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Four new silver-based complexes constructed from 3-nitrophthalic acid and pyrazine-like ligands: syntheses, crystal structures and photodegradation activities

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Abstract. Four Ag-based coordination polymers, $Ag_4(H_2O)_2(npth)_2$ (1), $Ag_4(epyz)_2(npth)_2$ (2), $[Ag(pyz)(Hnpth)] \cdot H_2O$ (3) and $Ag(epyz)_{0.5}(Hnpth)$ (4) ($H_2npth = 3$ -nitrophthalic acid, pyz = pyrazine, epyz = 2,3,5,6-tetramethylpyrazine), have been synthesized by ultrasonic or hydrothermal reactions of Ag(I) salts with H_2npth and various pyrazine derivatives ligands. Compound 1 presents a 2D 4⁴-sql network with Ag_4 units, and compound 2 features novel cage-like Ag_8 SBUs (secondary building unit), which are linked by epyz ligands to form a 3D framework. Compound 3 shows a 1D chain and compound 4 exhibits a 2D coordination polymer construction. The photocatalytic properties for the degradation of organic dye molecules have been examined, and the experiments show that compound 3 has a good degradation effect to Rhodamine B.

Keywords: Silver(I); Ag. Ag interaction; Coordination polymers; Luminescence; Degradation

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1. Introduction

The rational design and construction of metal-organic coordination polymers is attracting considerable attention in the fields of crystal engineering and supramolecular chemistry [1], due to their enormous variety of intriguing structures, topological architectures and their potential applications in various fields, including gas storage [2], luminescence [3], magnetism [4], antitumor/antibacterial activity [5], degradation of organic pollutants [6] and so on. As we known, it is still a huge challenge to control the final structures of desired crystalline products, since many factors affect the self-assembly process, such as the solvent system, metal-ligand ratio [7], temperature, counter ions [8], pH, template and so on [9]. Hence, we can change those conditions to obtain coordination polymers with novel structures.

Among these polymers, Ag(I)-based coordination polymers have attracted great interest [10]. The silver(I) ion has a very flexible coordination sphere, the coordination numbers of Ag(I) ions can vary greatly from two to six, forming diverse Ag(I) aggregates, such as T-shaped [11], trigonal [12], trigonal bipyramidal, tetragonal [13], square pyramidal, octahedral and so on. On the other hand, Ag(I) ions tend to form silver-silver bonds, so-called argentophilicity [14], which play an important role in the construction of multi-nuclear silver clusters, and further form diverse structures and fascinating topologies. From a synthetic point of view, carboxylate ligands have been shown to be good building blocks in preparing coordination polymers with desired topologies [15]. In this paper, we chose 3-nitrophthalic acid (H₂npth) [14d,16] as the ligand, which contains two carboxylate groups and exhibits a great diversity of coordinate modes through complete or partial deprotonation. Besides, the carboxylate groups show a strong ability to act as hydrogen bonding acceptors and donors.

This results in it often being chosen as an important organic ligand. To date, a total of 12 complexes of Ag-H₂npth have been reported, exhibiting rich coordination modes (Scheme 1) [14c,14d,15,16a-16c]. On the basis of these articles, we hoped that we could design more novel multinuclear silver architectural complexes. Moreover, according to the HSAB (hard soft acid-base) concept [17], the silver(I) ion can be classified as a soft acid, which can coordinate to soft bases, such as ligands containing N donor ligands. Therefore, pyrazine and its derivatives can be a kind of excellent organic ligand, which has attracted great interest in the construction of coordination polymers [18].

On the basis of the above consideration, In this paper, the self-assembly of Ag(I) ions with H₂npth and pyrazine-like ligands is reported and four coordination polymers, Ag₄(H₂O)₂(npth)₂ (**1**), Ag₄(epyz)₂(npth)₂ (**2**), [Ag(pyz)(Hnpth)]·H₂O (**3**) and Ag(epyz)_{0.5}(Hnpth) (**4**), have been synthesized using different pyrazine derivatives and synthesis conditions. What is more, the luminescence properties of complexes **1-4** are also presented. Compound **3** display photocatalytic properties in the degradation of organic dyes under UV and simulated daylight irradiation.

2. Experimental

2.1. *Materials*. All chemicals of reagent grade were commercially available and used without further purification.

2.2. Physical Methods. Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity. The C, N and H micro analyses were performed with a Perkin Elmer 2400II elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400cm⁻¹ on a Shimadzu FTIR–8900

spectrometer. Thermogravimetric measurement was performed under a flow of nitrogen gas from room temperature to 900 °C at a heating rate of 10 °C/min using a Seiko Exstar 6000 TG/DTA 6300 apparatus. Single crystal X-ray diffraction data were collected by a Rigaku R-Axis Rapid X-ray diffractometer. Photoluminescence properties were investigated in the solid state at room temperature with an F-7000 FL spectrophotometer. Photocatalytic tests were performed with a Bilon BL-GHX-V photochemical reaction instrument.

2.3. Synthesis of the complexes

2.3.1. Synthesis of complex 1

A mixture of AgNO₃ (33.4 mg, 0.2 mmol), pyrazine (pyz) (16.0 mg, 0.2 mmol) and 3-nitrophthalic acid (H₂npth) (42.2 mg, 0.2 mmol) were dissolved in methanol-H₂O-DMF (N,N-dimethylformamide) solvents (6 ml, v/v/v = 1:1:1) in the presence of ammonia (0.5 mL, 14 M) under ultrasonic treatment (160 W, 40 kHz, 30 min) at 40 °C. The resultant colorless solution was allowed to evaporate slowly at room temperature in the dark. Colorless crystals of compound **1** were obtained after several days. The crystals were isolated by filtration, washed with deionized water and dried in air. Yield based on silver is 58.71%. Elemental analysis, anal. calc. (found) for $Ag_4C_{16}H_{10}N_4O_{14}$: C, 21.64 (21.67); H, 1.14 (1.12); N, 3.20 (3.16) %. IR (KBr, cm⁻¹): 3355 (m), 3099 (w), 1591 (vs), 1519 (m), 1461 (m), 1399 (s), 1343 (m), 1157 (w), 924 (w), 826 (w), 753 (m), 717 (m).

2.3.2. Synthesis of complex 2

The synthesis of **2** was similar to that of **1**, but with 2,3,5,6-tetramethylpyrazine(epyz) (27.2 mg, 0.2 mmol) in place of pyz. The resultant solution was allowed to evaporate slowly in the dark at room temperature for several days to give colorless crystals of **2**. Yield based on

silver is 68.87%. Elemental analysis, anal. calc. (found) for Ag₄C₃₂H₂₉N₆O₁₂: C, 34.19 (34.26); H, 2.54 (2.58); N, 7.51 (7.49) %. IR (KBr, cm⁻¹): 3361 (m), 3097 (w), 2943 (w), 2861 (w), 1643 (m), 1596 (vs), 1534 (s), 1460 (m), 1405 (s), 1343 (s), 1161 (w), 924 (w), 760 (m), 717 (m).

