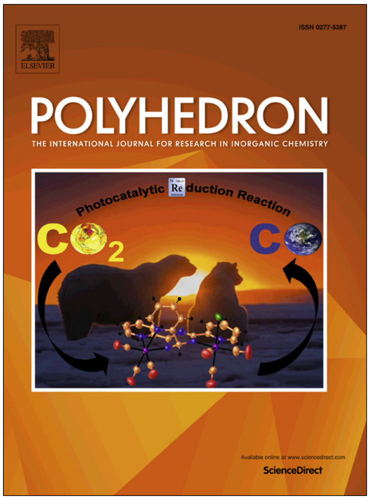

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A novel hexanuclear silver(I) complex with photoluminescence properties

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Abstract

A hexanuclear complex of d^{10}-d^{10} transition metal with organosulfur ligand, $Ag_6(py2t)_6$ (py2t = pyrazine-2-thiol), has been synthesized using diffusion methodology at room temperature. Crystal structure was revealed using single crystal X-Ray diffraction and data indicate that the complex synthesized containing Ag-Ag bonds in the silver cluster. The density function theory (DFT) calculation was performed to investigate the molecular orbital and photoluminescence potential. The photoluminescence properties of the complex have been further investigated, and a favorable fluorescence property was observed from the complex.

Key Words: Silver complex, Ag-Ag interaction, DFT calculation, photoluminescence

Introduction

During the past decades, more and more attention has been paid to the construction of metal-organic complexes. One of the main reasons for the current interest in those complexes is their remarkable structural variations[1] and potential for many areas as luminescent materials,[2] and drug delivery[3]. Besides, such complexes can be applied to explain the active sites of some metalloproteins.[4, 5] Among the large numbers of works reporteds, luminescent transition-metal complexes are under substantial investigations due to their versatile metal-metal interactions, leading to different spectroscopic behaviors and emission energies.[6, 7] In fact, a rapid growth of interest has been shown in the development of luminescent materials based on d^{10} metal. Different from the noble and rare earth metals, d^{10} metals used in synthesizing the luminescent complexes are much more abundant and cheaper. d^{10} metals including copper(I), silver(I), gold(I), zinc(II), and cadmium(II) have been utilized in most research works and many complexes with attractive luminescence properties and potentials as novel luminescent materials have been synthesized.[8-11]

In this work, the synthesis of a silver complex with a pyrazine-2-thiol as a ligand was carried out. The system was chosen for several reasons. Among a wide range of ligands applied, electron-rich sulfur-containing ligands have superior ability of generating different novel structural motifs.[12] Therefore, a diversity of complex structure in can be achieved. The presence of sulfur in the silver clusters enhances the luminescence properties due to the electron transition between the metal ligand. In the meantime, the orbital energies of sulfur and silver are better matched and there will be greater delocalization of the spin electron density towards the bridging atoms.[13, 14] The chemistry of silver-sulfur complex has attracted significant attention due to the ability to adopt geometries of variable nuclearity and great structural complexity.

S. Natarajan and co-workers[15] reported several new inorganic coordination polymers using $Ag_6S_6N_6$ core as metalloligands through a sequential crystallization. In the work of Singh,[16] new homoleptic hexanuclear silver(I) was synthesized and characterized. Although many silver complexes of silver(I) mono- and multinuclear complexes have been studied,[17] little research has been reported on the polymeric neutral silver(I) complexes with pyrazine-2-thiol as a ligand. The three-dimensional strucutres of such complexes is barely seen due to the poor solubility and the difficulties in obtaining highly-diffracted single crystals.

In this investigation, the synthesis and properties of a hexanuclear silver complex with a pyrazine-2-thiol as a ligand is reported. The ligand is chosen due to rigid structure and rich coordination atoms. The density function theory (DFT) calculation was performed to investigate the molecular orbital. Further study of photoluminescence properties shows that the silver complex $Ag_6(py2t)_6$ (py2t = pyrazine-2-thiol) produces red emission at room temperature.

