A Comparative Study of $[Ag_{11}(^{i}PrS)_9(dppb)_3]^{2+}$ and $[Ag_{15}S(^{s}BuS)_{12}(dppb)_3]^{+}$: Templating effect on Structure and Photoluminescence

Yang-Lin Shen,‡[a] Pei Zhao,‡[b] Jun-Ling Jin,[c] Jun Han,[a] Chen Liu,[a] Zheng Liu,[a] Masahiro Ehara,[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]Research Center for Computational Science, Institute for Molecular Science, Okazaki 444-8585, Japan.

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

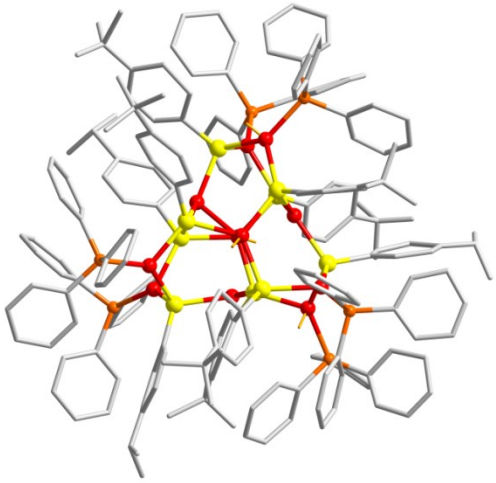

Figure S1. The overview structure of **Cu_{11}**. Color codes: Cu, red; S, yellow; C, grey; P, orange.[1]

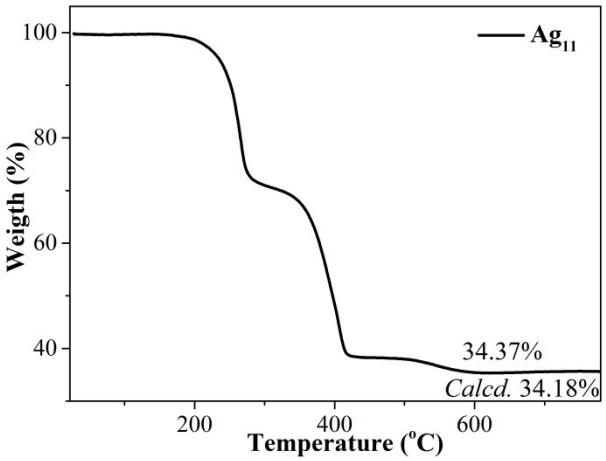

Figure S2. The TGA analysis of **Ag_{11}**.

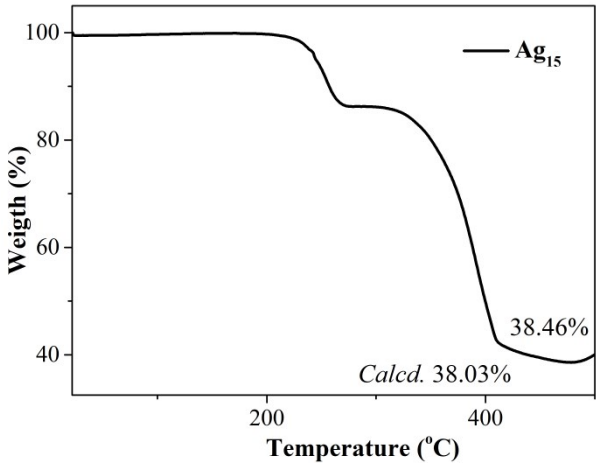

Figure S3. The TGA analysis of **Ag_{15}**.

