

**A robust wave-like silver-thiolate chain based metal-organic
network: synthesis, structure and luminescence**

Jie Wang, Yan-Ling Li, Zhao-Yang Wang,* and Shuang-Quan Zang*

*College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001,
China.*

E-mail: zangsqzg@zzu.edu.cn

wangzy@zzu.edu.cn

Experiment details

Materials: The precursor ^tBuSAg was prepared from the reaction of equivalent amounts of Ag₂O and ^tBuSH in Et₃N. The ligand (DPBZ-NH₂) was synthesized according to the literature method.¹ All other reagents were purchased from commercial sources and used without further purification.

Synthesis of {[Ag₅(^tBuS)₄(CF₃COO)(DPBZ-NH₂)_{1/2}]_n} (1). CF₃COOAg was slowly added to a suspension of ^tBuSAg (0.02 g, 0.10 mmol) in a mixture of ethanol/acetonitrile (1:1, 4 mL) until the solution became clear. CF₃COOH (10 μL, 0.135 mmol) and 1,4-Bis(4-pyridyl)aniline (DPBZ-NH₂) (0.010 g, 0.04 mmol) were sequentially added under stirring over 10 min at room temperature. The resulting yellow solution was allowed to evaporate slowly in the dark at room temperature for a week to give strip yellow crystals of **1**. Yield: ca. 35%. Elemental analysis Calc.(%) for Ag₅C₂₆H₄₂N_{1.5}O₂F₃S₄: C 14.17, H 2.68, N 2.32, S 11.23; Found: C 14.12, H 2.71, N 2.38, S 11.27.

Physical Measurements. ¹H NMR was carried out on a Bruker 400 spectrometer. Elemental Analysis (EA) was carried out at on a FLASH EA 112 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm⁻¹ on a Nicolet NEXUS 470-FTIR spectrometer. Thermogravimetric (TG) analyses were performed on a SDT 2960 thermal analyzer from room temperature to 350 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Powder X-ray diffraction (PXRD) data for **1** was collected on a Rigaku D/Max-2500PC diffractometer with Cu-Kα radiation (λ = 1.5418 Å) over the 2θ range of 3–50° at room temperature. UV-visible absorption spectra were recorded using a Hitachi UH4150 UV-visible spectrophotometer in the range 240-800 nm. Luminescence lifetime was measured on an Edinburgh FLS980 fluorescence spectrometer equipped with a 330 nm-laser, operating in time-correlated single photon counting mode (TCSPC) with a resolution time of 200 ps.

Crystallographic studies. Single-crystal X-ray diffraction data for **1** was performed on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ = 1.54184 Å) at 150 K. The intensities were corrected for absorption using empirical method implemented in SCALE3 ABSPACK scaling algorithm.² Data collection and reduction were performed using the program CrysAlisPro.³ The

structure of **1** was solved with direct methods (*SHELXS-2015*)⁴ and refined by full-matrix least squares on F^2 using *OLEX2*,⁵ which utilizes the *SHELXL-2015* module.⁶ All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included on idealized positions. The crystallographic data and selected bond distances and angles are listed in Supplementary **Table S1** and **Table S2**.

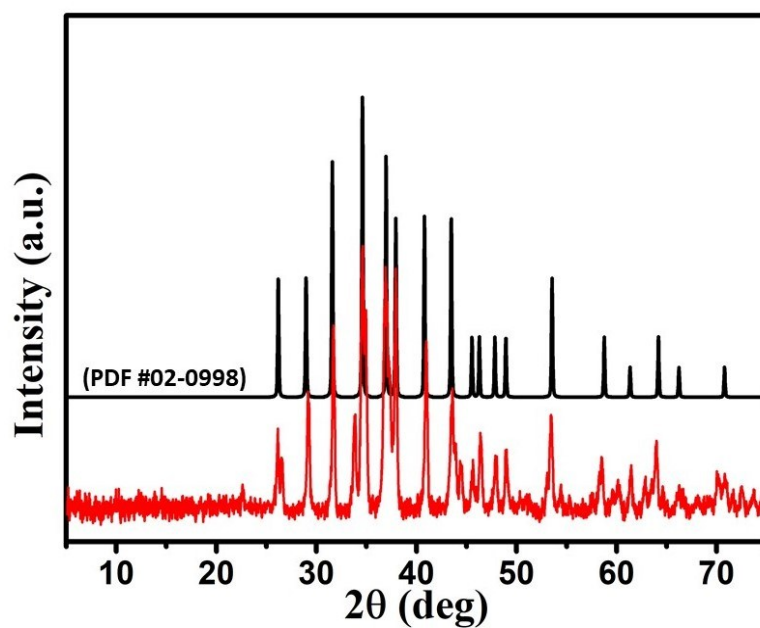


Figure S1 PXRD pattern of the final residue of **1** after TG analysis (red line) and Ag_2S (black line).

