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Synthesis and Characterization of Two Silver Iodides with One- and Three-Dimensional Hybrid Structures Constructed From Ag···Ag Interactions and Organic Templates

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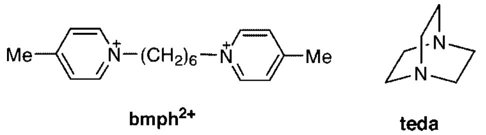
Two new organically templated silver iodides, namely $[(bmph)(Ag_5I_7)]_n$ (**1**) and $[(Hteda)_4(Ag_{12}I_{16})]_n$ (**2**), have been synthesized with $bmph^{2+}$ and teda [$bmph^{2+}$ = 1,6-bis(4-methylpyridinio)hexane, Hteda = protonated triethylenediamine] as structure-directing agents. Complex **1** consists of a one-dimensional polymer that can be described as edge-sharing AgI_4 tetrahedra, whereas **2** is the first example of a three-dimensional Ag/I framework based on Ag···Ag weak interactions and an organic template. Electrostatic interactions between the organic countercations and inorganic moieties are present and contribute to the crystal packing. Both compounds have been further characterized by IR spectroscopy, elemental analysis, TGA, and optical limiting measurements.

Introduction

There has been remarkable progress and interest in the synthesis and characterization of hybrid organic-inorganic molecular materials owing to their enormous variety of intriguing structural topologies and their fascinating properties, as well as their potential applications in many fields, such as catalysis, materials science, medicine, and magnetochemistry,[1] and the optical properties of polymer hybrids have attracted particular interest from chemists recently.[2] Among the various families of hybrid functional materials, the family of metal halides is an important one. As a branch of the metal halides, silver(I) halides occupy an important position.

In general, predicting the structures of self-assembled Ag^I compounds is difficult because the silver ion is known to adopt a myriad of bonding modes and coordination geometries. So far, considerable progress has been made towards the goal of obtaining specific architectures, such as the recently reported [4 × 5] Ag_{20} grid,[3a] an Ag_{10} quadruple helicate,[3a] and a chiral Ag^I diamondoid polymer,[3a,3b] all of which were prepared on the basis of rational design principles. Most of the reports involve metal-organic compounds that have variable dimensions and topologies, and compounds that contain organic-inorganic hybrid Ag^I/amino systems are much less common and only zero- or one-dimensional structures are known.[4] A recent advance in this system is to design the coordination frameworks of silver(I) halides by incorporating various organic structure-directing agents (SDA). It is noteworthy that the introduction of new organic template agents always leads to a dramatic structural change of the basic inorganic phases.[5] It seems that the structure of the inorganic moiety becomes more complicated when the space volume of the SDA increases. Furthermore, the inorganic structure can be different even with the same SDA. In all, the coordination chemistry of silver halides is versatile and the study in this field is in the ascendant. We aim to probe the impact of organic quaternary ammonium cations on the structure of the inorganic moiety. In this paper, we report the preparation, crystal structures, and some physical properties of the one-dimensional hybrid complex $[(bmph)(Ag_5I_7)]_n$ and the first three-dimensional Ag/I coordination polymer $[(Hteda)_4(Ag_{12}I_{16})]_n$, assembled from $bmph^{2+}$ [$bmph^{2+}$ = 1,6-bis(4-methylpyridinio)hexane] and $Hteda^+$ ($Hteda^+$ = protonated triethylenediamine) with Ag^I (Scheme 1).



Scheme 1. Structure of the two SDAs.

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Results and Discussion

Preparation of the Complexes

Variation of the SDA leads to the formation of two silver(I) inorganic components with different stoichiometries. They present dissimilar dimensions whose structures differ greatly in their linkage modes. Colorless block crystals of complexes **1** and **2** crystallize in a weakly acidic environment with pH = 5.0. In particular, **1** must be synthesized by slow condensation of diethyl ether into the DMF solution. The two complexes grow in solutions enriched with NaI, otherwise the crystals are of low quality or even do not form. Overall, many factors determine the anionic substructures, including the concentration and molar ratio of the starting materials, nature of the solvent, and, most importantly, the size, shape, and charge of the counterions.