2.3.3. Synthesis of complex 3

A mixture of AgNO₃ (33.4 mg, 0.2 mmol), H₂npth (42.2 mg, 0.2 mmol), pyz (16 mg, 0.2 mmol) and H₂O (10 mL) was stirred for a few minutes, then sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 100 °C for 72 h. After cooling to room temperature, pale yellow crystals were obtained in a yield of 51.91% based on Ag. Elemental analysis, anal. calc. (found) for AgC₁₂H₁₀N₃O₇: C, 34.63 (34.61); H, 2.41 (2.40); N, 10.09 (10.10) %. IR (KBr, cm⁻¹): 3443 (w), 3092 (w), 1720 (m), 1653 (s), 1630 (m), 1540 (vs), 1384 (s), 1348 (vs), 1151 (m), 784 (m), 707 (m).

2.3.4. Synthesis of complex 4

The synthesis of **4** was similar to that of **3**, but with epyz (27.2 mg, 0.2 mmol) in place of pyz. After cooling to room temperature, pale yellow crystals were obtained. Yield based on silver is 62.03%. Elemental analysis, anal. calc. (found) for $AgC_{12}H_{10}N_2O_6$: C, 37.28 (37.30); H, 2.59 (2.60); N, 7.25 (7.25) %. IR (KBr, cm⁻¹): 3430 (m), 3069 (w), 2924 (w), 2852 (w), 1685 (s), 1556 (m), 1534 (vs), 1419 (m), 1353 (s), 1274 (m), 921 (w), 806 (m), 703 (m).

2.4. X-ray crystallography

Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibers, which were then mounted on a Rigaku R-Axis Rapid diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) for cell

determination and subsequent data collection. The reflection intensities in the suitable θ ranges were collected at 293 K using the scan technique. The employed single crystals exhibit no detectable decay during the data collection. The data were corrected for Lp and absorption effects. The direct method employing SHELXS-97 [19] gave the initial positions for some non-hydrogen atoms, and the subsequent difference Fourier syntheses using SHELXL-97 [20] program resulted in the initial positions for the remaining non-hydrogen atoms. The hydrogen atoms on the organic ligands were geometrically generated, while the remaining hydrogen atoms were located from successive difference Fourier syntheses. Finally, the full-matrix least-squares technique was applied for refinement of positions and anisotropic displacement parameters of all the non-hydrogen atoms, and positions of the hydrogens were refined using a riding mode by fixing the initial distances to the associated heavier atoms with isotropic displacement parameters set to 1.5 times the values of the associated atoms. The crystal structure of 2 contains solvent-accessible voids of 875 Å, but showed no residual electron density in the voids. This might indicate that the crystal lost its solvent of crystallization without collapse of the structure. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Tables S1-S4.

2.5 Photocatalytic activity measurements

The photocatalytic activities of the as-prepared samples were evaluated by the degradation of Rhodamine B (RhB), Methyl orange (MO) and Methylene blue (MB) under different light sources: (1) UV light using a 300W Hg lamp, (2) visible light irradiation using a 300 W Xe lamp. 50 mg of the compounds was mixed together with 50 mL of 10 mg/L RhB

solution in a quartz beaker, then magnetically stirred in the dark for about 30 min to ensure the establishment of an adsorption/desorption equilibrium. After that, the mixtures were stirred and continuously exposed to light irradiation from different lamphouses. 5 ml of the sample were continually taken from the reaction beaker and collected by centrifugation with 30 min or 1 h intervals during the irradiation. The suspensions were centrifuged with a HC-3518 high speed centrifuge at 9000 rpm for 5 min to remove the compound, which was then analyzed using a Shimadzu UV-vis 2501PC recording spectrophotometer.

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3. Results and discussion

3.1. Description of the ccrystal structures

3.1.1. Structure of complex 1

X-ray crystallography of **1** revealed that it crystallizes in the space group $P2_1/c$. In the asymmetric unit, four crystallographically independent Ag(I) ions, two npth ligands (that containing the O1 atom is named npth1 and that containing the O7 atom is named npth2) and two coordinated water molecules were identified. The coordination environments of **1** are depicted in Fig. 1a, where all the Ag1, Ag2, Ag3, and Ag4 atoms are located in a distorted T-shaped geometry. The coordination environments of the Ag1 and Ag3 atoms are completed by three O atoms belonging to two different npth ligands and one H₂O molecule, and that of the Ag2 and Ag4 atoms are completed by three O atoms are completed by three O atoms from three different npth ligands. The Ag–O bond lengths fall in the range 2.116(4)-2.618(3) Å. The largest bond angles around the Ag1, Ag2, Ag3 and Ag4 atoms are 167.90(17), 168.25(13), 168.25(18) and 167.99(13) °. Each npth ligand adopts the same bridging mode to link five silver atoms in the $\mu_5-\eta^2:\eta^1:\eta^1:\eta^1$

2-position carboxylate groups links to two metal atoms in a $\mu_3\eta^2$ bridging/mondentate bridging fashion.

The O1 atom of the 1-position carboxylate group in npth1 and the O7 atom from the 2-position of carboxylate in npth2 are coordinated with the Ag1 atom, in addition the O4 atom from the 2-position carboxyl group in npth1 and the O9 atom of the 1-position carboxylate group in npth2 are coordinated with Ag3, which together form the 14-membered ring unit. Notably, the carboxylate oxygen atom O10 of the resultant 14-membered rings unit are coordinate to the Ag4 atom, extending into a 1D chain along the *b* axis (Ag4–O8^{#6} = 2.162(4) Ag4–O10 = 2.190(4) Ag4–O4^{#6} = 2.618(3) Å). The 1D chains are assembled into a 2D sheet parallel to *ab* plane via coordination of distorted T-shaped geometry Ag2 atoms, as observed in Fig. 1b (Ag2–O2^{#2} = 2.195(3), Ag2–O3 = 2.162(4) and Ag2–O7 = 2.610(4) Å). The resulting sheets are held together by interlayer hydrogen bonds between the carbon atoms of npth ligands and aqua ligands, leading to a 3D supramolecular architecture (C14–H14A···O12^{#7} = 3.335 Å), as described in Table S1.

There are five kinds of Ag···Ag interactions in complex **1** that form the Ag₄ unit $[Ag1-Ag2^{#3} = 2.967(1) Ag1-Ag4^{#4} = 3.332(1) Ag2-Ag3^{#3} = 3.355(1) Ag3-Ag4 = 2.962(1)$ and Ag4-Ag2^{#2} = 3.271(1) Å]. The distances of the Ag···Ag interactions are between 2.962(1) and 3.355(1) Å, which are shorter than twice the van der Waals radius of silver ions (3.44 Å), indicating the presence of argentophilic interactions. All the npth ligands adopt the $\mu_5-\eta^2:\eta^1:\eta^1:\eta^1$ bridging mode to link rhombic Ag₄ units, giving a 2D network. To better understand the structure of **1**, topological analysis was used. According to Wells, it is a platonic uniform net and can be represented by the symbol (n, p), where n is the size of the

shortest circuit and p is the connectivity of the nodes. All the Ag_4 units could be simplified to a 4-connected node, so this 2D sheet can be simplified to a 4^4 -sql net.