Experimental

Materials and instrumentation

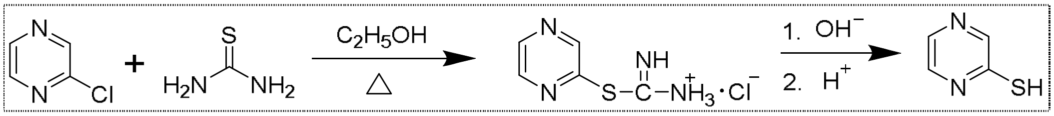
All chemicals were purchased from standard commercial sources and used as received. Solvents were reagent grade and used without further purification. All the synthesis in this work were carried out under autogenous pressure. The elemental analysis was performed on EA 3100 elemental analyzer. Raman spectrum was recorded from 100 to 1000 cm-1 with a Raman instrument. The phase purity and crystallinity of the product were checked by powder X-ray diffraction (PXRD) using a diffractiometer with Cu-K_α radiation. The fluorescence spectrum was measured with crystalline samples at room temperature using Fluoromax-4 (USA).

Computational Details

All the theoretical calculations were performed using the Gaussian 09 program.[18] The ground-state equilibrium geometries of the complex were fully optimized using the hybrid functional B3P86 and the LANL2DZ ECP basis set.

Synthesis of pyrazine-2-thiol (py2t)

A mixture of 2-chloropyrazine (28.6 g, 0.25 mol) and thiourea (19 g, 0.25 mol) were added into 200 mL ethanol. The mixture was refluxed for 3 h under vigorous stir in a 500 mL three-necked flask. After alcohol was removed by the evaporation, diluted sodium hydroxide solution (30 wt%, 300 g) was gradually added into the flask. The mixture was heated with reflux for another 5 hours and a large amount of ammonia was released. After cooled to ambient temperature, the pH of the solution was adjusted to 6.5 by adding quantitatively diluted hydrochloric acid. Extraction was carried out with dichloromethane. Dichloromethane layer was collected and washed with water for several times. Yellow powder was obtained through evaporation in 68% (*wt*) yield. The whole synthesis is illustrated in Scheme 1. The elemental analysis result for C_4HN_2S in mass %: C, 35.82; H, 2.25; N, 20.89. Experiment: C, 36.13; H, 2.01; N, 20.56.



Scheme 1. Preparation of pyrazine-2-thiol (py2t).

Preparation of $Ag_6(py2t)_6$

The yellow crystals of complex **$Ag_6(py2t)_6$** were prepared by diffusion method. $AgNO_3$ (34 mg, 0.2 mmol) and pyrazine-2-thiol (28 mg, 0.25 mmol) were mixed in a MeOH/MeCN solution (4:1, 5 mL) under vigorous stir in a radius flask. Triethylamine was added later. The mixture was stirred at 90 °C for 2 hours, and a yellow colored solution was obtained via filtration afterwards. The resulting solution was subjected to diffusion of anhydrous ether and crystals were generated after 7 days. The yellow crystals of the complex were collected and washed with MeCN and MeOH. The crystals obtained were stable in air, water and common organic solvents and the yield was 14%.

Crystal structure determination

Single crystals of the complex were carefully selected and separated. Crystal structure data were measured on an Agilent Super nova and a Bruker APEXII CCD diffractometer with Mo-Kα radiation source (λ = 0.71073 Å). The absorption corrections were employed by the program SADABS.[19] Structure was solved by direct method and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program.[20] The SQUEEZE procedure was applied to eliminate the disordered solvent molecules. The crystal structure was inspected through the Addsym subprogram of PLATON[21] to ensure that no attached symmetry should be used for the models. The topological analysis and graphs were generated by applying the TOPOS program. [22] The crystallographic data and refinement are summerized in Table 1.

Table 1 Crystallographic data of the $Ag_6(py2t)_6$

Empirical formula	$C_{24}H_{18}Ag_6N_{12}S_6$	F(000)	1248
Formula weight	1314.08	Crystal size / mm	0.1*0.1*0.2
Crystal system	Monoclinic	Temperature / K	293(2)
Space group	P21/c	θ range for date collection / (°)	3.10 to 28.53

a / Å	8.2259(2)	Limiting indices	-11≤h≤10, -29≤k≤26, -12≤l≤11
b / Å	22.3698(6)	Reflections collected / unique (Rint)	9763 / 3966 [R(int) = 0.0434]
c / Å	9.5415(3)	Goodness-of-fit on F 2	1.046
Volume / Å^3	1730.72(9)	Final R indices (I>2σ(I))	R_1= 0.0569, wR_2= 0.1607
γ / (°)	90	R indices (all dates)	R_1= 0.0919, wR_2= 0.1918
Z	2		
Absorption coefficient μ (Mo-Kα) / mu^{-1}	3.730		

