Supporting Information

Tert-butyl Thiol and Pyridine Ligands Co-protected 50-Nuclei Cluster: The Effect of Pyridines on Ag–SR Bonds

Yang-Lin Shen,[a] Jun-Ling Jin,[b] Yun-Peng Xie,[a] and 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. E-mail: xieyp@hust.edu.cn, lux@hust.edu.cn.

[b]Henan Key Laboratory of Functional Salt Materials, Center for Advanced Materials Research, Zhongyuan University of Technology, Zhengzhou, 450007, China.

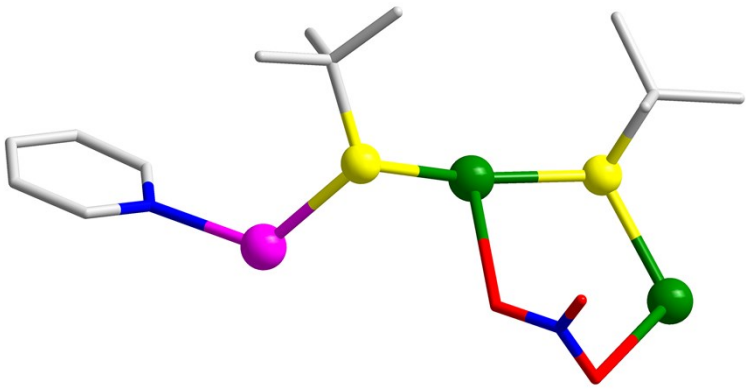

Fig. S1. The asymmetric unit of **1**. Hydrogen atoms are omitted for clarity. Color codes: Ag, purple and green; S, yellow; C, grey; N, blue.

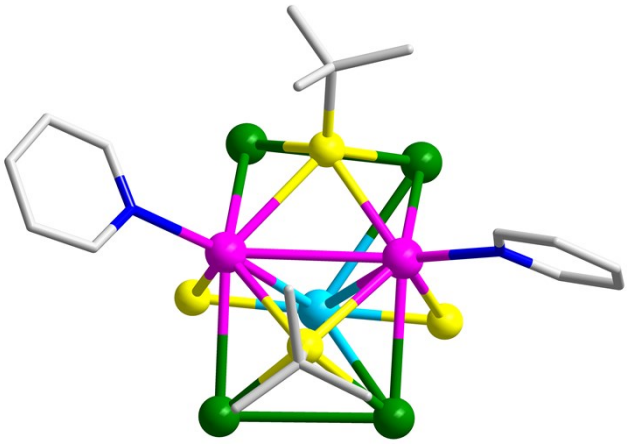

Fig. S2. Butterfly-like motif of the external shell structure in **6**. Hydrogen atoms are omitted for clarity. Color codes: Ag, purple, green and sky blue; S, yellow; C, grey; N, blue.

FT-IR spectrums

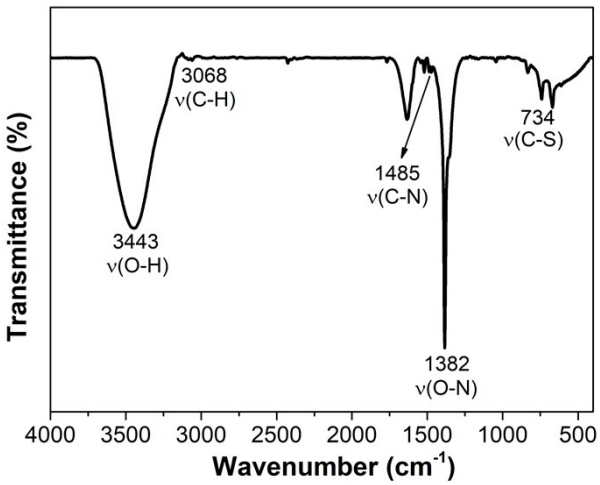

Fig. S3. IR spectrum of **1**.

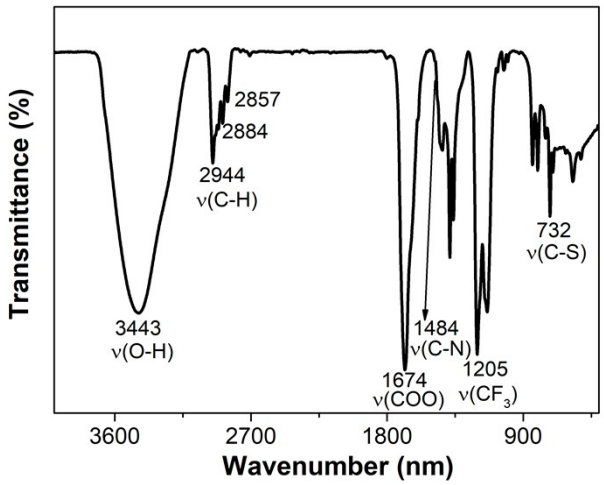

Fig. S4. IR spectrum of **2**.