Crystal Structures

[(bmph)(Ag$_5$I$_7$)]$_n$ (1)

According to the structural analysis, the crystal structure of **1** shows a one-dimensional arrangement constructed from (bmph)$^{2+}$ fragments and $(Ag_5I_7)_n^{2-}$ chains, which are held together by electrostatic forces. The (bmph)$^{2+}$ units are discrete, but the inorganic moiety $(Ag_5I_7)_n^{2-}$ is polymeric and exists in the crystal as an extended chain along the *a* axis [Figure 1(a)]. In other words, this structure is a one-dimensional infinite polymeric anion accompanied by discrete cations. It should be mentioned that the chain is almost linear. As shown in Figure 1(b), the $(Ag_5I_7)_n^{2-}$ chain can be discussed in terms of an Ag_5I_{10} building block in which each silver atom has an I_4 donor set and tetrahedral geometry when the Ag···Ag interactions are not taken into account. The Ag_5I_{10} building block can be described as the result of five edge-sharing AgI_4 tetrahedra and

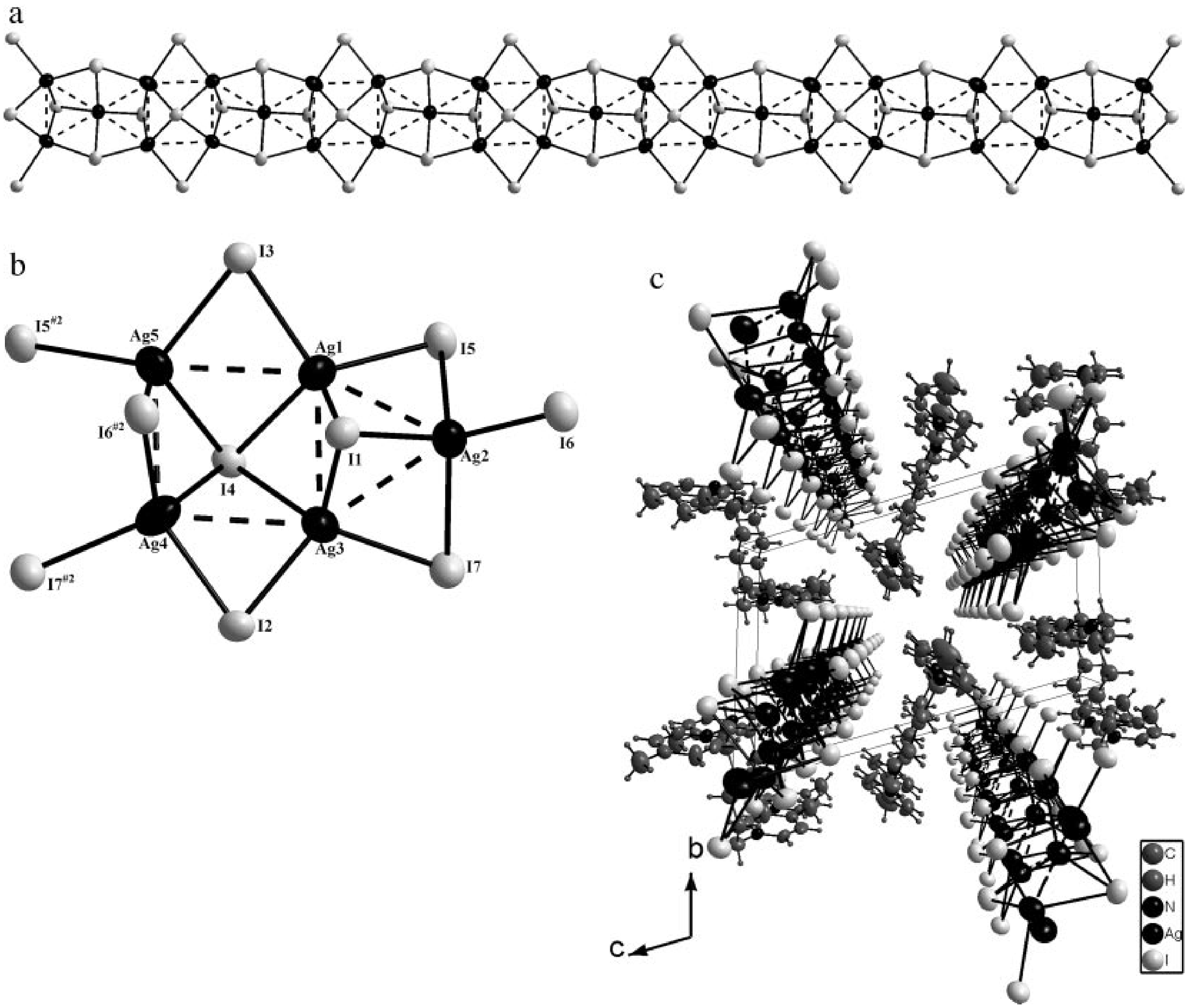

Figure 1. (a) View of the 1D zigzag chain structure of $[Ag_5I_7]_n^{2-}$ along the *a* axis. (b) Diagram of the Ag_5I_{10} building block. (c) Packing diagram of **1** showing SDA molecules contained in the cavities formed by the inorganic chains.