3.1.2. Structure of complex 2

The X-ray diffraction study reveals that the asymmetric unit of **2** consists of four Åg(I) ions, two epyz ligands (the epyz ligand containing the N1 atom is named epyz1 and that containing the N3 atom is named epyz2), two npth anions (the npth ligand containing the O1 atom is named npth1, and that containing the O3 atom is named npth2). As shown in Fig. 2a, there are three kinds of Ag(I) centers in compound **2**. Each Ag1 center is five coordinated by one epyz1 nitrogen atom [Ag1–N1 = 2.270(2) Å] and four oxygen atoms from two individual npth ligands with Ag–O distances ranging from 2.364(6) to 2.509(4) Å. The Ag2 center is seven coordinated by one epyz1 nitrogen atom [Ag2–N2^{#5}= 2.284(3) Å] and six oxygen atoms from two individual npth ligands. The Ag–O bond distances are in the range 2.379(7)-2.560(8) Å. The Ag3 atom is located in a distorted tetrahedral geometry and is coordinated by one N3 atom from an epyz2 ligand and three O atoms from three different npth ligands, with Ag–O distances ranging from 2.303(8) to 2.496(9) Å. The epyz ligands take a bidentate bridging mode, while the two different npth anions take a μ_4 - η^3 : η^1 : η^3 : η^1 and a μ_6 - η^2 : η^2

As shown in Fig. 2a, the npth1 and npth2 ligands bridge four Ag(I) centers (the Ag1, Ag2 and two Ag3 atoms) to form a Ag₄(epyz)₂(npth)₂ unit. Then cage-like Ag₈ SBU (secondary building unit) can be regarded as two centrosymmetric Ag₄(epyz)₂(npth)₂ units connected to each other by the Ag1–O3 (2.509(4) Å), Ag1–O3^{#4} (2.509(4) Å), Ag3–O1 (2.303(8) Å), Ag3–O2^{#3} (2.350(6) Å) and Ag3–O3^{#3} (2.496(9) Å) interactions, and is reinforced by an

Ag...Ag interaction (Ag3...Ag3^{#3} = 3.1702 (6) Å). The resulting _{Ag8} SBU is a new cage-like unit, which is different from that previously reported in the literature [21]. Each Ag₈ SBU is connected to four adjacent such clusters through epyz1 ligands to form a 2D grid-like layer parallel to the *ab* plane (Fig.2b). Simultaneously, the 2D layers are assembled into a 3D network structure through interlayer epyz2 ligands (Fig. 2c). From a topological point of view, each Ag₈ SBU serves as a six-connected node, while the epyz ligands can act as bridging ligands (Fig. 2d). Consequently, on the basis of this simplification, the 3D frameworks present a NaCl topological net with the point symbol $(4^{12} \cdot 6^3)$.

3.1.3. Structure of complex 3

Complex **3** is a 2D supermolecular structure, which crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig. 3a, the asymmetric unit of **3** consists of one Ag(I) ion, one pyz ligand, one half of a completely deprotonated Hnpth anion and one uncoordinated water molecule. The Ag(I) ions, in a distorted T-shaped coordination geometry, are coordinated by the two nitrogen atoms from two different pyz ligands (Ag–N1 = 2.185(2) and Ag–N2^{#3} = 2.183(2) Å; N1–Ag–N2^{#3} = 161.90(10) °) and one oxygen atom from one Hnpth anion (Ag–O1 = 2.480(2) Å).

The Ag(I) ions are bridged by pyz ligands *via* the μ_2 -N:N' coordination mode to form a 1D infinite chain structure and the terminal Hnpth ligands decorate alternately on the two sides of the chains. A weak Ag···Ag interaction (Ag···Ag^{#1} = 3.196(1) Å) extends the 1D chain into a 2D sheet parallel to the *bc* plane (Fig. 3c), which is reinforced by the uncoordinated water molecule via inter-chain hydrogen-bonding interactions (O6–H6···O7^{#3} = 2.616, O7–H72···O2^{#1} = 2.832, O7–H71···O1^{#4} = 2.758 Å). These neighboring 2D sheets are

interconnected to form the 3D supramolecular architecture by C-H···O hydrogen bonds.

3.1.4. Structure of complex 4

The asymmetric unit of **4** consists of one Ag(I) ion, one Hnpth anion and half an epyz ligand in the monoclinic space group $P2_1/c$. As shown in Fig. 4a, the half completely deprotonated Hnpth ligand adopts the $\mu_3\eta^4$ bridging mode to link three silver atoms with the 2-position carboxylate group chelating one silver ion and simultaneously acting as a monodentate donor to another Ag atom. Ag(I) shows a five-coordinated distorted square-pyramidal coordination environment, being bonded to four O atoms from three different Hnpth ligands and one N atom from one epyz ligand (Ag–O1 = 2.424(2), Ag–O3^{#1} = 2.443(2), Ag–O2^{#4} = 2.642(2), Ag–O2 = 2.705(3) and Ag–N2 = 2.257(2) Å). The structural distortion index tau (τ), as an index of the degree of distortion, is calculated as 0.61 ($\tau = (\alpha - \beta)/60$, where α and β correspond to the two largest angles between the donor atoms forming the basal plane in the square-pyramidal geometry). The value of τ indicates that the Ag center exhibits a configuration between distorted square pyramidal and trigonal bipyramid (for ideal square pyramidal geometry, $\tau = 0$) [22].

Two Ag atoms are interlinked by the oxygen O2 atoms of the 2-position carboxylate group to form a centrosymmetric binuclear unit; such units are connected to one another to build a 1D chain via bridging Hnpth ligands along the [100] direction (Fig. 4b). The resulting chains are further interlinked *via* the μ_2 –N: N' coordination mode of the epyz ligand into 2D layers parallel to the (010) plane (Fig. 4c). The layers are held together by interlayer hydrogen bonds (C6–H6A···O6^{#3}), leading to a 3D supramolecular architecture.

3.2. Effect of different pyrazine derivatives and synthesis conditions on the assembly of Ag(I)

As is shown in the description above, four Ag(I) complexes, 1-4, with the npth/Hnpth anion and different pyrazine derivatives were successfully synthesized and characterized. Complexes 1 and 2 are obtained by ultrasonic treatment with the addition of ammonia solution, and complexes 3 and 4 are synthesized via a hydrothermal method at 100 °C for 72 h. To gain an insight into the influence of the pyz ligand in 1, a similar method was followed by absenting the pyz ligand, affording an amorphous precipitate, thus indicating the pyz ligand plays a major role in the synthesis of complex 2. By way of a review of the characteristic structures, complex 1 exhibits a 2D structure which presents tetranuclear units, complex 2 contains a cage-like Ag₈ SBU to build up a 3D framework, complex 3 displays a 1D infinite chain and complex 4 encompasses binuclear units which form a 2D layer. From a methodological point of view, the method of ultrasonic irradiation synthesis is more likely to obtain multinuclear complexes or high-dimensional compounds. It is superior to the traditional mixing, heating and other thermodynamic methods, and ultrasonic irradiation synthesis has become a convenient, rapid, effective, safe synthetic technology for the synthesis of complexes.