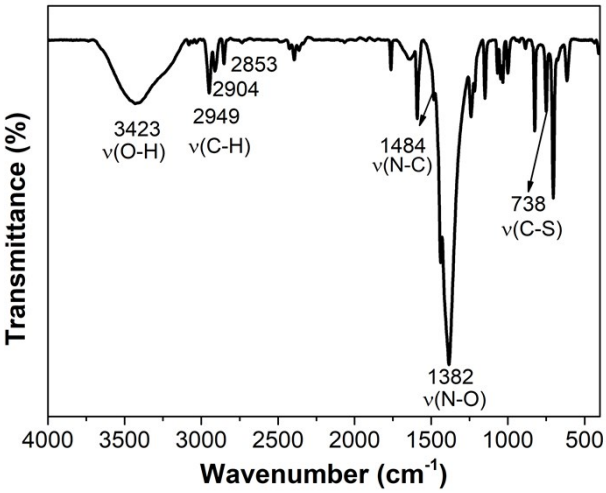

Fig. S5. IR spectrum of **3**.

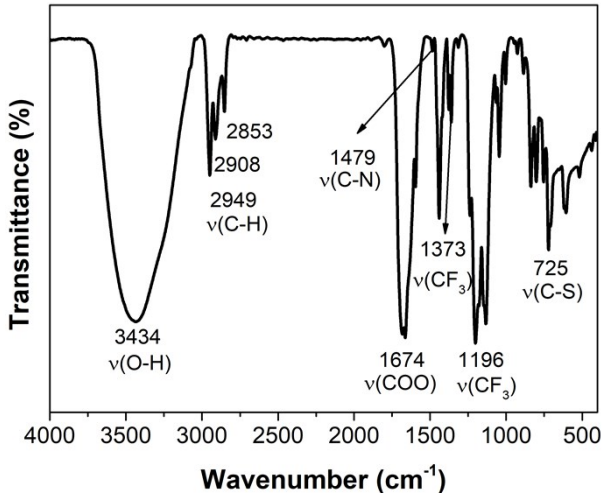

Fig. S6. IR spectrum of **4**.

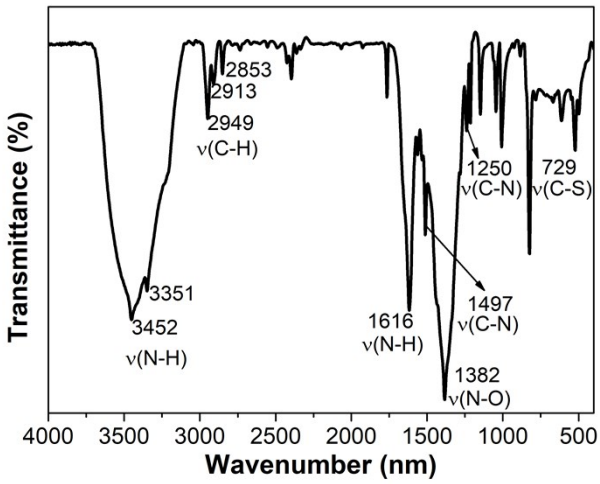

Fig. S7. IR spectrum of **5**.