argentophilic interactions. The infinite chain is built up by *cis*-edge-sharing Ag_5I_{10} building blocks, where the shared edges are I(5)–I(6) and I(6)–I(7).

Ag···Ag interactions have been found in many silver complexes, and the term argentophilicity has been adopted to describe this metal–metal interaction. The attraction between d^{10}–d^{10} closed-shell metal atoms promotes the aggregation of silver(I) centers, as supported by spectroscopic and structural evidence.[6] In this work the Ag···Ag distances in **1** range from 3.038(3) [Ag(2)–Ag(4)#1, Ag(4)–Ag(2)#2] to 3.361(3) Å [Ag(3)–Ag(4)], which are longer than that of metallic silver (2.88 Å) but shorter than the van der Waals radius sum of silver (3.44 Å).[7] The Ag···Ag separations [3.312(2)–3.556(3) Å] in $[(Et_4N)_3Ag_6(\mu\text{-}2Br)_6(\mu\text{-}4Br)_3]_n$[8] suggest that weak Ag···Ag interactions may exist. Compounds possessing argentophilicity can be potentially used in silver-containing antibacterial agents.[9]

This polymeric anion contains several very interesting features, the most extraordinary of which is the local environment of the Ag(4) atom. This atom is surrounded by I(2), I(4), I(6)#2, and I(7)#2, although in order to form stable polyanions the distances of Ag(4)–I(4) and Ag(4)–I(7)#2 [3.007(3) and 3.067(3) Å, respectively] are relatively long in comparison with the normal Ag–I distance. The $Ag(4)I_4$ tetrahedron is therefore highly distorted with Ag–I lengths ranging from 2.779(2) to 3.067(3) Å. The distorted pseudo-tetrahedron of $Ag(4)I_4$ can also be extracted from the data of I(2)–Ag(4)–I(6)#2 [125.83(9)°], I(2)–Ag(4)–I(7)#2 [103.16(7)°], and I(2)–Ag(4)–I(4) [96.31(7)°], and furthermore, because Ag(4) is pseudo-tetrahedral, it leads to the tetrahedron of corner-shared Ag(5) to be distorted with three short and one long Ag–I distances [2.826(2), 2.859(2), 2.933(2), and 3.000(3) Å, respectively].

The stacking of **1** is intimately associated with the role played by the electrostatic interaction between the $(bmph)^{2+}$ cations and the silver halide polyanions in the crystal. As can be seen from Figure 1(c), groups of $(bmph)^{2+}$ cations girdle the columnar stacks, and it is this slippage and kinking of the stacks that leads to the recombinatorial structure of the compound, thus forming a so-called organic-inorganic hybrid structure.

[(Hteda)$_4$(Ag$_{12}$I$_{16}$)]$_n$ (2)

