)	Ag1-Ag27	3.264(2)	Ag2-Ag3	2.951(2)
Ag2-Ag4	2.830(2)	Ag2-Ag10	2.816(2)	Ag2-Ag11	2.976(2)
Ag2-Ag15	3.232(2)	Ag2-Ag25	2.971(2)	Ag2-Ag26	2.702(2)
Ag3-Ag4	3.255(2)	Ag3-Ag5	2.962(2)	Ag3-Ag23	2.965(2)
Ag3-Ag25	2.696(2)	Ag3-Ag27	2.840(2)	Ag3-Ag28	2.824(2)
Ag4-Ag5	2.833(2)	Ag4-Ag6	2.836(2)	Ag4-Ag10	2.966(2)
Ag4-Ag25	2.784(2)	Ag5-Ag6	2.813(2)	Ag5-Ag7	3.190(2)
Ag5-Ag25	2.764(2)	Ag5-Ag28	2.847(2)	Ag6-Ag7	2.948(2)
Ag6-Ag9	2.837(2)	Ag6-Ag10	3.222(2)	Ag6-Ag25	2.770(2)
Ag7-Ag9	2.826(2)	Ag7-Ag14	2.825(2)	Ag7-Ag21	2.960(2)
Ag7-Ag24	3.008(2)	Ag7-Ag25	2.695(2)	Ag8-Ag11	2.838(2)
Ag8-Ag12	2.956(2)	Ag8-Ag15	2.845(2)	Ag8-Ag17	3.161(2)
Ag8-Ag19	2.837(2)	Ag8-Ag26	2.752(2)	Ag9-Ag10	2.972(2)
Ag9-Ag12	2.962(2)	Ag9-Ag13	3.150(2)	Ag9-Ag14	3.009(2)
Ag9-Ag24	2.703(2)	Ag9-Ag25	3.010(2)	Ag10-Ag11	2.830(2)
Ag10-Ag12	2.959(2)	Ag10-Ag25	2.687(2)	Ag10-Ag26	2.996(2)
Ag11-Ag12	3.230(2)	Ag11-Ag15	2.845(2)	Ag11-Ag26	2.775(2)
Ag12-Ag13	2.830(2)	Ag12-Ag19	2.816(2)	Ag12-Ag24	2.967(2)
Ag12-Ag26	2.707(2)	Ag13-Ag14	2.825(2)	Ag13-Ag19	3.003(2)

Ag13-Ag20	2.795(2)	Ag13-Ag24	2.770(2)	Ag14-Ag20	2.844(2)
Ag14-Ag21	3.081(2)	Ag14-Ag24	2.767(2)	Ag15-Ag17	2.946(2)
Ag15-Ag26	2.778(2)	Ag16-Ag17	2.837(2)	Ag16-Ag18	2.835(2)
Ag16-Ag22	3.167(2)	Ag16-Ag23	2.761(2)	Ag16-Ag27	2.847(2)
Ag17-Ag19	2.980(2)	Ag17-Ag22	2.945(2)	Ag17-Ag23	3.027(2)
Ag17-Ag26	2.681(2)	Ag18-Ag21	2.823(2)	Ag18-Ag22	2.909(2)
Ag18-Ag23	2.764(2)	Ag18-Ag27	2.829(2)	Ag18-Ag28	3.217(2)
Ag19-Ag20	3.077(2)	Ag19-Ag22	2.955(2)	Ag19-Ag24	2.698(2)
Ag19-Ag26	3.032(2)	Ag20-Ag21	2.988(2)	Ag20-Ag22	2.824(2)
Ag20-Ag24	2.762(2)	Ag21-Ag22	2.812(2)	Ag21-Ag23	3.008(2)
Ag21-Ag24	2.682(2)	Ag21-Ag28	2.983(2)	Ag22-Ag23	2.686(2)
Ag22-Ag24	2.991(2)	Ag23-Ag24	2.865(2)	Ag23-Ag25	2.863(2)
Ag23-Ag26	2.865(2)	Ag23-Ag27	2.772(2)	Ag23-Ag28	2.670(2)
Ag24-Ag25	2.869(2)	Ag24-Ag26	2.852(2)	Ag25-Ag26	2.872(2)
Ag25-Ag28	3.017(2)	Ag27-Ag28	2.947(2)		