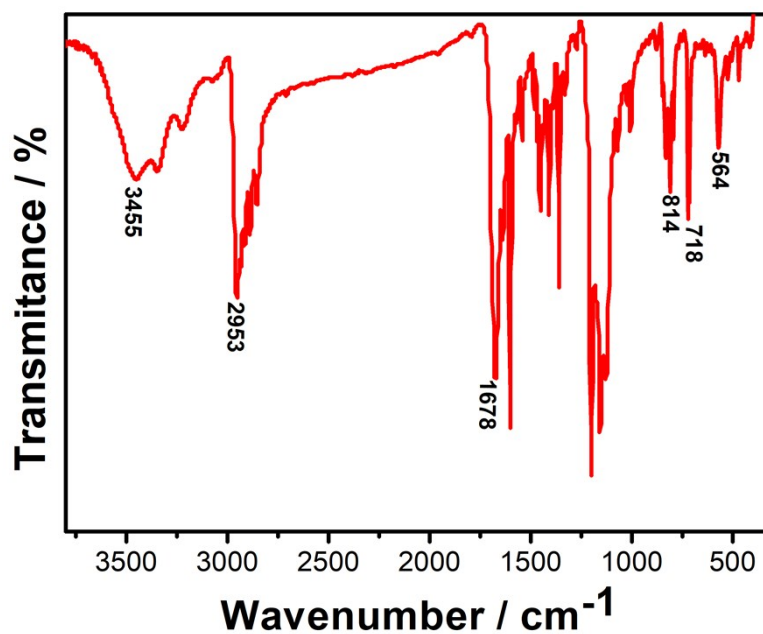


Figure S2 Fourier transform infrared spectrum of **1**.