The single-crystal X-ray analysis reveals that the crystal structure of complex **2** represents a three-dimensional arrangement. As shown in Figure 2, the basic structural unit of **2** is an $Ag_{12}I_{12}@I$ building block [Figure 2(a)]. If the terminal I(1) atoms are eliminated, the $Ag_{12}I_6@I$ unit forms a quasi-hexagonal antiprism [Figure 2(b)] in which the top and bottom Ag_3I_3 hexagons are not coplanar but take on a chair-like configuration. The Ag–I–Ag angles in this Ag_3I_3 chair-like arrangement are 116.61(5)° and I–Ag–I angles are 120.70(4)°, so the hexagon is distorted to a small extent. An IAg_6 octahedron in the middle of the $Ag_{12}I_6@I$ hexagonal antiprism links two Ag_3I_3 hexagons through μ_3-I(2) and Ag···Ag interactions. This IAg_6 octahedron is greatly distorted, with Ag(2A) and Ag(2A)#6 occupying the axial positions and Ag(2A)#1, Ag(2A)#2, Ag(2A)#3, and Ag(2A)#4 comprising the equatorial plane [symmetry transformations: #1: $-y, x-y, z$; #2: $x-y, x, -z$; #3: $y, -x+y, -z$; #4: $-x+y, -x, z$; #6: $-x, -y, -z$; Ag(2) is distorted therefore only Ag(2A) is discussed]. The μ_6-I(3) atom is located at the center of the octahedron (on a $\bar{3}$ site) and is σ-bonded to six Ag atoms, with six equivalent contacts with Ag(2A) of 2.872(3) Å. These values are much shorter than that in $\{I@[AgI(inh)]_6\}$(3.09 Å).[10] The Ag···Ag distances in **2** range from 2.915(3) Å [Ag(1)–Ag(2A)] to 3.286(4) Å [Ag(2A)–Ag(2A)#2], thereby indicating that weak Ag···Ag interactions may exist. The peripheral terminal I(1) atoms bond with Ag(2A) to complete its tetrahedral coordination geometry.

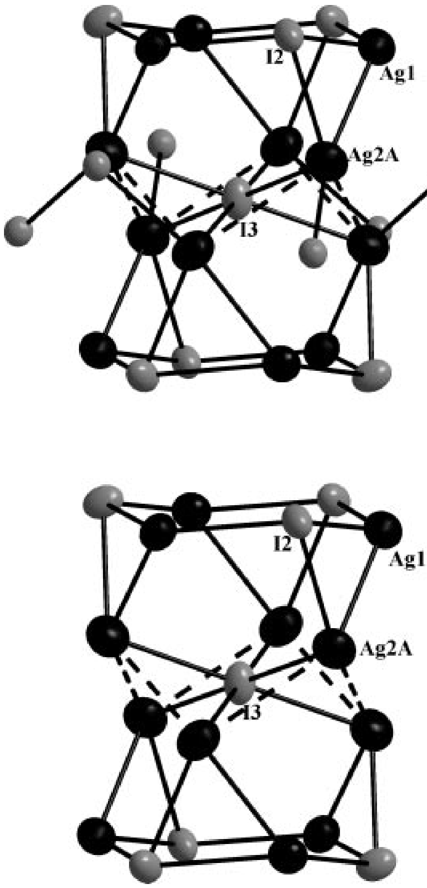

Figure 2. (a) Structure of the $Ag_{12}I_{12}@I$ building block. (b) View of the $Ag_{12}I_6@I$ quasi-hexagonal antiprism.

Although a series of monomeric Ag_6 octahedral clusters[11] and polymeric Ag_6 octahedral units centered by anions such as μ_6-I,[10] μ_6-C_2^{2-}, μ_6-F, μ_3-F, and μ_3-CF_3SO_3[12] have been reported, this $Ag_{12}I_{12}@I$ hexagonal prism cluster centered by μ_6-I was unknown until now. The hexagonal surfaces of the hexagonal prism are parallel to the *ab* plane, and each $Ag_{12}I_{12}@I$ building block links six $Ag_{12}I_{12}@I$ prisms through μ_2-I(4) into a three-dimensional arrangement (Figure 3). The triethylenediamine-based countercations arrange in a parallel fashion between the $Ag_{12}I_{12}@I$ hexagonal prism building blocks and play an important structural direction role. The half-protonation of