UV-Vis spectrums

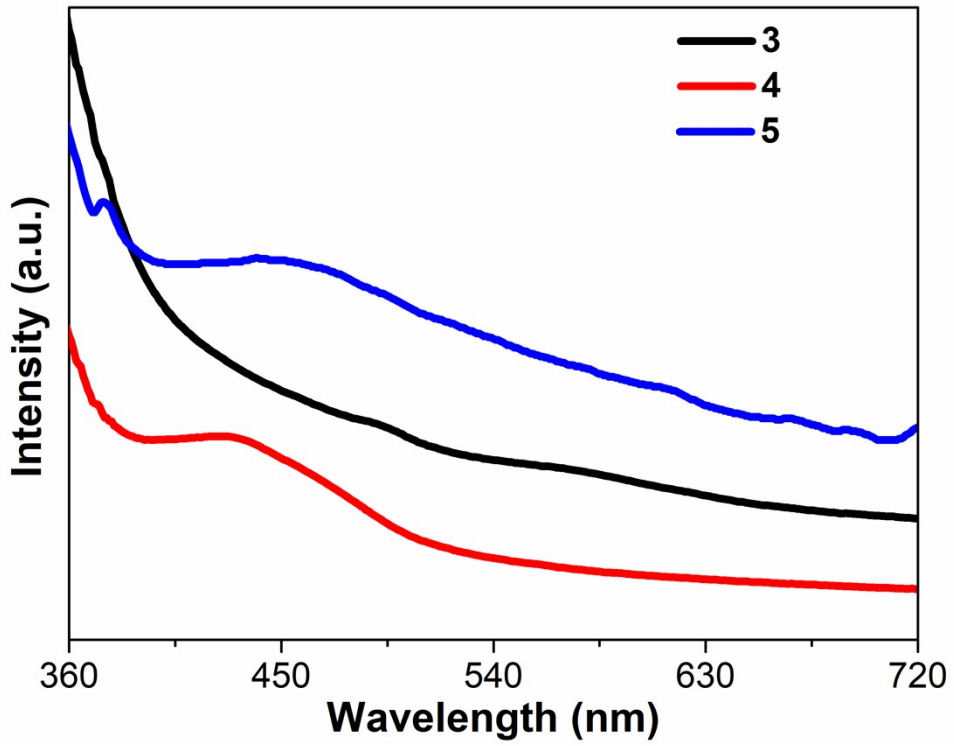

Fig. S8. UV-Vis spectrums of **3-5**.

PL spectrums

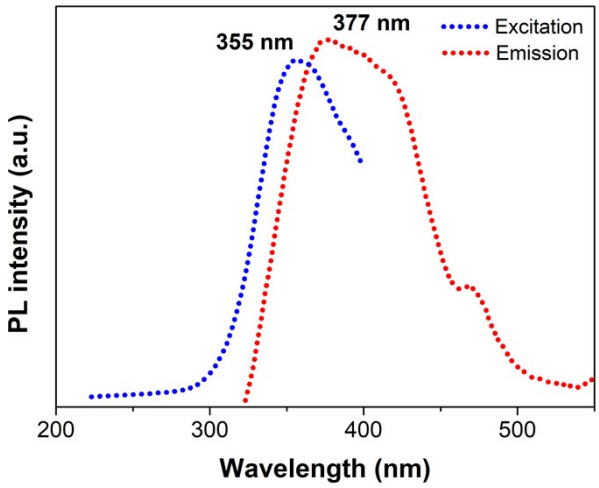

Fig. S9. Fluorescence spectrum of **3**.

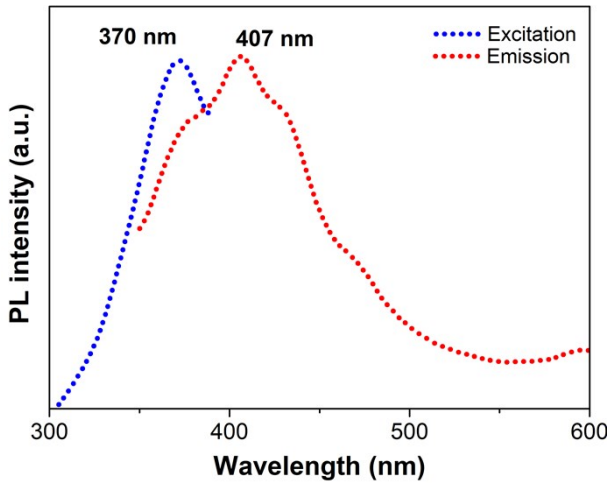

Fig. S10. Fluorescence spectrum of **4**.