$R_1 = \sum\left||F_o| - |F_c|\right| / |\sum o|$. $\omega R_2 = \{\sum[\omega(F_o^2 - F_c{}^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

Synthesis and Characterization

Ag(I) complex was obtained in good yield by the treatment of a solution of the ligand py2t and metal salt $AgNO_3$. The complex is air- and moisture-stable and insoluble in water, common organic solvents including alcohols, acetonitrile, acetone, DMSO and DMF. The Raman spectrum of the complex (Fig. S1) shows two bands at 750 cm^{-1} and 650 cm^{-1}, which can be assigned to the breathing vibration of the C-N ring. Phase purity of the complex was confirmed by comparison of the powder diffraction pattern (Fig. S2) with the data calculated from the single-crystal X-ray study, despite minor differences can be seen in the intensities and widths of some peaks.

Crystal Structure of [Ag_6(py2t)$_6$]

The exact structure of Ag_6(py2t)$_6$ was revealed by single crystal X-ray crystallography. The ORTEP diagram of $Ag_6(py2t)_6$ with 30% thermal ellipsoids and hydrogen atoms omitted for clarity is shown in Fig. 1. The selected bond distances and angles are given in the Table S1. Single-crystal analysis has revealed that the hexanuclear cluster $Ag_6(py2t)_6$ has six Ag centers bridged by the py2t ligands which exhibits as a distorted octahedron as shown in Fig. 2. As can be seen from the structure, each Ag(I) is bonded by two sulfur atoms and one nitrogen atom from three py2t ligands, yielding an approximately monoclinic geometry. Such three-coordinate metal center is not common for Ag(I), even though similar core structures have, been found with 2-mercaptobenzothiazole in hexanuclear Ag(I) complexes. With pyrazine-2-thiol in Ag(I) complex is much less frequent and has not been reported. The py2t molecule works as a μ_3-bridging ligand to link three Ag(I) ions. The nitrogen atom from the py2t molecule links to one Ag(I) ion and the axial μ_2-sulfur to two Ag(I) ions, forming one face of the octahedron and shortening the distances between Ag(I) ions.

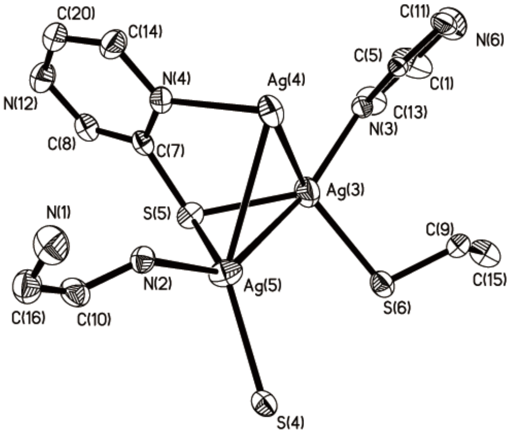


Fig. 1 An ORTEP view of the structure of complex with 30% thermal ellipsoids, hydrogen atoms omitted for clarity.

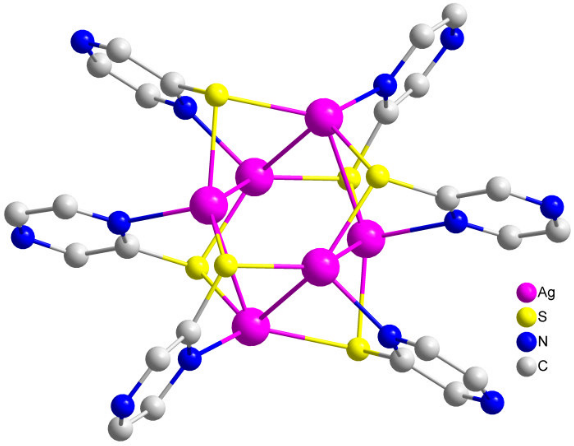


Fig. 2 The molecular structure of complex.