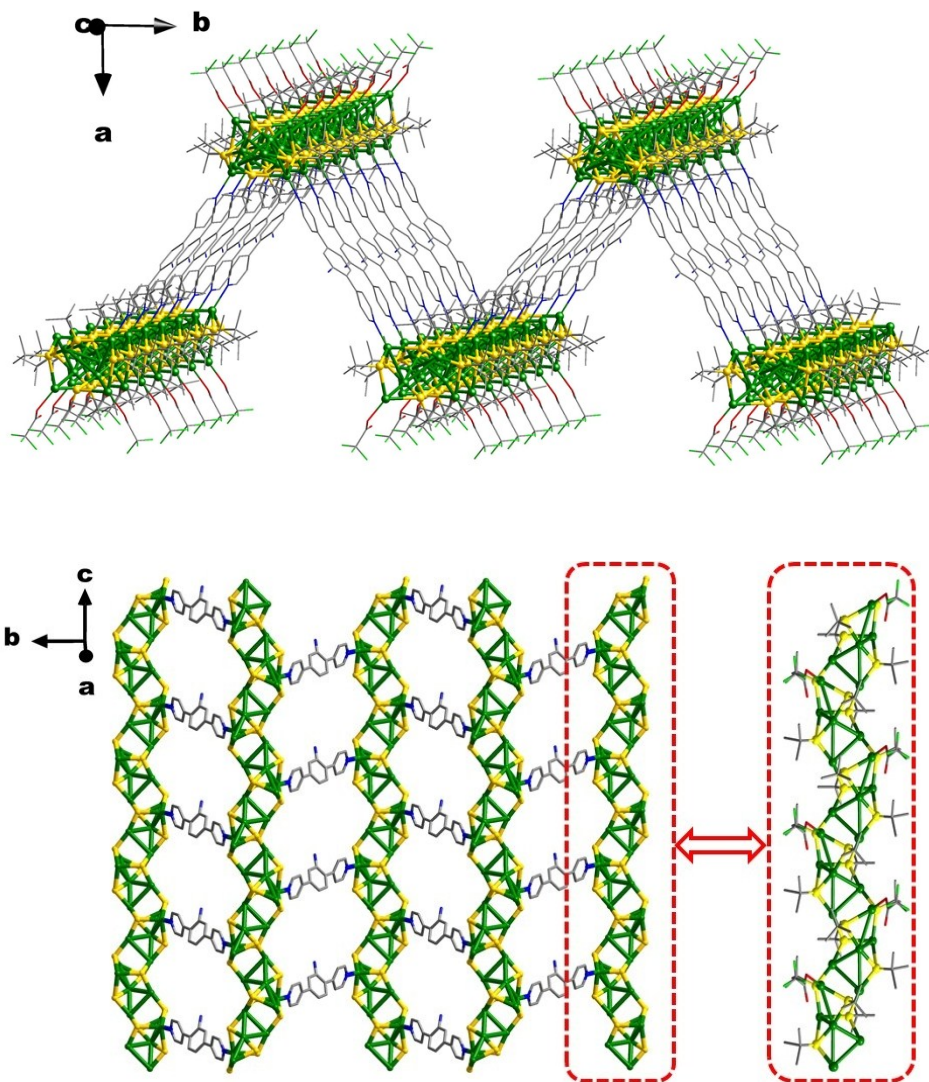


Figure S3 Side (top) and top (bottom) view of the 2D network in **1** ($t\text{BuS}^-$ and CF_3COO^- are omitted for clarity).

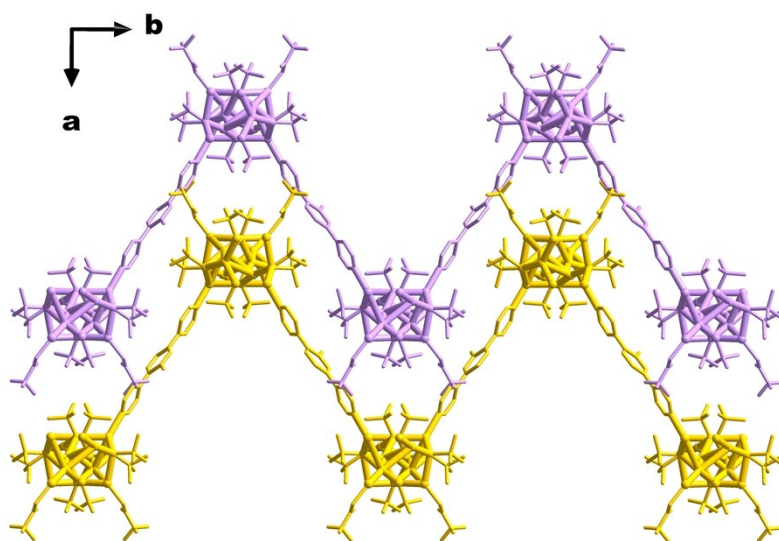


Figure S4 Stacking of the 2D network structure of complex **1** viewed along the c -axis.