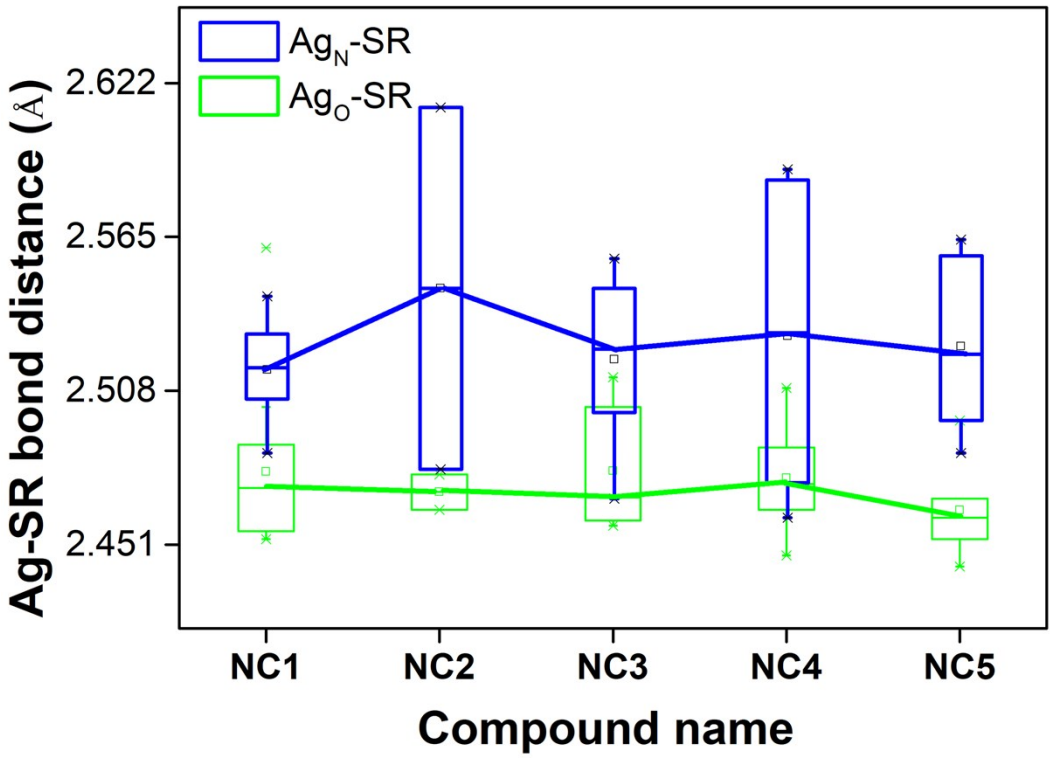

Fig. S11. Statistical bond length studies of Ag_N-SR and Ag_O-SR in pyridine-ligated clusters that reported by the Zang group[S1].

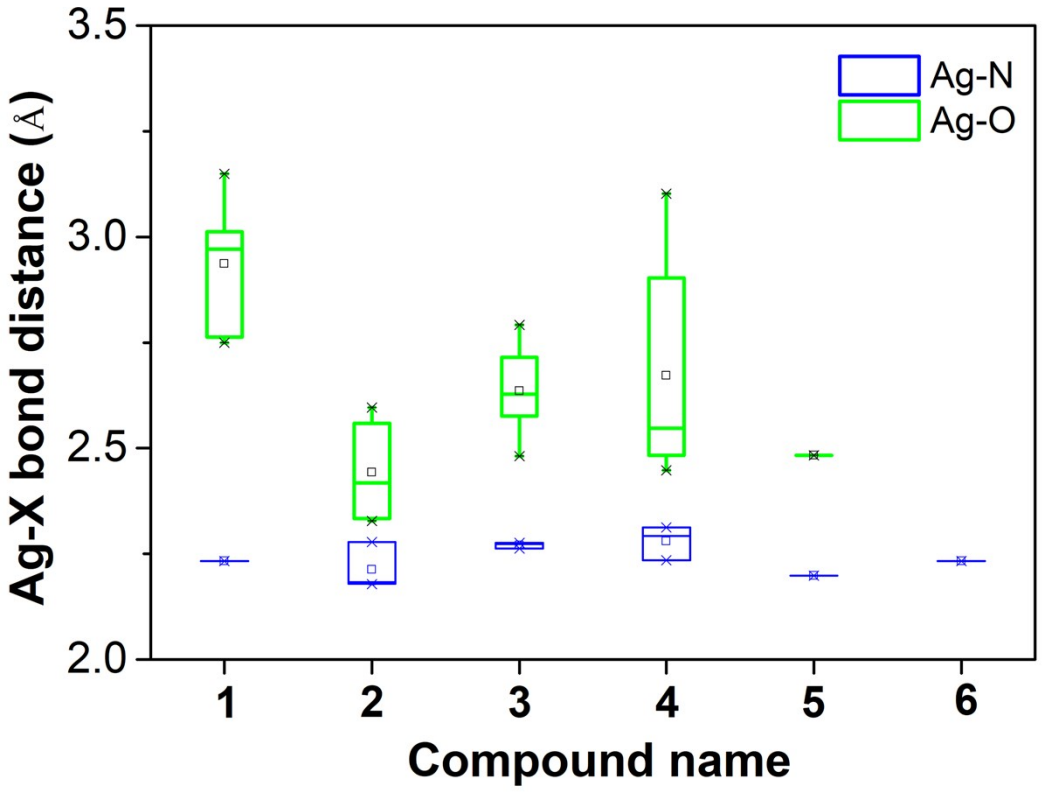

Fig. S12. Statistical bond length studies of Ag–O and Ag–N bond lengths of **1**-**6**.