The Ag-S bond distances of complex $Ag_6(py2t)_6$ are within the range of 2.346(3) ~ 2.511(3) Å (Table S2), which are similar to those distances found in other silver complexes.[23-25] The Ag-N bond distances of complex $Ag_6(py2t)_6$ are in the range of 2.198(6) ~ 2.338(7) Å, which are in consistence with the reported complex $[\{Ag(SR)\}_6]$ (2.331(11) Å).[23, 26] The Ag···Ag distances in the $Ag_6(py2t)_6$ complex are in a wide range from 2.969 to 3.789 Å. The L(S, N)-Ag(3)-L(S, N) angles are in the range of 91.80(19) ~ 153.67(19)°. The Ag(4, 5)-Ag(3)-Ag(5, $5^{\#}$) angles are in the range of 62.13(3) ~ 82.66(3)°. All the bond lengths and angles are consistent with the similar complexes, such as $[Ag_2Cl_2(4\text{-pdtH})]$.[27]

In order to make the hexanuclear silver cluster more clear, the distorted octahedron consisting of six Ag(I) without other atoms is shown in Fig. 3. The Ag-Ag distances vary from 2.969 Å to 3.789 Å, and are mostly shorter than the sum of the Van der Waals radii of two Ag atoms (3.44 Å).The interaction of Ag-Ag might be best considered as weak interactions, since some of the values are very close to those presented in metallic silver (2.88 Å).[28] This indicates reasonable argentophilic (Ag···Ag) interactions, which have been observed in other related structures as well.[29, 30]

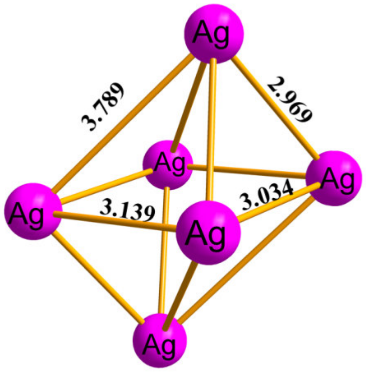


Fig. 3 Distorted octahedral Ag cluster formed by the hexanuclear cores in complex

When expanding the molecules to a bulk network in the b axis, it can be clearly observed in Fig. 4(a) that the stack of the $Ag_6(py2t)_6$ with Ag···S interaction and the weak π···π stack interaction produce a three-dimensional network structure. The distance between two adjacent aromatic ring centers and the distance between nitrogen atom and the adjacent aromatic ring were determined and considered to be the versatile Ag···S interaction and the aromatic ring π···π stack interaction, respectively. The weak Ag···S interaction between the adjacent complexes was further evaluated and a Ag···S distance of 3.1218 Å was found as shown in Fig. 4(b). In a word, the self-assembly of supramolecular networks of the complex is driven by the multiple intermolecular Ag···S interactions between Ag(I) centers and sulfur atom of ligands as well as the weak π···π interaction.

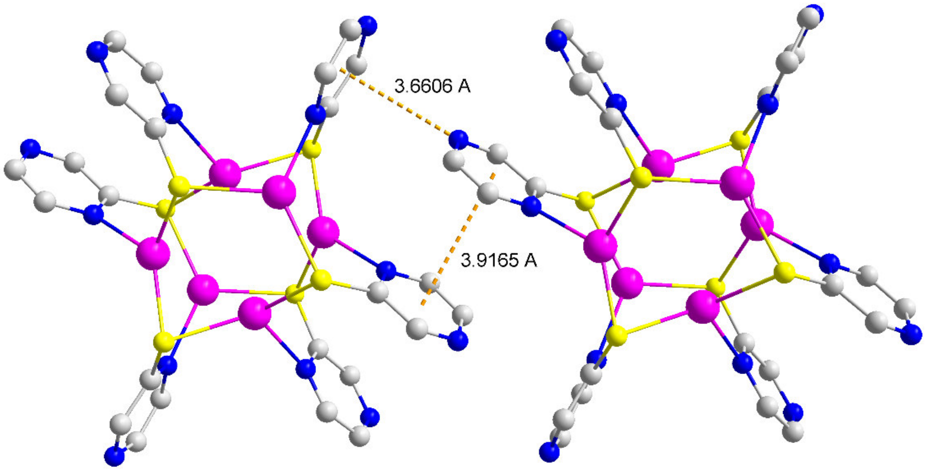


Fig. 4 (a) Two adjacent complexes showing the very weak π-π stack interaction.