Ag-Ag bond list of **2**					
Ag1-Ag11	2.701(2)	Ag1-Ag18	2.964(3)	Ag1-Ag20	2.825(3)
Ag1-Ag17	2.852(2)	Ag1-Ag27	3.175(3)	Ag1-Ag28	2.928(3)
Ag1-Ag22	2.949(3)	Ag1-Ag23	3.028(3)	Ag2-Ag15	2.695(3)
Ag2-Ag22	2.840(3)	Ag2-Ag9	2.846(3)	Ag2-Ag16	2.947(2)
Ag2-Ag12	2.957(3)	Ag2-Ag3	2.989(3)	Ag2-Ag23	3.052(2)
Ag2-Ag19	3.122(3)	Ag3-Ag10	2.688(2)	Ag3-Ag4	2.814(3)
Ag3-Ag19	2.846(2)	Ag3-Ag16	2.963(3)	Ag3-Ag14	2.981(3)
Ag3-Ag15	3.002(2)	Ag3-Ag24	3.203(2)	Ag4-Ag15	2.692(2)
Ag4-Ag14	2.862(2)	Ag4-Ag5	2.963(3)	Ag4-Ag6	2.964(3)
Ag4-Ag10	3.000(2)	Ag4-Ag19	3.048(3)	Ag4-Ag26	3.181(2)
Ag5-Ag11	2.695(2)	Ag5-Ag18	2.824(3)	Ag5-Ag26	2.873(3)
Ag5-Ag27	2.957(3)	Ag5-Ag6	2.992(2)	Ag5-Ag15	3.032(3)
Ag5-Ag25	3.159(3)	Ag6-Ag10	2.689(3)	Ag6-Ag8	2.807(3)
Ag6-Ag25	2.848(3)	Ag6-Ag11	3.000(2)	Ag6-Ag7	3.006(3)
Ag6-Ag14	3.150(3)	Ag7-Ag10	2.763(2)	Ag7-Ag24	2.844(3)
Ag7-Ag14	2.849(3)	Ag7-Ag8	2.860(3)	Ag7-Ag13	3.083(3)
Ag8-Ag11	2.677(2)	Ag8-Ag17	2.937(3)	Ag8-Ag13	2.977(3)
Ag8-Ag25	2.979(3)	Ag8-Ag10	3.027(2)	Ag8-Ag28	3.211(3)
Ag9-Ag23	2.767(3)	Ag9-Ag21	2.840(3)	Ag9-Ag20	2.841(3)
Ag9-Ag22	2.941(3)	Ag9-Ag16	3.159(3)	Ag10-Ag13	2.683(2)

Ag10-Ag14	2.758(2)	Ag10-Ag24	2.811(2)	Ag10-Ag23	2.855(2)
Ag10-Ag15	2.874(2)	Ag10-Ag11	2.895(2)	Ag10-Ag16	2.976(3)
Ag11-Ag27	2.776(3)	Ag11-Ag25	2.779(3)	Ag11-Ag28	2.784(3)
Ag11-Ag23	2.859(3)	Ag11-Ag15	2.879(2)	Ag11-Ag18	2.999(2)
Ag11-Ag17	3.016(3)	Ag12-Ag15	2.812(2)	Ag12-Ag22	2.832(3)
Ag12-Ag19	2.846(3)	Ag12-Ag26	2.860(3)	Ag12-Ag18	3.203(3)
Ag13-Ag16	2.837(3)	Ag13-Ag21	2.839(3)	Ag13-Ag24	2.979(3)
Ag13-Ag17	2.990(3)	Ag13-Ag23	2.990(2)	Ag14-Ag24	2.877(3)
Ag15-Ag18	2.698(2)	Ag(15)-Ag(26	2.756(2)	Ag15-Ag19	2.781(2)
Ag15-Ag23	2.869(2)	Ag15-Ag22	2.985(2)	Ag16-Ag23	2.682(3)
Ag16-Ag24	2.841(3)	Ag16-Ag21	2.996(3)	Ag17-Ag23	2.695(2)
Ag17-Ag28	2.856(3)	Ag17-Ag20	2.945(3)	Ag17-Ag21	3.176(3)
Ag18-Ag27	2.839(3)	Ag18-Ag26	2.953(3)	Ag18-Ag22	2.959(3)
Ag19-Ag26	2.840(3)	Ag20-Ag23	2.764(2)	Ag20-Ag21	2.838(3)
Ag20-Ag22	3.155(3)	Ag21-Ag23	2.769(3)	Ag22-Ag23	2.684(2)
Ag25-Ag27	2.836(3)	Ag25-Ag28	2.884(3)	Ag27-Ag28	2.815(3)