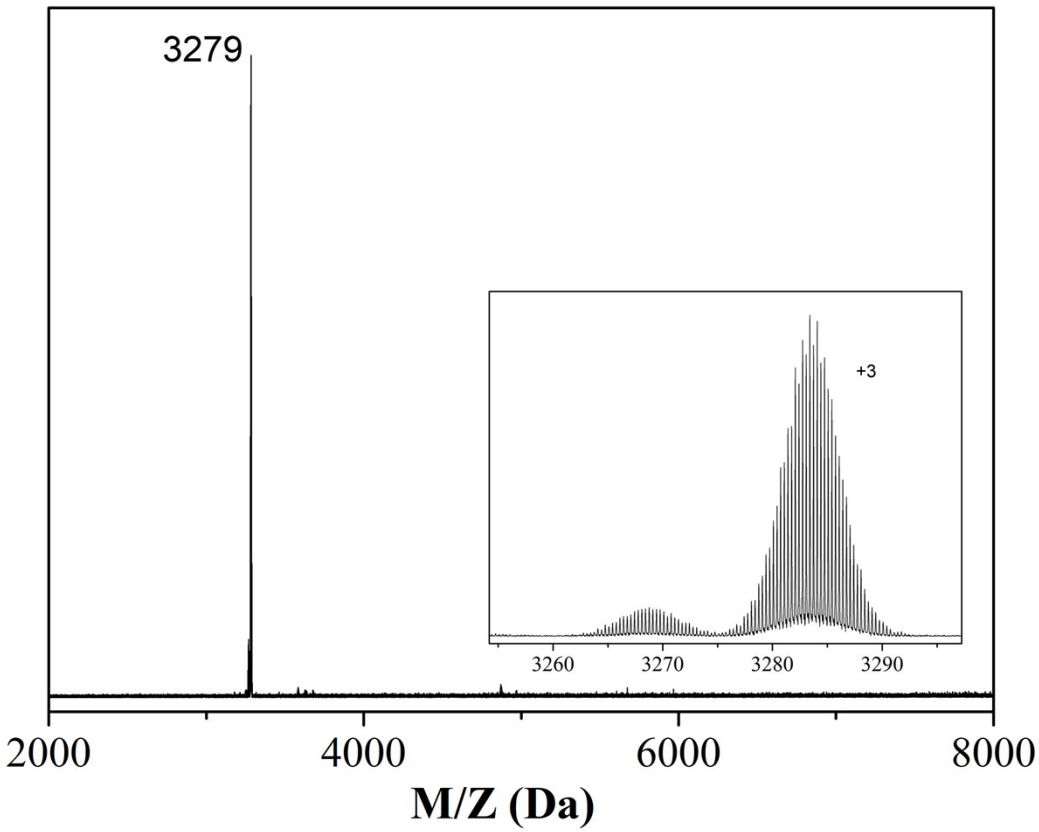

Fig. S13. The ESI-MS analysis of raw product.

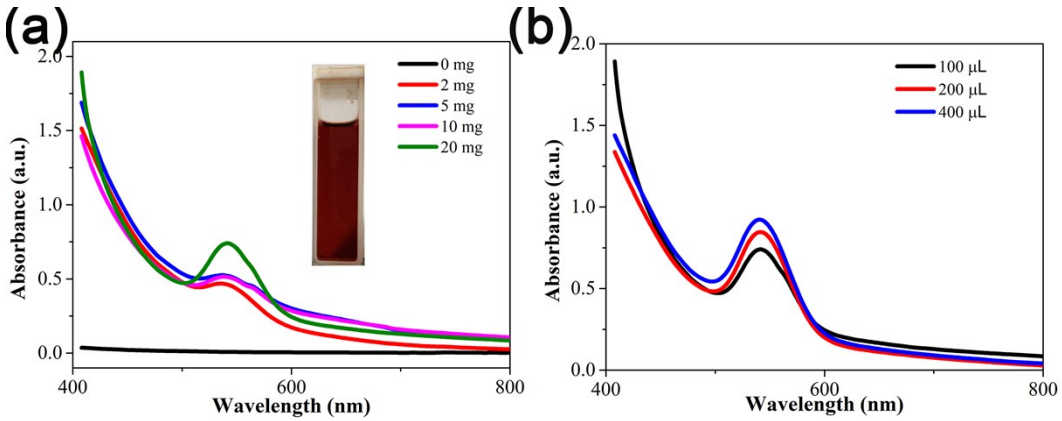

Fig. S14. The UV-vis spectrums of raw product obtained with different amount of thioacetamide (a) and pyridine (b).

Table S1. Crystal data and structure refinement for **1**	
Empirical formula	$C_{13}H_{23}N_2O_3S_2Ag_3$
Formula weight	643.07
Crystal system	Monoclinic
Space group	$P2_1/n$
a	11.6560(10) Å
b	7.3664(6) Å
c	24.205(2) Å
α	90°
β	103.522(2)°
γ	90°
Volume	2020.7(3) $Å^3$
Z	4
ρ_{calc}	2.114 Mg/m^3
Absorption coefficient	3.097 mm^{-1}
F(000)	1248
Crystal size	0.215 x 0.106 x 0.087 mm^3
Crystal color and habit	colorless strip
Theta range for data collection	2.898 to 25.027°
Index ranges	-13<=h<=13, -8<=k<=8, -28<=l<=25

Reflections collected	13333
Independent reflections	3560
Observed reflections (I > 2sigma(I))	3129
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0637
R indices (all data)	R1 = 0.0308, wR2 = 0.0667
Largest diff. peak and hole	1.194 and -0.690 e.Å-3
CCDC number	1999533