The H_2 npth ligand contains two protons, and thus could be deprotonated to the Hnpth⁻ and npth²⁻ anions. According to the reference reported, there are 12 silver- H_2 npth complexes

complexes with H₂npth

3.3. Luminescent properties

The photoluminescence properties of the coordination polymers have been investigated extensively because of the potential applications in chemical sensors, photochemistry and electroluminescence. At room temperature, the solid-state excitation and emission spectra of complexes **1-4** and the corresponding original ligand H₂npth were measured (Fig. 5). The emission spectra were recorded with the light of λ = 300 nm as the excitation source. The free ligand H₂npth displays photoluminescence with two shoulder peaks centered at 425 and 466 nm. Complexes **1-4** show emission spectra with two peaks at 423 and 466 nm for **1**, 421 and 467 nm for **2**, 420 and 467 nm for **3** and 421 and 468 nm for **4**. The emission spectra of **1-4** are similar to that of the H₂npth ligand, indicating that the ligand-centered (n– π * or π – π *)

transitions play a leading role.

3.4. Photodegradation activities

Photocatalysts have attracted much attention due to their potential applications in purifying water and air by decomposing organic molecules [23]. As we know, TiO₂ has been studied extensively as a semiconductor photocatalyst [24]. More recently, there have been a few contributions about new photocatalytic materials based on coordination polymers that are successfully accomplished, which indicate that this area is a new application for coordination polymer materials [25]. Rhodamine B (RhB) is commonly used as a representative of widespread organic dyes that are very difficult to decompose in waste streams. Thus, we choose rhodamine B as a model model dye pollutant and the photocatalytic activity of the as-prepared complexes **1-4** was tested under simulated UV light by a 300W Hg lamp. For comparison, the photodegradation of RhB without any photocatalyst was also studied under the same conditions and no RhB degradation was observed.

The experimental results show that compound **3** can degrade 81.8% of rhodamine B in 3.5 h under UV light irradiation. Unfortunately, RhB solutions with complexes **1**, **2** and **4** showed no obvious degradation effects (Fig.S4-S6). Additionally, we also carried out experiments to degrade other dyes (MO and MB) with complex **3**. In Fig.6, MB, MO and RhB were analyzed by UV/Vis absorption at 664, 464 and 554 nm respectively. In the presence of complex **3**, the degradation rate of MB, MO and RhB is 33.2, 44.2 and 81.8% after 3.5 h with 30 minutes intervals under UV irradiation, respectively, indicating that RhB shows the best effect for degradation. In addition, we tested the RhB degradation of **3** under the condition of simulated visible light using a 300W Xe lamp (Fig. 7.), and the degradation

ratio of RhB reached 44.2% after 7 h. The experimental results demonstrate that complex **3** is a potential candidate for the photo-degradation organic dyes in visible irradiation.

It is well known that many factors affect the complexes for the degradation of organic pollutants. A variety of conditions from external factors will influence the degradation effect, such as, PH value, temperature and light source in the catalytic system, the concentrations of the dye and so on. From the catalyst itself, its catalytic effect not only relates to the specific surface area of the catalyst, but also to the structure of the catalyst itself. From the characteristic structures of silver clusters, a total of 20 cases of silver complexes have been investigated, as shown in Table 3 [26], there are 13 cases of mononuclear silver complexes, 4 cases of binuclear complexes, 2 cases of Ag₄ clusters and the last one is an Ag₇ cluster. It is easily to see that mononuclear silver complexes have more advantages in the photocatalytic degradation of organic pollutants. It is known to all that the recombination of electrons (e-) and holes (h+) have a great influence on the efficiency of complexes on the degradation of dyes [27]. The Ag centers in multinuclear silver clusters are mostly connected via O and N atoms mostly, hence, electron transfer between silver atoms is through O and N atom, However, in mononuclear silver complexes, electronic transfer may need to proceed through organic ligands, so it is more difficult compared with multi-core silver clusters. Therefore, we speculate that electron transfer between Ag atoms is much easier in most multi-core silver clusters, with an easy recombination between the electrons (e-) and holes (h+). At the same time, it also can reduce the effect of photocatalysis.

4. Conclusions

In this manuscript, four related coordination polymers based on silver nitrate,

3-nitrophthalic acid and pyrazine-like ligands are synthesized and characterized. Compound **1** presents Ag_4 units, and compound **2** features a cage-like Ag_8 SBU (secondary building unit), which is the first time such a multinuclear polymer has been reported. Furthermore, the 3-nitrophthalic acid exhibits three new coordination modes, which also have never been reported by others. In addition, the methods of ultrasonic synthesis are more likely to obtain multi-nuclear complexes or high-dimensional compounds. Furthermore, we have tested the photochemical properties of complexes **1-4** and we found the mononuclear silver complexes may have more advantages for the degradation of organic pollutants.

Supporting Information Available

Crystallographic data for compounds **1-4** are deposited with the Cambridge Crystallographic Data Center, 1498925-1498928 [CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom. Fax: (44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk. Website: http://www.ccdc.cam.ac.uk]. Experimental and simulated PXRD patterns of **1-4**; IR spectra of **1-4**; TG curves of **1-4**; Selected inter-atomic distances and bond angles for **1-4**.

Disclosure statement

No potential conflict of interest is reported by the authors.