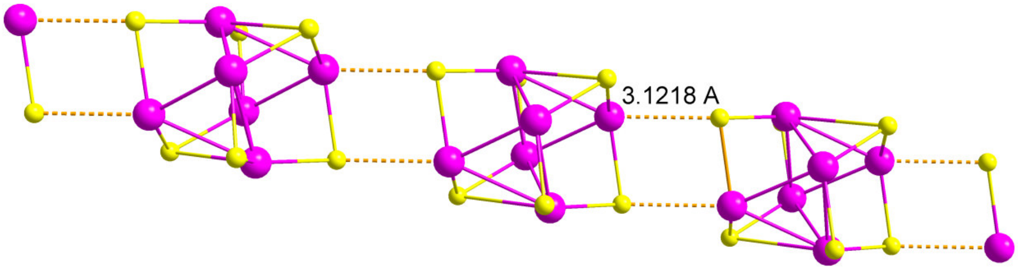


Fig. 4 (b) The Ag-S interaction of adjacent complexes.

As shown in Fig. 5, the formation of bulk structure may be a result from the weak π···π interactions between different one-dimensional chain structures. This may be considered as a new synthetic strategy of framework coordination in contrast with the existing methods, self-assembled with simple rigid linear ligands, and therefore may contribute to a better understanding of inorganic crystal design for predictable, multi-dimensional infinite networks of various topologies.

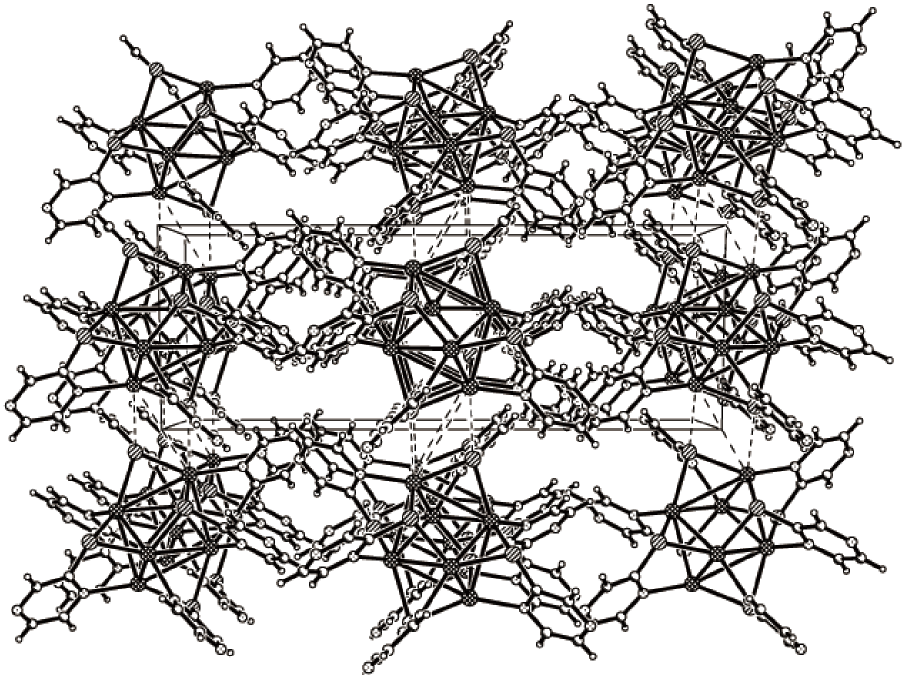


Fig. 5 View down the crystallographic b axis of CDHAB of the packing diagram

Theoretical studies

Density function theory (DFT) calculations were performed with the ground-state geometries adapted from the analytical processing X-ray data. Geometry was optimized using the B3P86 functional with two bases set: 3-21g for C, H, N, S atoms and LanL2DZ for Ag atom. According to the frontier molecular orbital theory, HOMO (the highest occupied molecular orbital) and its nearby occupied orbits can give priority to donor electron, while LUMO (the lowest unoccupied molecular orbital) and its nearby free orbits are easy to be the acceptor. The energy gap between these orbitals has significant influences on the activity of the compounds. Therefore, the relationships between the aforementioned orbits are very important because they are related to not only the charge transfer properties but also the photoluminescent properties of the complex.

As shown in Fig. 6, the LUMO mainly composed of s orbitals of Ag(I), while the HOMO mainly consists of p orbitals of ligand py2t as well as d orbitals of Ag^I. The photoluminescent properties of this complex are mainly due to the intramolecular electron transition. Therefore, when excited, the electron density has moved from Ag d orbitals together with py2t p orbitals to Ag s orbitals. It is assumed that the emission of $Ag_6(py2t)_6$ is a ligand to metal charge transfer.