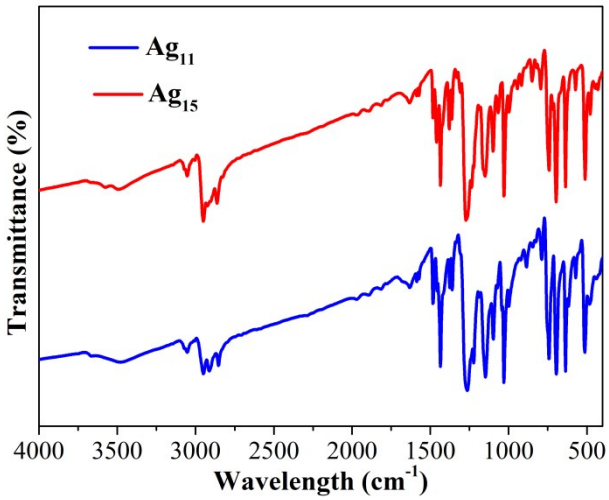

Figure S4. The IR spectra of **Ag_{11}** and **Ag_{15}**.

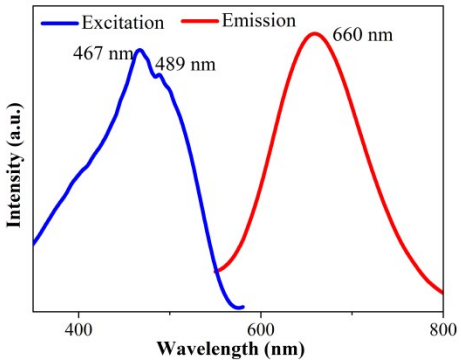

Figure S5. The PL spectra of **Ag_{11}** in solid state.

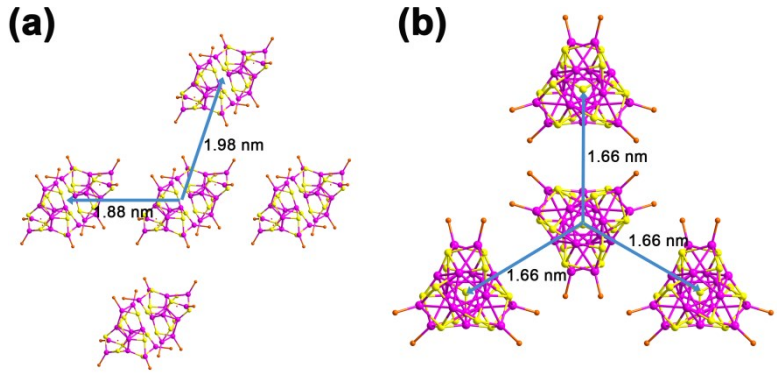

Figure S6. Packing patterns of cluster **Ag_{11}** (a) and **Ag_{15}** (b) viewing along c axis. The numbers refer to the distances between clusters. The alkyl groups are omitted for clarity. Color codes: Ag, purple; S, yellow; C, grey; P, orange.

Table S1. Crystal data and structure refinement for **Ag_{11}**	
Empirical formula	$Ag_{11}C_{114}H_{147}O_7F_6P_6S_{11}$
Formula weight	3468.36
Crystal system	Triclinic
Space group	P-1
a	18.842(12) Å
b	19.773(13) Å
c	21.523(13) Å
α	80.980(2)°
β	69.874(2)°
γ	70.541(2)°
Volume	7091.3(8) $Å^3$
Z	2

ρ_{calc}	1.626 Mg/m^3
Absorption coefficient	1.766 mm^{-1}
F(000)	3448
Crystal color and habit	yellow block
Theta range for data collection	2.578 to 30.508°
Index ranges	-25<=h<=26, -17<=k<=28, -30<=l<=30
Reflections collected	78739
Independent reflections	43199 [R(int) = 0.0175]
Observed reflections (I > 2sigma(I))	33826
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1252
R indices (all data)	R1 = 0.0563, wR2 = 0.1360
Largest diff. peak and hole	2.936 and -2.324 $e.Å^{-3}$
CCDC number	2040190