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References

- [1] (a) G. Dura, M. Carmen Carrion, F.A. Jalon, B.R. Manzano, A.M. Rodriguez, K. Mereiter, Cryst. Growth Des. 15 (2015) 3321;
- (b) H.A. Mohamed, B.R.M. Lake, T. Laing, R.M. Phillips, C.E. Willans, Dalton Trans. 44 (2015) 7563;
 - (c) L.Mei, Q.Y. Wu, S.W. An, Z.Q. Gao, Z.F. Chai, W.Q. Shi, Inorg. Chem. 54 (2015) 10934;
 - (d) P. Smolenski, C. Pettinari, F. Marchetti, M.F.C. Guedes da Silva, G. Lupidi, G.V.B. Patzmay, D. Petrelli, L.A. Vitali, A.J.L. Pombeiro, Inorg. Chem. 54 (2015) 434.
- [2] (a) J. Janczak, D. Prochowicz, J. Lewinski, D. Fairen-Jimenez, T. Bereta, J. Lisowski, Chem. Eur. J. 22 (2016) 598;
 - (b) X. Jiang, K.Q. Hu, H.Z. Kou, CrystEngComm 18 (2016) 4084;
 - (c) A. Pal, S. Chand, S. Senthilkumar, S. Neogi, M.C. Das, CrystEngComm 18 (2016) 4323;
 - (d) X.B. Liu, H. Lin, Z.Y. Xiao, W.D. Fan, A. Huang, R.M. Wang, L.L. Zhang, D.F. Sun, Dalton Trans. 45 (2016) 3743;
 - (e) R.A. Agarwal, S. Mukherjee, Polyhedron 106 (2016) 163.
- [3] (a) S. Feng, H. Yang, X. Jiang, Y. Wang, M. Zhu, J. Mol. Struct. 1081 (2015) 1;
 (b) Z.X. Si, W. Xu, Y.Q. Zheng, J. Solid State Chem. 239 (2016) 139;
 - (c) J. Lee, Y. Kang, N.S. Cho, K.M. Park, Cryst. Growth Des. 16 (2016) 996.
- [4] (a) L.Z. Chen, Q.J. Pan, X.X. Cao, F.M. Wang, CrystEngComm 18 (2016) 1944;
 (b) G.T. Wang, J.C. Zhang, Z.Y. Tang, H.T. Zhou, L. Zhang, R.W. Yang, P. Zou, Y.H. Yu, J.S. Gao, G.F. Hou, CrystEngComm 18 (2016) 2437;
- (c) L. Jiang, D.Y. Zhang, J.J. Suo, W. Gu, J.L. Tian, X. Liu, S.P. Yana, Dalton Trans. 45 (2016) 10233;
 - (d) J. Tong, S. Demeshko, M. John, S. Dechert, F. Meyer, Inorg. Chem. 55 (2016) 4362;
 (e) Q.J. Niu, Y.Q. Zheng, H.L. Zhu, W. Xu, Transition Met. Chem. 41 (2016) 365.
- [5] (a) J.M. Cardoso, A.M. Galvao, S.I. Guerreiro, J.H. Leitao, A.C. Suarez, M.F. Carvalho, Dalton Trans. 45 (2016) 7114;
 - (b) X. Lu, J. Ye, Y. Sun, R.F. Bogale, L. Zhao, P. Tian, G. Ning, Dalton Trans. 43 (2014)

10104;

- (c) S.W. Jaros, M.F.C. Guedes da Silva, J. Król, M. Conceição Oliveira, P. Smoleński,A.J.L. Pombeiro, A.M. Kirillov, Inorg. Chem. 55 (2016) 1486;
- (d) F. Marchetti, J. Palmucci, C. Pettinari, R. Pettinari, S. Scuri, I. Grappasonni, M. Cocchioni, M. Amati, F. Lelj, A. Crispini, Inorg. Chem. 55 (2016) 5453;
- (e) P.A. Papanikolaou, A.G. Papadopoulos, E.G. Andreadou, A. Hatzidimitriou, P.J. Cox,A.A. Pantazaki, P. Aslanidis, New J. Chem. 39 (2015) 4830;
- (f) S. Roca, D. Vikić-Topić, J. Plavec, P. Šket, Z. Mihalić, D. Matković-Čalogović, Z. Popović, Polyhedron 109 (2016) 166.
- [6] (a) X.S. Zhai, W.G. Zhu, W. Xu, Y.J. Huang, Y.Q. Zheng, CrystEngComm 17 (2015) 2376;
 (b) X.Y. Wu, H.X. Qi, J.J. Ning, J.F. Wang, Z.G. Ren, J.P. Lang, Appl. Catal. B: Environ.
 168 (2015) 98;
 - (c) Y.J. Huang, Y.Q. Zheng, H.L. Zhu, J.J. Wang, J. Solid State Chem. 239 (2016) 274;
 (d) T.T. Li, J. Qian, Y.Q. Zheng, RSC Adv. 6 (2016) 77358.
- [7] X. Zhang, Y.G. Liu, Z.C. Hao, G.H. Cui, J. Coord. Chem. 69 (2016) 1514.
- [8] J.Y. Hu, J.S. Zhang, J.A. Zhao, L.L. Hu, S.F. Chen, J. Coord. Chem. 694 (2016) 57.
- [9] (a) H.L. Li, W. Yang, X.H. Wang, L.J. Chen, J.R. Ma, L.W. Zheng, J.W. Zhao, Cryst. Growth Des. 16 (2016) 108;
 - (b) S. Roy, H.M. Titi, B.K. Tripuramallu, N. Bhunia, R. Verma, I. Goldberg, Cryst. Growth Des. 16 (2016) 2814;
 - (c) B. Xu, Y. Cheng, H.M. Hu, C. Bai, X.F. Wang, M.L. Yang, G.L. Xue, CrystEngComm 18 (2016) 4613;
 - (d)Z.L. Bai, Y.L. Wang, Y.X. Li, W. Liu, L.H. Chen, D.P. Sheng, D.W. Juan, Z.F. Chai, T.E. Albrecht-Schmitt, S. Wang, Inorg. Chem. 55 (2016) 6358;
 - (e) J.M. Hu, K. Van Hecke, B.Y. Yu, G.H. Cui, Inorg. Chem. Commun. 61 (2015) 217;
 - (f) S.M. Jansze, G. Cecot, M.D. Wise, K.O. Zhurov, T.K. Ronson, A.M. Castilla, A. Finelli,
 - P. Pattison, E. Solari, R. Scopelliti, G.E. Zelinskii, A.V. Vologzhanina, Y.Z. Voloshin, J.R.Nitschke, K. Severin, J. Am. Chem. Soc. 138 (2016) 2046;
 - (g) L.Y. Yin, H.W. Wu, M.J. Zhu, Q. Zou, Q. Yan, L.L. Zhu, Langmuir 32 (2016) 6429;
 - (h) F. Semerci, O.Z. Yesilel, F. Yuksel, O. Sahin, Polyhedron 111 (2016) 1.

- [10] (a) J.R. Gardinier, J.S. Hewage, J. Hoffman, S.V. Lindeman, D.E. Williams, N.B. Shustova, Eur. J. Inorg. Chem. (2016) 2615;
 - (b) S.W. Jaros, M. da Silva, M. Florek, P. Smolenski, A.J.L. Pombeiro, A.M. Kirillov, Inorg. Chem. 55 (2016) 5886.
- [11] W.M. Bloch, C.J. Sumby, Supramol. Chem. 27 (2015) 807.
- [12] (a) M.J. Baena, S. Coco, P. Espinet, Cryst. Growth Des. 15 (2015) 1611;
 (b) N.I. Sulaiman, N.R. Salimin, R.A. Haque, M.A. Iqbal, S.W. Ng, M.R. Razali, Polyhedron 97 (2015) 188; (c) K. Potgieter, M.J. Cronje, R. Meijboom, Inorg. Chim. Acta 437 (2015) 195.
- [13] (a) M.N. Tahir, A.A. Isab, F. Afzal, K. Raza, S. Muhammad, M. Hanif, S. Ahmad, T. Gul, S. Ahmad, Z. Naturforsch., B-a: Chem. Sci. 70 (2015) 541;
 - (b) V. Charra, P. de Fremont, P.-A.R. Breuil, H. Olivier-Bourbigou, P. Braunstein, J. Organomet. Chem. 795 (2015) 25.
- [14] (a) R.W. Huang, Y. Zhu, S.Q. Zang, M.L. Zhang, Inorg. Chem. Commun. 33 (2013) 38;
 (b) X.W. Lei, F.X. Zhou, M.F. Wang, H.P. Zhang, C.Y. Yue, M.C. Hong, Inorg. Chem. Commun. 27 (2013) 171;
 - (c) D.F. Wang, T. Zhang, S.M. Dai, R.B. Huang, L.S. Zheng, Inorg. Chim. Acta 423 (2014) 193;
 - (d) T. Zhang, D.F. Wang, R.B. Huang, L.S. Zheng, Inorg. Chim. Acta 427 (2015) 299;
 - (e) Y. Zorlu, H. Can, J. Mol. Struct. 1076 (2014) 629;
 - (f) S.C.K. Hau, T.C.W. Mak, J. Organomet. Chem. 792 (2015) 123;
 - (g) A. Espinosa Ferao, F. Afzal, S. Aslam, I.K. Muhammad, Ejaz, I.U. Khan, M. Fettouhi, A.A. Isab, S. Ahmad, Polyhedron 110 (2015) 299.
- [15]Z.H. Wang, D.F. Wang, T. Zhang, R.B. Huang, L.S. Zheng, CrystEngComm 16 (2014) 5028.