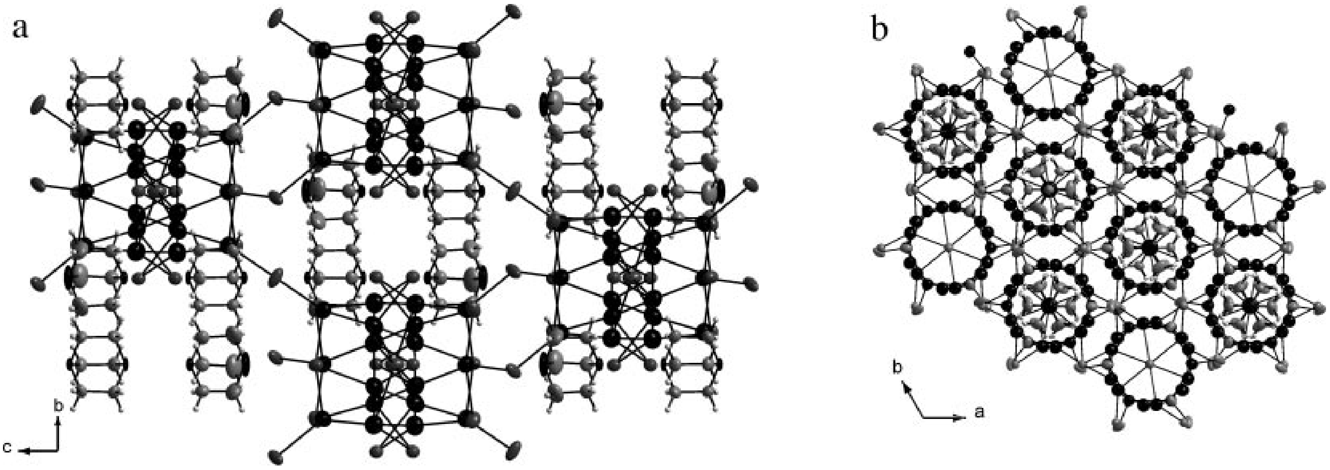

Figure 3. 3D perspective view of **1** based on $Ag_{12}I_{12}@I$ building blocks [(a): side view; (b): top view].

triethylenediamine was determined from the charge-balance requirements, although, to our disappointment, the hydrogen atom of the protonated amine could not be found in the Fourier map. The organic cations line up with intermolecular N···N contacts of about 2.8 Å, which clearly indicate H-bonding distances.

A particularly obvious feature of the polymeric structure is the charge-balanced $Hteda^+$ cations trapped within the cavity of the three-dimensional cavities, which act as the nut and bolt of the tube-like combination (Figure 3). It is worth noting that the formation of the 3D polymeric cluster could be a good illustration of a cation-induced self-assembly reaction. In addition, although there are many examples of self-assembly induced or controlled by cations {such as $[(Et_3NC_6H_{12}NEt_3)_2(Ag_5I_7)]_n$ (unpublished work) and $[Ag^{II}(tmc)(BF_4)]_\infty{}^+$},[13] complex **2** represents the first three-dimensional product of an Ag/I assembly induced by a cation.

It is known that the formation of anionic complexes of the type $[Ag_lX_k]^{(k-l)-}$ is strongly dependent on the countercation and the nature of the halide.[14] In the case of iodide, the ions $[AgI_3]^{2-}$, $[Ag_2I_4]^{2-}$, and $[Ag_4I_8]^{4-}$ have been reported.[3] To the best of our knowledge, polymer **1** is a new example of a 1D Ag/I coordination polymer, and, more importantly, **2** is the first example of a three-dimensional product of Ag/I assembly based on weak Ag···Ag interactions and an organic template.

Optical Limiting Effect Measurement

The optical limiting results of **1** and **2** are depicted in Figure 4. The result shows that the present compounds exhibit a good optical limiting capacity. The response of the composite is linear to the input energy intensity at the beginning, obeying Beer's law. However, as input energy intensity increases, the light transmittance starts to deviate from the linear response expected due to Beer's law when the input light fluence rises to 0.86 and 0.62 $J\,cm^{-2}$ for **1** and **2**, respectively. The limiting threshold can be defined as the incident fluence at which the solution transmittance falls to 50% of the linear transmittance. The limiting threshold value of **1** and **2** was measured as 1.12 and 0.7 $J\,cm^{-2}$ according to the experimental data. A lower limiting threshold and saturation level provide a greater safety margin for device protection. A comparison of this new compound