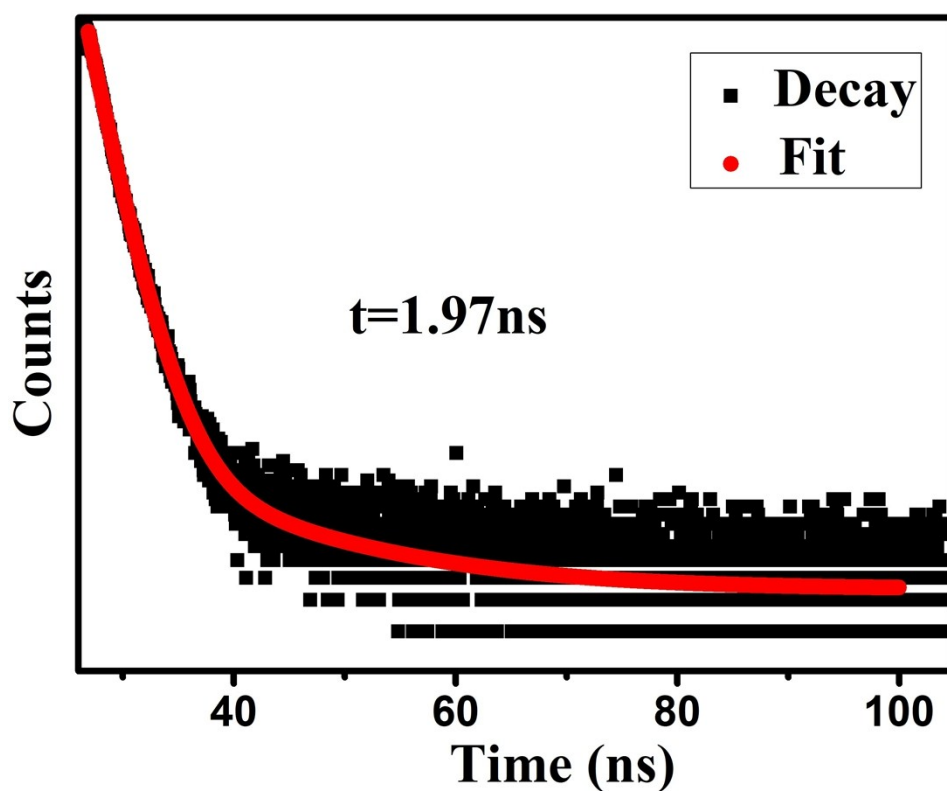
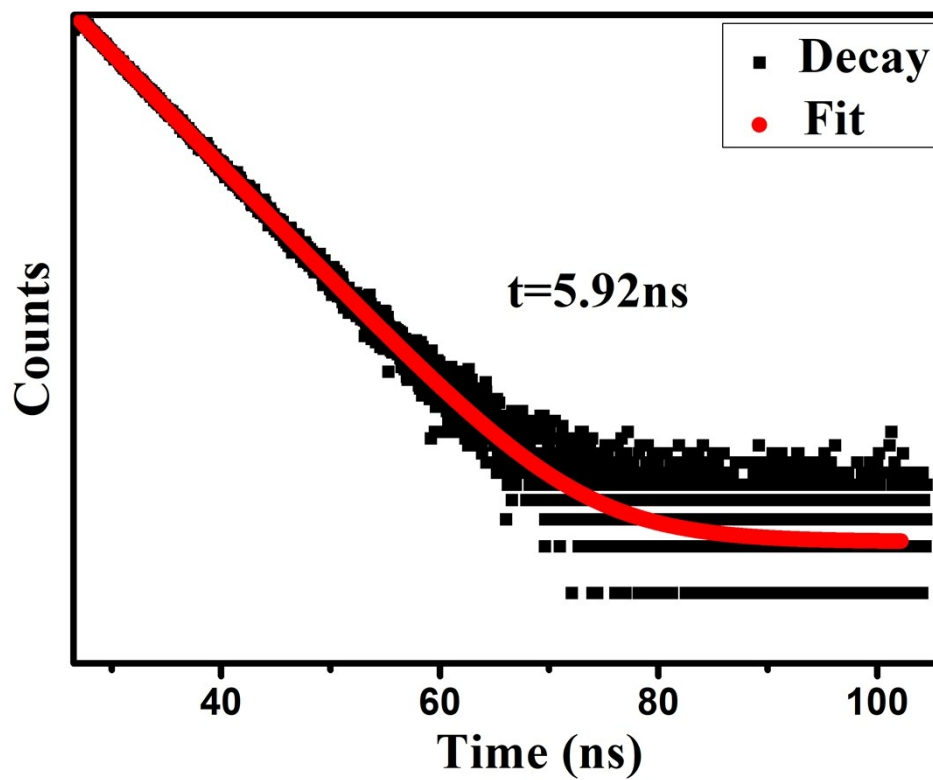


Figure S5 The decay time at room temperature for **1** (top) and DBPZ-NH₂ (below).