Ag-Ag bond list of **3**					
Ag1-Ag2	2.856(2)	Ag1-Ag3	2.844(2)	Ag1-Ag4	3.033(2)
Ag1-Ag5	2.865(2)	Ag1-Ag6	2.772(2)	Ag1-Ag7	3.029(2)
Ag2-Ag3	2.862(2)	Ag2-Ag4	2.990(2)	Ag2-Ag6	2.776(2)
Ag2-Ag9	2.995(2)	Ag2-Ag10	2.871(2)	Ag3-Ag6	2.789(2)
Ag3-Ag7	3.088(2)	Ag3-Ag8	2.836(2)	Ag3-Ag9	3.057(3)
Ag4-Ag5	3.008(2)	Ag4-Ag6	2.680(2)	Ag4-Ag10	2.815(2)
Ag4-Ag16	3.010(2)	Ag4-Ag17	3.047(2)	Ag4-Ag18	2.817(2)
Ag5-Ag6	3.019(2)	Ag5-Ag7	2.797(2)	Ag5-Ag11	3.047(2)
Ag5-Ag15	2.685(2)	Ag5-Ag17	2.967(2)	Ag5-Ag27	3.129(2)
Ag6-Ag7	2.681(2)	Ag6-Ag8	2.987(2)	Ag6-Ag9	2.681(2)
Ag6-Ag10	3.058(2)	Ag6-Ag14	2.853(2)	Ag6-Ag15	2.876(2)
Ag6-Ag16	2.859(2)	Ag7-Ag8	3.054(2)	Ag7-Ag11	2.858(2)
Ag7-Ag12	2.997(2)	Ag7-Ag15	3.012(2)	Ag8-Ag9	2.802(2)
Ag8-Ag12	2.990(2)	Ag8-Ag13	3.032(2)	Ag8-Ag14	2.687(2)
Ag8-Ag26	3.059(2)	Ag9-Ag10	2.973(2)	Ag9-Ag13	2.847(2)
Ag9-Ag14	3.038(2)	Ag9-Ag22	3.018(2)	Ag10-Ag16	2.682(2)
Ag10-Ag18	2.988(2)	Ag10-Ag19	3.004(2)	Ag10-Ag22	2.990(2)
Ag11-Ag12	3.125(2)	Ag11-Ag15	2.773(2)	Ag11-Ag25	2.857(2)
Ag11-Ag27	2.860(2)	Ag12-Ag14	2.998(2)	Ag12-Ag15	2.683(2)
Ag12-Ag24	2.792(2)	Ag12-Ag25	3.059(2)	Ag12-Ag26	2.874(2)
Ag13-Ag14	2.768(2)	Ag13-Ag22	2.998(2)	Ag13-Ag23	2.889(2)

Ag13-Ag26	2.832(2)	Ag14-Ag15	2.882(2)	Ag14-Ag16	2.862(2)
Ag14-Ag21	3.028(2)	Ag14-Ag22	2.681(2)	Ag14-Ag23	2.798(2)
Ag14-Ag24	2.671(2)	Ag14-Ag26	2.787(2)	Ag15-Ag16	2.863(2)
Ag15-Ag17	3.029(2)	Ag15-Ag24	3.004(2)	Ag15-Ag25	2.798(2)
Ag15-Ag27	2.781(2)	Ag15-Ag28	2.693(2)	Ag16-Ag17	2.679(2)
Ag16-Ag18	2.814(2)	Ag16-Ag19	2.762(2)	Ag16-Ag20	2.780(2)
Ag16-Ag21	2.689(2)	Ag16-Ag22	3.067(2)	Ag16-Ag28	2.998(2)
Ag18-Ag19	2.871(2)	Ag18-Ag20	2.864(2)	Ag19-Ag20	2.828(2)
Ag19-Ag21	2.990(2)	Ag19-Ag22	2.855(2)	Ag20-Ag21	3.115(2)
Ag20-Ag28	2.874(2)	Ag21-Ag22	2.815(2)	Ag21-Ag23	2.853(2)
Ag21-Ag24	3.025(2)	Ag21-Ag28	2.981(2)	Ag22-Ag23	3.013(2)
Ag23-Ag24	3.059(2)	Ag23-Ag26	2.878(2)	Ag24-Ag25	2.852(2)
Ag24-Ag26	3.069(2)	Ag24-Ag28	3.030(2)	Ag25-Ag27	2.864(2)
Ag25-Ag28	3.138(2)	Ag27-Ag28	2.997(2)		

References

(S1) Z. G. Jiang, K. Shi, Y. M. Lin and Q. M. Wang, *ChemComm*. **2014**. *50*. 2353-2355.
(S2) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112.