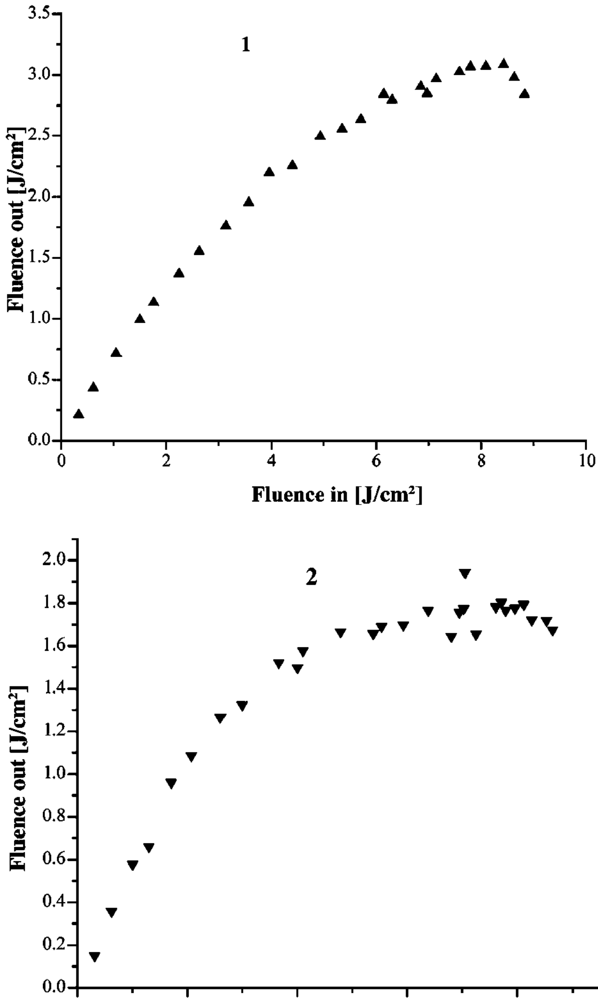

Figure 4. Optical limiting effect of $[(bmph)(Ag_5I_7)]_n$ (**1**) and $[(Hteda)_4(Ag_{12}I_{16})]_n$ (**2**) in a 1.0×10^{-5} M DMF solution.

Table 1. Limiting thresholds of polymeric compounds measured at 532 nm with ns laser pulses.

Polymeric compound	Structure type	Solvent	Limiting threshold [J cm^{-2}]	Ref.
C_{60}		toluene	1.6	[15a]
$\{I@[AgI(inh)]_6\}$	1D polymer	DMF	0.53	[9]
$\{[La(Me_2SO)_8][(\mu\text{-}WSe_4)_3Ag_3]\}_n$	1D polymer	DMF	0.7	[15b]
$[MoS_4Cu_6I_4(py)_4]_n$	2D microporous	DMSO	0.6	[15c]
$[Et_4N]_2[MoS_4Cu_6(CN)_4]_n$	3D cross-framework	DMF	0.28	[15d]
$[(bmph)(Ag_5I_7)]_n$	1D polymer	DMF	1.12	this work
$[(Hteda)_4(Ag_{12}I_{16})]_n$	3D cross-framework	DMF	0.7	this work

with other well-known optical limiting materials will be interesting. Table 1 gives the limiting thresholds of **1**, **2**, polymeric clusters, and C_{60}.[15] It is clear that the limiting performance of **1** in DMF solution is two times better than that displayed by C_{60}. It has been universally accepted that the assembly of monomeric cluster units into a polymer will bring an enhancement of the optical limiting effect.[16] Among the structure–optical limiting (OL) property correlation of clusters and polymers, the heavy atom effect also plays an important role.[2] So, as far as this work is concerned, the heavier atoms Ag and I, together with the polymeric aggregation, play a vital role in determining its OL properties. The successful synthesis of coordination polymeric clusters containing a polyiodide complex paves the way for the quick and facile preparation of novel OL materials.

Thermogravimetric Analysis

The thermogravimetric analysis (TGA) results for **1** show that the weight loss between 40 and 240 °C is 1.76%, which might correspond to the loss of DMF solvent molecules absorbed on the crystal surface. This complex is thermally stable until around 260 °C, and then loses 30.38% of its weight in the temperature range 260–450 °C. Because isolated $(bmph)^{2+}$ molecules take the role of countercations, the framework collapses during the removal of the organic components. This stage can be attributed to the loss of $(bmph)\cdot I_2$ (calcd. 30.85%).

The polymeric cluster **2** shows remarkable thermal stability. Thermal gravimetric analysis for **2** shows no weight loss up to 310 °C. Weight loss under heating starts at 355 °C and finishes at 980 °C.

Conclusions

Two organically templated hybrid silver iodides, namely $[(bmph)(Ag_5I_7)]_n$ (**1**) and $[(Hteda)_4(Ag_{12}I_{16})]_n$ (**2**), have been obtained as good quality single crystals by a direct method. Structural analyses indicate that both compounds consist of uncoordinated structure-directing molecules and an inorganic moiety that is tuned by organic SDAs. Complex **1** presents a one-dimensional chain structure, whereas the inorganic moiety of **2** is the first example of an Ag/I coordination polymer based on Ag···Ag weak interactions and an organic template. Both compounds possess optical limiting activity.