[16](a) D. Sun, F.J. Liu, R.B. Huang, L.S. Zheng, CrystEngComm 15 (2013) 1185;

- (b) D.F. Wang, Z.H. Wang, B.W. Lu, S.F. Chen, T. Zhang, R.B. Huang, L.S. Zheng, J. Mol. Struct. 1059 (2014) 81;
- (c) X.Y Lu, J.W Ye, YSun, R.F. Bogale, L.M. Zhao, P. Tian, G.L. Ning, Dalton Trans.43
 (2014)10104; (d) Z.X. Si, W. Xu, J. Cluster Sci. 27 (2015) 603.

- [17]R.G. Pearson, Inorg. Chim. Acta 240 (1995) 93.
- [18] (a) T. Zhang, H.Q. Huang, H.X. Mei, D.F. Wang, X.X. Wang, R.B. Huang, L.S. Zheng, J.
 Mol. Struct. 1100 (2015) 237;
 - (b) O. Rivada-Wheelaghan, A. Dauth, G. Leitus, Y. Diskin-Posner, D. Milstein, Inorg. Chem. 54 (2015) 4526;
 - (c) R. Biswas, S. Mukherjee, S. Ghosh, C. Diaz, A. Ghosh, Inorg. Chem. Commun. 56 (2015) 108;
 - (d) S.K. Dey, M. Hazra, L.K. Thompson, A. Patra, Inorg. Chim. Acta 443 (2016) 224.
- [19] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- [20] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [21] (a) T. Guchhait, B. Barua, A. Biswas, B. Basak, G. Mani, Dalton Trans. 44 (2015) 9091;
 (b) J. Yang, T. Hu, T.C.W. Mak, Cryst. Growth Des. 14 (2014) 2990;
 (c) Y.P. Xie, T.C.W. Mak, Dalton Trans. 42 (2013) 12869.
- [22] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [23] (a) X. Bai, C. Sun, D. Liu, X. Luo, D. Li, J. Wang, N. Wang, X. Chang, R. Zong, Y. Zhu, Appl. Catal. B: Environ. 204 (2017) 11;
 - (b) A. Cortez-Lorenzo, L. Escamilla-Perea, K. Esquivel-Escalante, R. Velazquez-Castillo, Catal. Today 282 (2017) 159.
- [24] (a) F. Shiraishi, D. Maruoka, Y. Tanoue, Sep. Purif. Technol. 175 (2017) 185;
 - (b) Y. Chen, K. Liu, J. Alloys Compd. 697 (2017) 161;
 - (c) I. Ali, S.R. Kim, S.P. Kim, J.O. Kim, Catal. Today 282 (2017) 31.
- [25] (a) Z.X. Si, W. Xu, Y.Q. Zheng, J. Solid State Chem. 239 (2016) 139;
 - (b) D. Sun, N. Zhang, R.B. Huang, L.S. Zheng, Cryst. Growth Des. 10 (2010) 3699;
- [26] (a) Q. Zhang, D. Chen, X. He, S. Huang, J. Huang, X. Zhou, Z. Yang, J. Li, H. Li, F. Nie, CrystEngComm 16 (2014) 10485;
 - (b) J.F. Wang, S.Y. Liu, C.Y. Liu, Z.G. Ren, J.P. Lang, Dalton Trans. 45 (2016) 9294;
 - (c) J. Zhang, C.C. Wang, P. Wang, X.X. Guo, S.J. Gao, Transition Met. Chem. 41 (2016)

637-645;

CC C

(d) D. Marcinkowski, M. Walesa-Chorab, V. Patroniak, M. Kubicki, G. Kadziolka, B. Michalkiewicz, New J. Chem. 38 (2014) 604;

(e) M. Wałęsa-Chorab, V. Patroniak, M. Kubicki, G. Kądziołka, J. Przepiórski, B. Michalkiewicz, J. Catal. 291 (2012) 1;

(f)C.C. Wang, H.P. Jing, P. Wang, J. Mol. Struct. 1074 (2014) 92;

(g) D. Marcinkowski, M. Walesa-Chorab, M. Kubicki, M. Hoffmann, G. Kadziolka, B. Michalkiewicz, V. Patroniak, Polyhedron 90 (2015) 91;

(h) S.E.-d.H. Etaiw, M.M. El-Bendary, Inorg. Chim. Acta 435 (2015) 167;

(i) L.D. Chen, L.X. Zhou, Y.Q. Zheng, H.L. Zhu, Polyhedron 126 (2017) 150;

(j) X.Y. Wu, H.X. Qi, J.J. Ning, J.F. Wang, Z.G. Ren, J.P. Lang, Appl. Catal. B: Environ. 168 (2015) 98;

(k) J.M. Hao, B.Y. Yu, K. Van Hecke, G.H. Cui, CrystEngComm 17 (2015) 2279;

(1) W.Q. Kan, B. Liu, J. Yang, Y.Y. Liu, J.F. Ma, Cryst. Growth Des. 12 (2012) 2288.

[27] (a) L. Liu, J.T. Deng, T.J. Niu, G. Zheng, P. Zhang, Y. Jin, Z.F. Jiao, X.S. Sun, J Colloid Interface Sci. 493 (2017) 281;

(b) H. Tang, S.F. Chang, G.G. Tang, W. Liang, Appl. Surf. Sci. 391 (2017) 440;

(c) X.J. Chen, Y.Z. Dai, J. Guo, T.H. Liu, X.Y. Wang, Ind. Eng. Chem. Res. 55 (2016) 568.