Table S2. Crystal data and structure refinement for **2**

Empirical formula	$C_{77}H_{99}N_9O_8F_{12}S_6Ag_{10}$
Formula weight	2777.71
Crystal system	Triclinic
Space group	P-1
a	12.36(6) Å
b	13.39(6) Å
c	14.98(7) Å
α	70.25(13)°
β	82.72(12)°
γ	89.18(14)°
Volume	2313(18) $Å^3$
Z	1
ρ_{calc}	1.991 Mg/m^3
Absorption coefficient	2.282 mm^{-1}
F(000)	1357
Crystal size	0.148 x 0.124 x 0.105 mm^3
Crystal color and habit	colorless bulk
Theta range for data collection	2.914 to 25.026°

Index ranges	-14<=h<=8, -15<=k<=15, -17<=l<=17
Reflections collected	13362
Independent reflections	7987 [R(int) = 0.0212]
Goodness-of-fit on F^2	1.183
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1106
R indices (all data)	R1 = 0.0730, wR2 = 0.1268
Largest diff. peak and hole	1.730 and -1.035 e.$Å^{-3}$
CCDC number	1999534

Table S3. Crystal data and structure refinement for **3**

Empirical formula	$C_{58}H_{86}N_{14}O_{20}S_6Ag_{12}$
Formula weight	2786.19
Crystal system	Monoclinic
Space group	C2/c
a	22.4694(10) Å
b	22.3474(8) Å
c	17.3851(7) Å
α	90°
β	92.6030(10)°
γ	90°
Volume	8720.6(6) $Å^3$
Z	4
ρ_{calc}	2.122 Mg/m^3
Absorption coefficient	2.842 mm^{-1}
F(000)	5408
Crystal color and habit	colorless bulk
Theta range for data collection	2.861 to 23.255°

Index ranges	-24<=h<=24, -24<=k<=24, -19<=l<=17
Reflections collected	20719
Independent reflections	6105
Observed reflections (I > 2sigma(I))	4857
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0701
R indices (all data)	R1 = 0.0513, wR2 = 0.0771
Largest diff. peak and hole	0.774 and -0.662 e.$Å^{-3}$
CCDC number	1999535

Table S4. Crystal data and structure refinement for **4**

Empirical formula	$C_{70}H_{82}N_8O_{12}F_{18}S_6Ag_{12}$
Formula weight	3056.22
Crystal system	Monoclinic
Space group	$P2_1/n$
a	13.9007(10) Å
b	20.5190(16) Å
c	17.5600(13) Å
α	90°
β	107.023(2)°
γ	90°
Volume	4789.2(6) $Å^3$
Z	2
ρ_{calc}	2.119 Mg/m^3
Absorption coefficient	2.616 mm^{-1}
F(000)	2952
Crystal color and habit	colorless bulk

Theta range for data collection	2.975 to 25.026°
Index ranges	-16<=h<=16, -22<=k<=24, -20<=l<=20
Reflections collected	32609
Independent reflections	8437 [R(int) = 0.0228]
Observed reflections (I > 2sigma(I))	7387
Goodness-of-fit on F^2	1.170
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0807
R indices (all data)	R1 = 0.0463, wR2 = 0.0860
Largest diff. peak and hole	1.340 and -1.281 e.$Å^{-3}$
CCDC number	1999536

Table S5. Crystal data and structure refinement for **5**

Empirical formula	$C_{48}H_{78}N_{18}O_{18}S_6Ag_{12}$
Formula weight	2682.05
Crystal system	Trigonal
Space group	R-3
a	24.5159(7) Å
b	24.5159(7) Å
c	11.1964(6) Å
α	90°
β	90°
γ	120°
Volume	5827.8(5) $Å^3$
Z	3
ρ_{calc}	2.293 Mg/m^3
Absorption coefficient	3.184 mm^{-1}
F(000)	3888

Crystal color and habit	colorless bulk
Theta range for data collection	2.878 to 25.353°
Index ranges	-29<=h<=24, -28<=k<=29, -13<=l<=13
Reflections collected	14342
Independent reflections	2379 [R(int) = 0.0210]
Observed reflections (I > 2sigma(I))	2281
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R1 = 0.0144, wR2 = 0.0366
R indices (all data)	R1 = 0.0154, wR2 = 0.0369
Largest diff. peak and hole	0.322 and -0.375 e.$Å^{-3}$
CCDC number	1999537

Table S6. Crystal data and structure refinement for **6**

Empirical formula	$C_{164}H_{280}B_4O_6N_{16}F_{16}S_{33}Ag_{50}$
Formula weight	9370.84
Crystal system	Monoclinic
Space group	$P2_1/n$
a	20.8642(2) Å
b	22.8925(2) Å
c	27.241(2) Å
α	90°
β	93.205(2)°
γ	90°
Volume	12991.0(2) $Å^3$
Z	2
ρ_{calc}	2.390 Mg/m^3
Absorption coefficient	3.987 mm^{-1}