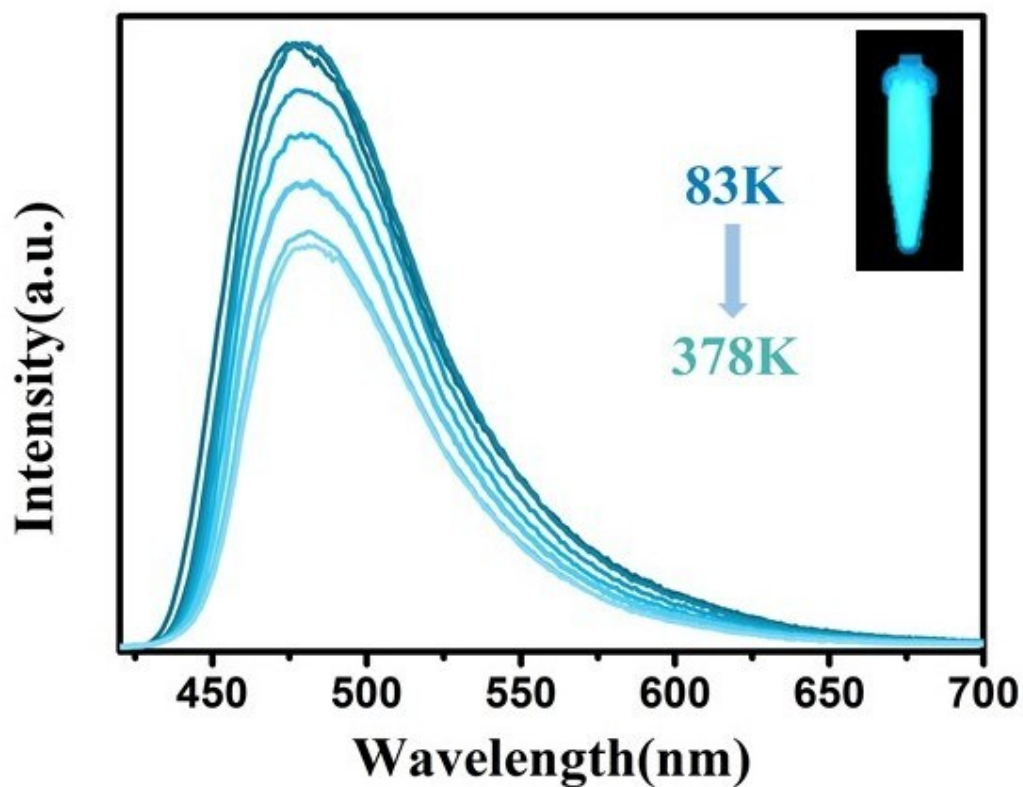


Figure S6 The temperature-dependent fluorescence spectra of **1** under 376 nm excitation. Inset: the photograph of **1** irradiated with 365 nm UV light at the temperature.