Figure captions

Fig. 1. (a) The coordination environment of Ag(I) ions and npth ligands in **1** with thermal ellipsoids at the 40% probability level. We marked the 14-membered ring unit with a green line. (b) Ball-and-stick view of the 2D sheet in compound **1** and the 4⁴-sql network incorporating rhombic Ag₄ units. (Symmetry codes: #1 = x, y+1, z; #2 = -x+2, y+1/2, -z+1/2; #3 = -x+2, y-1/2, -z+1/2; #4 = x, y-1, z; #5 = -x+1, y-1/2, -z+1/2; #6 = -x+1, y+1/2, -z+1/2)

Fig. 2. (a) The coordination environment of Ag(I) ions and npth ligands in **2** with thermal ellipsoids at the 40% probability level. The cage-like Ag₈ unit is marked by a blue line. (b) Ball-and-stick view of the 2D sheet in compound **2** along the *c* axis. The phenyl rings of all npth ligands and hydrogen atoms are omitted for clarity. (c) 3D framework of complex **2**. (d) A schematic view of the $(4^{12} \cdot 6^3)$ topological net of **2**. The purplish red balls represent 6-connecting Ag₈ SBUs, each blue line represents epyz ligands. (Symmetry codes: #1 = -x+1, -y, -z+1; #2 = x-1/2, -y+1/2, -z+1; #3 = -x+1, -y, z; #4 = x, y, -z+1; #5 = x+1/2, -y+1/2, -z+1; #6 = x, y, -z.)

Fig. 3. (a) The coordination environment of Ag(I) ions and npth ligands in **3** with thermal ellipsoids at the 40% probability level. (b) View of the structure of complex **3** showing the 1D sheet of Ag(I) ions with Hnpth anions and pyz ligands along the *c* axis. (c) Ball-and-stick view of the 2D sheet in the *bc* plane. All H and oxygen atoms of the nitro group are omitted for clarity. (Symmetry codes: #1 = -x+1, -y, -z, #2 = -x+1, y+1/2, -z+1/2, #3 = -x+1, y-1/2, -z+1/2)

Fig. 4. (a) The coordination environment of the Ag(I) ions and npth ligands in **4** with thermal ellipsoids at the 40% probability level. (b) Presentation of 1D infinite $[Ag_2(Hnpth)_2]_n$ units. (c) Ball-and-stick view of the 2D sheet in compound **4**. All hydrogen atoms are omitted for clarity. (Symmetry codes: #1 = -x-1, -y+1, -z+1, #2 = -x-1, -y+1, -z+1, #3 = x+1, 1/2+y, 1/2+z, #4 = -x, -y+1, -z+1, #5 = -x+1, -y+1, -z+2.)

Fig. 5. Emission spectra of 1-4 and H₂npth in the solid state at room temperature.

Fig. 6. Photocatalytic decomposition of RhB, MB and MO solutions with the change in C_t/C_0 of 3 under UV light.

Fig. 7. Absorption spectra of RhB solutions during the decomposition reaction with the use of complex 3 under a Xe lamp. Insert: photocatalytic decomposition of the RhB solution with the change in C_t/C_0 (%).

Scheme 1 Coordination modes of 3-nitrophthalic acid with Ag(I) ions.



















Graphic abstract

We report four new silver coordination polymers, $Ag_4(H_2O)_2(npth)_2$ (1), $Ag_4(epyz)_2(npth)_2$ (2), $[Ag(pyz)(Hnpth)] \cdot H_2O$ (3) and $Ag(epyz)_{0.5}(Hnpth)$ (4), synthesized by hydrothermal and ultrasonic treatment methods. Their luminescent and photocatalytic properties have been studied.



Compounds	$Ag_4(H_2O)_2(npth)_2$	$Ag_4(epyz)_2(npth)_2$	[Ag(pyz)(Hnpth)]·H ₂ O	Ag(epyz) _{0.5} (Hnpth)
Empirical formula	$C_{16}H_{10}Ag_4N_2O_{14}$	$C_{32}H_{29}Ag_4N_6O_{12}$	$C_{12}H_{10}AgN_3O_7$	$C_{12}H_{10}AgN_2O_6$
Formula weight	885.74	1121.09	416.10	386.09
Description	Colorless, platelet	Colorless, prism	Colorless, block	Yellow, block
Crystal size (mm)	$0.50 \times 0.28 \times 0.09$	0.46 imes 0.32 imes 0.25	0.41 imes 0.21 imes 0.20	$0.28 \times 0.18 \times 0.15$
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P 2_{1}/c$	P bam	$P 2_1/c$	$P 2_1/c$
<i>a /</i> (Å)	7.354(1)	14.702(3)	14.981(3)	6.685(1)
<i>b</i> / (Å)	10.943(2)	23.516(5)	13.994(3)	21.482(4)
c / (Å)	27.213(5)	12.725(3)	6.8505(14)	8.929(1)
$\beta/(^{\circ})$	92.15(3)	90.00	102.99(3)	99.04(3)
Volume (Å ³)	2188.4(7)	4399.4(17)	1399.4(5)	1266.2(4)
Z	4	4	4	4
$D_{\rm calc} / ({\rm g \ cm}^{-3})$	2.668	1.693	1.975	2.025
<i>F</i> (000)	1680	2188	824	764.0
$\mu (\mathrm{mm}^{-1})$	3.605	1.812	1.484	1.623
θ range (deg)	3.07-27.47	3.07–27.48	3.07–27.45	3.07-27.44
Reflections collected	20230	42091	13321	12316
Unique reflections (Rint)	5008 ($R_{\rm int} = 0.1064$)	$5270(R_{\rm int} = 0.0452)$	$3201 \ (R_{\rm int} = 0.0436)$	2898 ($R_{\rm int} = 0.1230$)
Data, restraints, parameters	3836, 0, 326	4882,268, 362	2621, 0, 220	2340, 0, 190
Goodness of fit on F^2	1.065	1.027	1.141	1.117
$R_1, wR_2 \left[I \ge 2\sigma(I)\right]^a$	0.0556, 0.1202	0.0939, 0.2069	0.0729, 0.1517	0.0280, 0.0280
R_1 , wR_2 (all data) ^{<i>a</i>}	0.0676, 0.1270	0.0973, 0.2080	0.1415, 0.1814	0.0410, 0.0648
A, B values in w^{b}	0.0484, 1.1806	0.0000, 144.0000	0.0865, 0.0000	0.0320, 1.0093
$\Delta ho_{ m max}, \Delta ho_{ m min}$ / (e Å ⁻³)	1.515, -1.417	1.835, -1.675	0.651, -0.625	0.597, -0.573

Table 1. Summary of the crystal data, data collection, structure solution and refinement details for complexes 1, 2, 3 and 4.