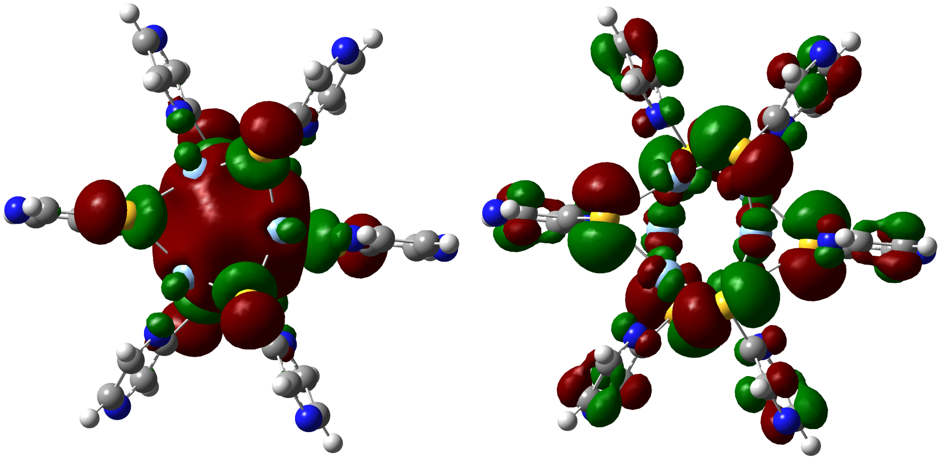


Fig. 6 Electron-density distribution of LUMO (left) and HOMO (right) frontier orbitals of the complex

Photoluminescent properties

For further evaluation on the solid-state photoluminescent properties of the complex, the fluorescence excitation and emission properties of $Ag_6(py2t)_6$ were investigated at room temperature. It is reported that only few of luminescence silver(I) compounds are luminescent at room temperature, while most of them exhibit such property at lower temperature.[31] Nevertheless, in this investigation, the red emission band with a maximum peak at 695 nm for complex $Ag_6(py2t)_6$ appeared clearly at room temperature. The excitation band with a peak at 372 nm, and a wide stokes shift 323 nm were observed. The fluorescence-emission of free ligand was investigated as well and no fluorescence emission peak of ligand was observed in all the experiments of excitation wavelength. The main reason of this property is ascribed to the chelation of nitrogen and sulphur atoms to the central metals and the increase of conjugation upon metal silver coordination.