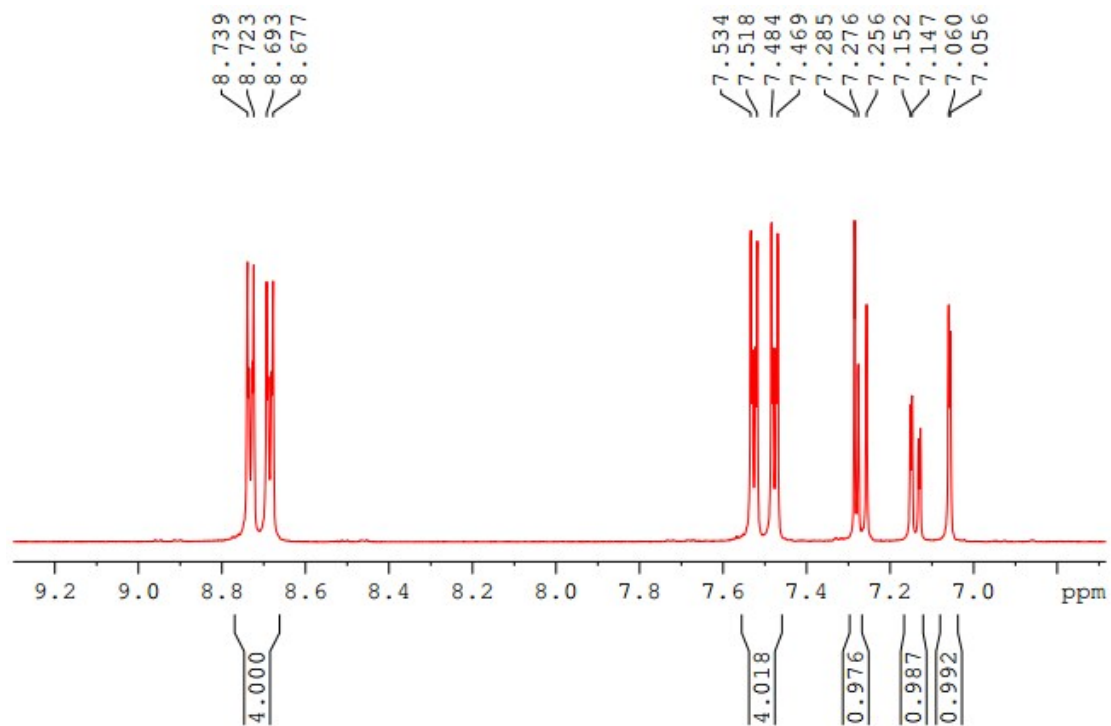


Figure S7 The $^1\text{H-NMR}$ spectrum of the DBPZ-NH_2 .

X-ray crystallography

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

Complex 1	
CCDC number	1880187
Empirical formula	C ₂₆ H ₄₂ Ag ₅ F ₃ N _{1.5} O ₂ S ₄
Formula weight	1132.20
Temperature / K	150.00(10)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.28107(12)
<i>b</i> (Å)	25.8112(3)
<i>c</i> (Å)	11.74661(12)
α (°)	90
β (°)	102.7277(10)
γ (°)	90
Volume (Å ³)	3632.06(6)
Z	4
ρ_{calc} g/cm ³	2.071
μ /mm ⁻¹	23.745
F(000)	2202.0
Crystal size/mm ³	0.171 × 0.136 × 0.109
Radiation	CuK α (λ = 1.54184)
2 θ range for data	6.85 to 134.16
Index ranges	-14 ≤ <i>h</i> ≤ 13, -30 ≤ <i>k</i> ≤ 11, -10 ≤ <i>l</i> ≤ 14
Reflections collected	16453
Independent reflections	6429 [R _{int} = 0.0242, R _{sigma} = 0.0272]
Data/restraints/parameters	6429/161/483
Goodness-of-fit on F ²	1.047
Final R indexes [<i>l</i> ≥ 2 σ (<i>l</i>)]	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.1369
Final R indexes [all data]	<i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.1389
Largest diff. peak/hole / e Å ⁻³	2.15/-2.58

$$R_1 = \frac{\sum \max(0, |F_o| - |F_c|)}{\sum |F_o|}, \quad wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S2 Selected bond distances (Å) for **1**

Complex 1			
Ag1-S4	2.149(4)	Ag4-S2	2.4477(19)
Ag1-S3 ¹	2.342(3)	Ag4-S4 ²	2.488(2)
Ag1-Ag2	2.742(2)	Ag4-S1 ²	2.5377(18)
Ag1A-O1	2.153(11)	Ag4A-S2	2.2231(15)
Ag1A-S3 ¹	2.566(2)	Ag4A-S1 ²	2.262(14)
Ag1A-S4	2.697(4)	Ag5-N1	2.301(6)
Ag1A-Ag2	3.2109(16)	Ag5-S3 ¹	2.5298(18)
Ag2-S2	2.352(2)	Ag5-S1	2.5742(18)
Ag2-S4	2.354(3)	Ag5-S2	2.7916(19)
Ag2-Ag4	3.1397(10)	S1-Ag4A ¹	2.262(14)
Ag2-Ag5	3.1602(8)	S1-Ag4 ¹	2.5377(18)
Ag2-Ag3	3.1837(8)	S3-Ag1 ²	2.342(3)
Ag2-Ag4A	3.293(15)	S3-Ag5 ²	2.5298(18)
Ag3-S3	2.3762 (17)	S3-Ag1A ²	2.566(2)
Ag3-S1	2.3776(16)	S4-Ag4 ¹	2.488(2)
Ag3-Ag4A	3.200(15)		

Symmetry codes: ¹+x, 1/2-y, -1/2+z; ²+x, 1/2-y, -1/2+z; ³-1-x, 1-y, 1-z

References

1. X. G. Guo, Z. Y. Zhang, S. Qiu, X. Su, Y. B. Wang, and X. Q. Sun, *Chem. Eur. J.*, 2017, **23**, 17727–17733.
2. SCALE3 ABSPACK in CrysAlis PRO.
3. CrysAlisPro 2012, Agilent Technologies. Version 1.171.36.31.
4. G. M. Sheldrick, *Acta Cryst. A* 2008, **64**, 112-122.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
6. A. L. Spek, *Acta Cryst. C* 2015, **71**, 9-18.