F(000)	8892
Crystal color and habit	yellow bulk
Theta range for data collection	2.778 to 23.256°
Index ranges	-23<=h<=23, -25<=k<=25, -30<=l<=27
Reflections collected	76939
Independent reflections	18604 [R(int) = 0.0299]
Observed reflections (I > 2sigma(I))	15089
Goodness-of-fit on F^2	1.129
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0862
R indices (all data)	R1 = 0.0563, wR2 = 0.0978
Largest diff. peak and hole	1.472 and -1.155 e.$Å^{-3}$
CCDC number	1999538

Table S7. Selected b					
Ag1–S1	2.499(9)	Ag1–S2	2.458(9)	Ag2–S1	2.370(9)
Ag2–S2	2.372(9)	Ag3–S2	2.382(9)	Ag2–Ag2#1	3.308(6)

Table S8. Selected b					
Ag1–S1	2.323(9)	Ag1–S2	2.350(9)	Ag2–S2	2.498(9)
Ag2–S3#1	2.521(11)	Ag3–S1	2.501(9)	Ag3–S3	2.331(8)
Ag4–S1#1	2.697(9)	Ag4–S2	2.649(12)	Ag4–S3	2.403(9)
Ag5—S1#1	2.511(10)	Ag5—S2	2.463(9)	Ag1—Ag1#1	3.316(10)
Ag1—Ag2	3.140(11)	Ag1—Ag3	3.175(11)	Ag1—Ag4	2.934(10)
Ag1—Ag4#1	3.056(14)	Ag2—Ag5	3.290(3)	Ag3—Ag5#1	3.310(3)
Ag4—Ag1#1	3.056(14)	Ag4—Ag5	2.887(11)		

Table S9. Selected b					
Ag1–S1	2.457(17)	Ag1–S2	2.486(17)	Ag2–S2	2.437(17)
Ag2–S3	2.438(17)	Ag3–S3	2.547(18)	Ag4–S1	2.552(18)
Ag4–S2#1	2.576(18)	Ag5–S2#1	2.547(18)	Ag5–S3	2.527(18)
Ag6–S1	2.575(19)	Ag6–S3#1	2.563(18)	Ag1—Ag2	2.906(7)
Ag1—Ag3	3.072(7)	Ag1—Ag5#1	3.234(7)	Ag1—Ag6	3.054(8)
Ag2—Ag3	3.018(8)	Ag2—Ag6#1	2.922(8)	Ag5—Ag1#1	3.234(7)
Ag6—Ag2#1	2.922(8)				

Table S10. Selected b					
Ag1–S1	2.454(12)	Ag1–S3	2.454(12)	Ag2–S2	2.453(12)
Ag2–S3	2.435(13)	Ag3–S1	2.532(13)	Ag3–S2	2.577(13)
Ag4–S3#1	2.551(4)	Ag5–S2#1	2.507(13)	Ag5–S3	2.501(13)
Ag6—S1#1	3.184(8)	Ag6—S2	2.512(13)	Ag1—Ag2	3.007(6)
Ag1—Ag3	3.050(6)	Ag1—Ag5	3.190(7)	Ag1—Ag6#1	3.184(8)
Ag2—Ag3	3.046(6)	Ag2—Ag6	2.945(7)	Ag3—Ag4	3.136(3)
Ag4—Ag5#1	3.357(4)	Ag6—Ag1#1	3.1847(8)		

Table S11. Selected b					
Ag1–S1	2.508(5)	Ag1–S1#1	2.575(5)	Ag2–S1	2.451(5)
Ag2–S1#3	2.466(5)	Ag1–Ag2	3.248(2)	Ag1–Ag2#2	3.072(2)
Ag2–Ag1	3.072(2)	Ag2–Ag2#3	3.011(3)	Ag2–Ag2#4	3.011(3)