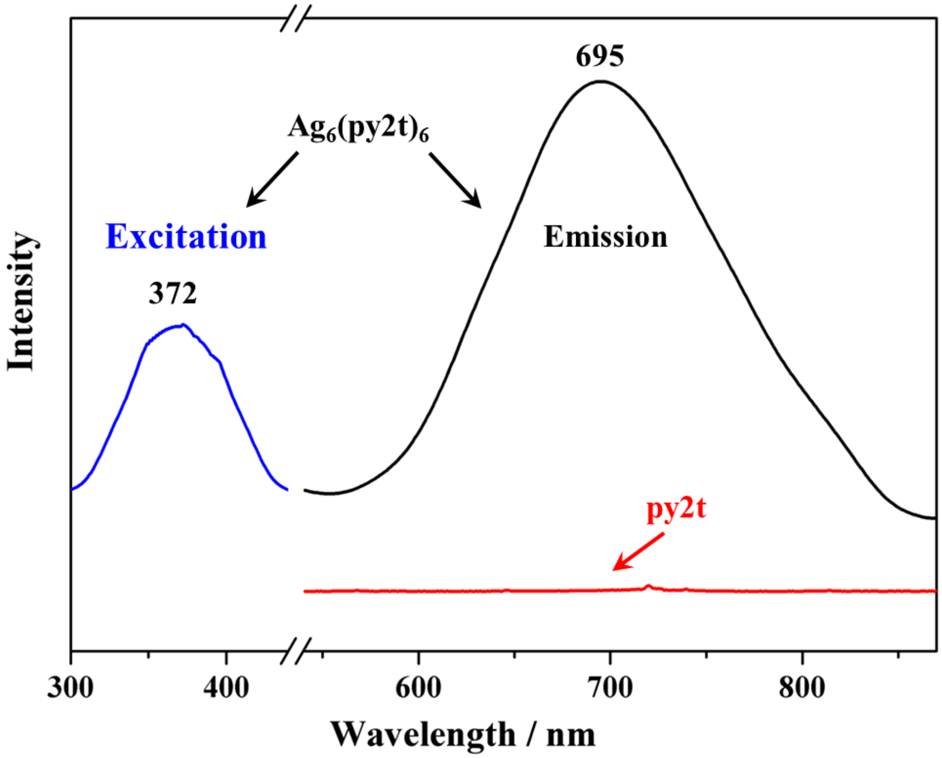


Fig. 7 Solid-state excitation and emission spectra for complex 1 at room temperature

Conclusion

In summary, a hexanuclear d^{10}-d^{10} transition metal complex $Ag_6(py2t)_6$ was synthesized with organosulfur ligands using diffusion method at ambient temperature. The exact structure was characterized by single crystal X-ray diffraction analysis. Meanwhile, the DFT calculation was used to characterize the electronic transition between HOMO and LUMO of $Ag_6(py2t)_6$. Photoluminescent property analysis reveals that the complex exhibits a strong fluorescence in the solid state at room temperature. The study provides a practical origin of photoluminescence materials. Based on the study above, further exploration of coinage metals and thiolate ligands is in progress.

Appendix A. Supplementary data

CCDC <1478950> contains the supplementary crystallographic data for < C24H18Ag6N12S6>. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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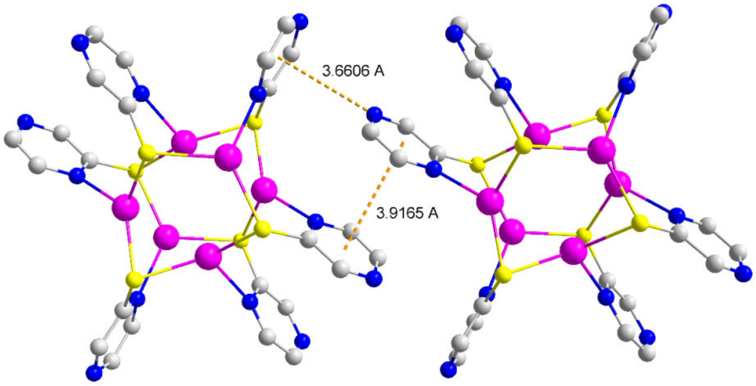
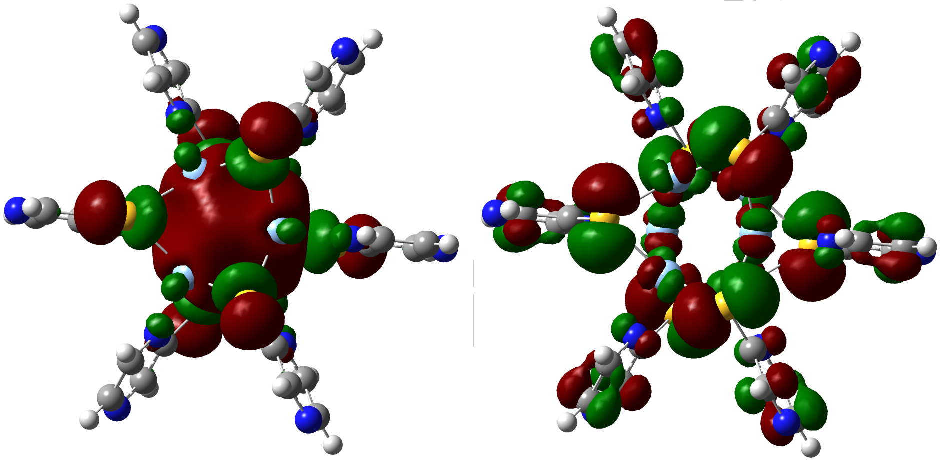


Two adjacent complexes showing the very weak π-π stack interaction.



Electron-density distribution of LUMO (left) and HOMO (right) frontier orbitals of complex

A hexanuclear complex of d^{10}-d^{10} transition metal with organosulfur ligand has been synthesized using diffusion methodology at room temperature. The DFT and photoluminescence properties of complex have been investigated, and a favorable fluorescence property was observed from the complex.