Table S2. Crystal data and structure refinement for **Ag_{15}**

Empirical formula	$Ag_{15}C_{133}H_{192}O_4F_3P_6S_{14}$
Formula weight	4164.56
Crystal system	Trigonal
Space group	P-31c
a	20.6961(19) Å
b	20.6961(19) Å
c	23.000(2) Å
α	90°
β	90°
γ	120°
Volume	8531.6(18) $Å^3$
Z	2
ρ_{calc}	1.621 Mg/m^3
Absorption coefficient	1.951 mm^{-1}
F(000)	4136
Crystal color and habit	brown bar
Theta range for data collection	2.439 to 26.481°
Index ranges	-25<=h<=12, 0<=k<=25, 0<=l<=28
Reflections collected	23275
Independent reflections	23275 [R(int) = 0.0347]
Observed reflections (I > 2sigma(I))	11841
Goodness-of-fit on F^2	0.984
Final R indices [I>2sigma(I)]	R1 = 0.1021, wR2 = 0.2427
R indices (all data)	R1 = 0.1845, wR2 = 0.2882
Largest diff. peak and hole	1.131 and -0.986 $e.Å^{-3}$
CCDC number	2040192

Table S3. Selected bond list of **Ag_{11}**			
g(1)-S(2)	2.4780(2)	Ag(1)-S(5)	2.4900(2)
Ag(1)-S(3)	2.5157(19)	Ag(2)-S(2)	2.4930(19)
Ag(2)-S(1)	2.5260(2)	Ag(3)-S(9)	2.4716(18)
Ag(3)-S(6)	2.5045(18)	Ag(3)-S(2)	2.5210(2)
Ag(4)-S(1)	2.4905(18)	Ag(4)-S(3)	2.5022(19)
Ag(4)-S(8)	2.5491(18)	Ag(5)-S(8)	2.4744(19)
Ag(5)-S(7)	2.5045(18)	Ag(5)-S(9)	2.5151(18)
Ag(6)-S(4)	2.5380(2)	Ag(7)-S(3)	2.5083(18)
Ag(7)-S(4)	2.5530(2)	Ag(8)-S(7)	2.5084(18)
Ag(8)-S(6)	2.5278(17)	Ag(9)-S(5)	2.4966(18)
Ag(9)-S(6)	2.5330(18)	Ag(10)-S(9)	2.5061(18)
Ag(10)-S(1)	2.5672(18)	Ag(11)-S(5)	2.4650(18)
Ag(11)-S(4)	2.5259(19)	Ag(11)-S(7)	2.5275(18)
Ag(1)-Ag(4)	3.0587(8)	Ag(1)-Ag(3)	3.1278(9)
Ag(1)-Ag(11)	3.2710(8)	Ag(2)-Ag(10)	3.1193(8)
Ag(3)-Ag(10)	3.0459(8)	Ag(3)-Ag(5)	3.1992(8)
Ag(4)-Ag(5)	2.9914(8)	Ag(5)-Ag(11)	3.0874(8)
Ag(8)-Ag(11)	3.2757(8)		

Table S4. Selected bond list of **Ag_{15}**			
Ag(1)-S(2)	2.4615(17)	Ag(1)-S(2)#1	2.4835(16)
Ag(1)-S(4)#2	2.7510(2)	Ag(2)-S(4)	2.3445(19)
Ag(2)-S(4)#4	2.3445(19)	Ag(5)-S(4)	2.5640(3)
Ag(5)-S(2)	2.6458(19)	Ag(5)-S(4)#2	2.8620(2)
S(2)-Ag(1)#3	2.4835(16)	S(4)-Ag(1)#2	2.7510(2)
S(4)-Ag(5)#2	2.8620(2)		
Ag(1)-Ag(1)#1	3.0961(10)	Ag(1)-Ag(1)#3	3.0961(10)
Ag(1)-Ag(5)	3.1115(7)	Ag(1)-Ag(2)#1	3.1952(8)
Ag(2)-Ag(1)#2	3.1953(8)	Ag(2)-Ag(1)#3	3.1953(8)
A(2A)-A(2A)#3	3.115(8)	A(2A)-A(2A)#1	3.115(8)

Reference

1 H. Li, H. Zhai, C. Zhou, Y. Song, F. Ke, W. W. Xu and M. Zhu, *J. Phys. Chem. Lett*. 2020, **11**, 4891−4896.