 $\frac{\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} / (e \check{A}^{-3})}{R_{1} = \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}|, wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2};}$ $b w = [\sigma^{2}(F_{o}^{2}) + (AP)^{2} + BP]^{-1} \text{ with } P = (F_{o}^{2} + 2F_{c}^{2}) / 3$

formula	the auxiliary ligand	dimensionality	point symbol	References
$Ag_4(H_2O)_2(npth)_2$		2 D	4^{4}	This work
$Ag_4(epyz)_2(npth)_2$	epyz = 2,3,5,6-tetramethylpyrazine	3 D	$4^{12} \cdot 6^3$	This work
$[Ag(pyz)(Hnpth)] \cdot H_2O$	pyz = pyrazine	2 D		This work
Ag(epyz) _{0.5} (Hnpth)	epyz = 2,3,5,6-tetramethylpyrazine	2 D		This work
$[Ag_2(pdz)(npth)]$	pdz = pyridazine	1 D		Ref [14c]
$[Ag_2(L_1)(npth)]$	$L_1 = 2$ -ethyl-3-methylpyrazine	2 D		Ref [14d]
[Ag ₂ (tpyz)(npth)]	tpyz = 2,3,5-trimethylpyrazine	2 D	4 ⁴	Ref [14d]
$[Ag_2(npth)(NH_3)_2]$		1 D		Ref [14d]
$[Ag_2(2,3-dmpyz)(npth)]$	2,3-dmpyz = $2,3$ -dimethylpyrazine	2 D		Ref [15]
$[Ag_2(NH_3)_2(npth)]$		1 D		Ref [16a]
$[Ag_2(NH_3)(npth)]$		2 D	4	Ref [16a]
$\{(NH_4)[Ag(npth) \cdot H_2O]\}$		2 D		Ref [16a]
$[Ag_4(NH_2)_4(npth)\cdot H_2O]$		2 D		Ref [16a]
$[Ag_4(mpyz)(npth)_2;(H_2O)_2]$	mpyz= methyl-pyrazine	$\frac{2}{2}$ D		Ref [16b]
$[Ag_4(mpy2)(npth)_2]$	mpyz= methyl-pyrazine	2 D		Ref [16b]
$[A g_2(npt)/(npt)/2]$	hipy=4.4'- $hipyridyl$	3 D	$(4^3)_2(4^6.6^{18}.8^4)$	Ref $[16c]$

Table 2. Summary of the relevant reported compounds based on silver-H₂npth complexes.

	Complexes	ligands	Organic pollutants	Light source	Time(C _t /C ₀)	References
Ag	$[Ag_2(en)_2(AT)]_n$	en = ethylenediamine, AT = 5, 5'-azotetrazolate	R6G	UV light	43 min (90.8 %)	Ref [26 a]
	[Ag(ATZ)] _n	ATZ = 5-amino-tetrazole	R6G	UV light	60 min (86.3%)	
	${Ag(Sal)(3-bdppmapy)}_n$	Sal = salicylate, 3-bdppmapy = N,N-bis(diphenylphosphanylmethyl)-3-amino pyridine	RhB	UV light	4 h (60%)	Ref [26 b]
	$[Ag_4(dpe)_4] \cdot (btec)$	dpe = 1,2-di(4-pyridyl)ethylene H ₄ btec = 1,2,4,5-benzenetetracarboxylic acid	МО	UV light	2 h (52.3%)	Ref [26 c]
	$[Ag_4(bpy)_4] \cdot (btec) \cdot 12H_2O$	bpy = 4,4'-bipyridine, H ₄ btec = 1,2,4,5-benzenetetracarboxylic acid	мо	UV light	2 h (26.5%)	
	${[AgL](CF_3SO_3)}_n$	L = 2,3-bis(6'-methyl-2,2'-bipyridin-6-yl)pyrazine	МВ	UV light Sun-light	6.7 h (100%) 133 h (90%)	Ref [26 d]
	$[Ag_2L_2](CF_3SO_3)_2 \cdot H_2O$	L = 6',6"-(2-phenylpyrimidine-4,6-diyl)bis(6-meth	MB	UV light Sun-light	6 h (100%) 252 h (100%)	Ref [26 e]
	$[Ag_2(dpe)_{1.5}(sbdc)_{0.5}](sbdc)_{0.5} \cdot 7H_2O$	H_2 sbdc = 4,4'-stilbenedicarboxylic acid dpe = 1,2-di(4-pyridyl)ethylene	MB	UV light	3 h (99.9%)	Ref [26 f]
	$[Ag_2(bpy)_2](npdc)\cdot 2H_2O$	H_2 npdc = 2,6-Naphthalenedicarboxylic acid bpy = 4,4'-bipyridine	MB	UV light	3 h (99.8%)	
	$[Ag_4(bpy)_4](ap)_2 \cdot 11H_2O$	$H_2ap = 5$ -aminophthalic acid bpy = 4,4'-bipyridine	MB	UV light	3 h (98.2%)	
	[AgL(NO ₃)]	L = 2,6-di(anthracen-9-yl)pyridine	MB	solar radiation	100h (90%)	Ref [26 g]
	[AgL(i-PrOH) ₂](BF ₄)	L = 2,6-di(anthracen-9-yl)pyridine	MB	solar radiation	100h (85%)	
	C					

Table 3 Comparison of the decomposition performances of different dyes for the reported silver-based catalysts.

	$[Ag_5(CN)_5(2,2'-bpy)_2]_n$	2,2'-bipyridine	MB	UV light	3 h (100%)	Ref [26 h]
Ag2	{ $[Ag_4(Sal)_2(\mu-\eta,\eta^2-Sal)_2](3-bdppm)$	Sal = salicylate	RhB	UV light	4 h (100%)	Ref [26 b]
	$apy)_2\}_n$	3-bdppmapy =				
		N,N-bis(diphenylphosphanylmethyl)-3-amino				
		pyridine				
	$[Ag_2(MA)_2(3-npa)] \cdot 2H_2O$	MA = melamine a. RhB L		LED lamp	a. 5h (61%)	Ref [26 i]
		H_2 npa = 3-nitrophthalic acid b. MB			b. 5h (85%)	
	$[Ag_2(MA)_2(2-nbd)] \cdot 2.5H_2O$	MA = melamine	a. RhB	LED lamp	a. 5h (49%)	
		H_2 nbd = 2-nitroterephthalic acid	b. MB		b. 5h (54%)	
	$[AgL(\mu-H_2O)AgL](BF_4)_2 \cdot 3CH_2Cl_2$	L = 2,6-di(anthracen-9-yl)pyridine	MB	solar	40h (50%)	Ref [26 g]
				radiation		
Ag4	[Ag ₄ (NO ₃) ₄ (dpppda)]	dpppda =	a. NB	UV light	a. 5h (100%)	Ref [26 j]
		1,4-N,N,N',N'-tetra(diphenylphosphanylmeth	b. PNP		b. 5h (100%)	
		yl) benzene diamine	c. 2,4-DNP		c. 6h (100%)	
	$[Ag_2(pbmb)(2,6-napdc)]_n$	$2,6-H_2$ napdc = 2,6- naphthalenedicarboxylic	МО	UV light	2 h (99%)	Ref [26 k]
		acid				
		pbmb = bis(2-methylbenzimidazole)				
Ag7	[Ag ₇ (4,4'-tmbpt)(HL) ₂ (L)(H ₂ O)]	$H_3L = 5-(4- carboxybenzyloxy)$ isophthalic	MB	UV light	1.5 h (49%)	Ref [26 1]
		acid, 4,4'-tmbpt =				
		1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-p				
		yridyl)-1,2,4-triazole				