Table S12. Selected b

Ag1–S4	2.412(2)	Ag1–S5	2.411(2)	Ag2–S14	2.440(2)
Ag2–S9#1	2.462(2)	Ag2–S6#1	2.948(2)	Ag3–S7	2.916(2)
Ag3–S8	2.445(2)	Ag3–S12	2.450(2)	Ag4–S3	2.955(2)
Ag4–S4#1	2.968(2)	Ag4–S12	2.451(3)	Ag4–S14	2.444(3)
Ag5–S2	2.908(2)	Ag5–S8	2.436(2)	Ag5–S17	2.441(2)
Ag6–S2#1	2.835(2)	Ag6–S10	2.437(2)	Ag6–S13	2.461(2)
Ag7–S14	2.441(3)	Ag7–S15	2.445(2)	Ag7–S6#1	2.938(2)
Ag8–S6#1	2.633(2)	Ag8–S12#1	2.966(12)	Ag8–S15	2.744(3)
Ag8–S17#1	2.634(3)	Ag8–S18#1	3.063(9)	Ag9–S3	2.878(2)
Ag9–S10	2.431(2)	Ag9–S15	2.445(2)	Ag10–S15	2.445(2)
Ag10–S6	2.882(2)	Ag10–S9	2.449(2)	Ag10–S11	2.431(2)
Ag11–S5	2.941(2)	Ag11–S10	2.417(3)	Ag11–S16	2.426(3)
Ag12–S7	2.823(2)	Ag12–S11	2.444(3)	Ag12–S17	2.450(3)
Ag13–S2	2.660(2)	Ag13–S15#1	2.674(2)	Ag13–S17	2.698(3)
Ag14–S5	2.902(2)	Ag14–S11	2.427(3)	Ag14–S16	2.446(3)
Ag15–S3	2.652(2)	Ag15–S12	2.670(2)	Ag15–S16	2.752(3)
Ag16–S5	2.551(2)	Ag16–S9	2.787(3)	Ag16–S13	2.630(3)
Ag17–S7	2.691(2)	Ag17–S12	2.672(3)	Ag17–S16	2.676(3)
Ag18–S2	2.406(2)	Ag18–S6	2.410(2)	Ag19–S3	2.418(2)
Ag19–S7	2.421(2)	Ag20–S5	2.602(2)	Ag20–S6	2.606(2)
Ag20–S7	2.618(2)	Ag21–S3#1	2.609(2)	Ag21–S4	2.627(2)
Ag21–S6	2.613(2)	Ag22–S2	2.603(2)	Ag22–S4#1	2.629(2)
Ag22–S7	2.611(2)	Ag23–S2#1	2.609(2)	Ag23–S3	2.622(2)
Ag23–S5	2.604(2)	Ag24–S4	2.660(2)	Ag24–S9	2.621(2)
Ag24–S13	2.696(2)	Ag25–S4	2.934(2)	Ag25–S8#1	2.446(2)
Ag25–S13	2.464(2)	Ag1–Ag16	3.048(10)	Ag1–Ag20	3.051(9)
Ag1–Ag21	3.009(9)	Ag1–Ag22#1	3.024(9)	Ag1–Ag23	3.047(9)
Ag1–Ag24	3.065(9)	Ag1–Ag25	3.368(10)	Ag2–Ag10#1	3.348(12)
Ag2–Ag21#1	3.186(10)	Ag2–Ag24#1	2.980(11)	Ag3–Ag17	3.245(12)
Ag3–Ag22	3.061(10)	Ag4–Ag15	3.140(12)	Ag4–Ag21#1	3.059(10)
Ag5–Ag12	3.307(11)	Ag5–Ag13	3.157(12)	Ag5–Ag22	3.123(10)
Ag6–Ag16	3.119(13)	Ag6–Ag23	3.102(10)	Ag6–Ag25	3.317(11)

Ag7–Ag8	3.177(12)	Ag7–Ag9	3.295(11)	Ag7–Ag21#1	3.142(10)
Ag8–Ag12#1	2.966(12)	Ag8–Ag18#1	3.063(9)	Ag9–Ag13#1	2.970(13)
Ag9–Ag18#1	3.346(10)	Ag9–Ag23	3.169(10)	Ag10–Ag2#1	3.348(12)
Ag10–Ag16	3.184(13)	Ag10–Ag20	3.105(10)	Ag11–Ag15	3.081(12)
Ag11–Ag23	3.109(10)	Ag12–Ag8#1	2.966(12)	Ag12–Ag18	3.377(10)
Ag12–Ag20	3.095(10)	Ag13–Ag9#1	2.970(13)	Ag13–Ag18	3.100(10)
Ag14–Ag17	3.008(13)	Ag14–Ag20	3.141(11)	Ag15–Ag19	3.046(10)
Ag15–Ag17	3.138(13)	Ag16–Ag24	3.371(11)	Ag17–Ag19	3.034(11)
Ag18–Ag8#1	3.063(9)	Ag18–Ag9#1	3.346(10)	Ag18–Ag20	2.986(9)
Ag18–Ag21	3.042(9)	Ag18–Ag22	3.070(9)	Ag18–Ag23#1	2.989(9)
Ag19–Ag20	3.008(9)	Ag19–Ag21#1	3.0327(9)	Ag19–Ag22	3.040(9)
Ag19–Ag23	3.009(9)	Ag21–Ag2#1	3.186(10)	Ag21–Ag4#1	3.059(10)
Ag21–Ag7#1	3.142(10)	Ag21–Ag19#1	3.032(9)	Ag22–Ag1#1	3.024(9)
Ag22–Ag25#1	3.144(9)	Ag23–Ag18#1	2.989(9)	Ag24–Ag2#1	2.980(11)
Ag24–Ag25	3.047(11)	Ag25–Ag22#1	3.144(9)		

Reference

[S1] Y.-L. Li, W.-M. Zhang, J. Wang, Y. Tian, Z.-Y. Wang, C.-X. Du, S.-Q. Zang and T. C. Mak, *Dalton Trans.*, 2018, **47**, 14884-14888.