Experimental Section

General Remarks: All chemicals except $bmph\cdot I_2$ were of reagent grade quality from commercial sources and were used without further purification. C, H, N analyses were carried out with a Vario EL III element analyzer. IR spectra were recorded with a Nicolet Co. Magna-IR 750 spectrometer as KBr pellets in the region 4000–400 cm^{-1}. Thermal stability (TG-DTA) studies from room temperature to 800 °C (for **1**) and 1200 °C (for **2**) under nitrogen with a heating rate of 10 °C min^{-1} were performed with a Perkin–Elmer TGA 7 instrument. The optical limiting behaviors were investigated by fluence-dependent transmittance measurements. Radiation with a wavelength of 532 nm was provided by a Q-switched Nd:YAG laser with a pulse duration of 8 ns.

Synthesis of $bmph\cdot I_2$: $bmph\cdot I_2$ was prepared as reported in the literature:[17]

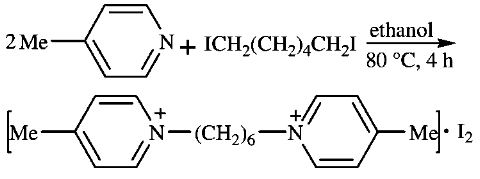

Table 2. Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	$C_{18}H_{26}Ag_5I_7N_2$	$C_{12}H_{24}Ag_6I_8N_4$
Formula mass	1698.06	1886.77
Crystal system	triclinic	hexagonal
Space group	$P\bar{1}$	$R\bar{3}c$
a [Å]	8.5704(17)	13.3373(19)
b [Å]	11.886(2)	13.3373(19)
c [Å]	18.170(4)	63.537(13)
α [°]	103.93(3)	90.00
β [°]	98.16(3)	90.00
γ [°]	102.05(3)	120.00
V [Å^3]	1720.4(6)	9788(3)
Z	2	12
D_c [g cm^{-3}]	3.278	3.841
μ [mm^{-1}]	9.087	11.111
F(000)	1508	9960
Reflections, total	13669	30308
Reflections, unique	6830	2510
Reflections, observed	3574	1570
Goodness-of-fit on F^2	0.964	0.925
No. of parameters refined	289	101
R_1 [$I > 2\sigma(I)$][a]	0.0589	0.0396
wR_2 [$I > 2\sigma(I)$][b]	0.1364	0.1131
Residual electron density [e Å^3]	2.213, –2.280	2.847, –2.788

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

Table 3. Selected bond lengths [Å] and angles [°] for **1** and **2**.

Compound **1**[a]			
Ag(1)–I(1)	2.866(2)	Ag(1)–I(3)	2.827(2)
Ag(1)–I(4)	2.968(2)	Ag(1)–I(5)	2.942(2)
Ag(2)–I(1)	2.867(2)	Ag(2)–I(5)	2.872(2)
Ag(2)–I(7)	2.891(2)	Ag(2)–I(6)	2.856(2)
Ag(3)–I(1)	2.887(2)	Ag(3)–I(2)	2.814(2)
Ag(3)–I(4)	2.967(2)	Ag(3)–I(7)	2.860(2)
Ag(4)–I(2)	2.779(2)	Ag(4)–I(4)	3.067(3)
Ag(4)–I(6)#2	2.839(3)	Ag(4)–I(7)#2	3.007(3)
Ag(5)–I(3)	2.826(2)	Ag(5)–I(4)	3.000(3)
Ag(5)–I(6)#2	2.859(2)	Ag(5)–I(5)#2	2.933(2)
Ag(1)–Ag(2)	3.086(2)	Ag(1)–Ag(3)	3.124(2)
Ag(1)–Ag(5)	3.333(2)	Ag(2)–Ag(4)#1	3.038(3)
Ag(2)–Ag(5)#1	3.140(2)	Ag(2)–Ag(3)	3.177(2)
Ag(3)–Ag(4)	3.361(3)	Ag(4)–Ag(2)#2	3.038(3)
Ag(4)–Ag(5)	3.149(3)	Ag(5)–Ag(2)#2	3.140(2)
Ag(1)–I(1)–Ag(2)	65.14(6)	Ag(1)–I(1)–Ag(3)	65.78(6)
Ag(1)–I(4)–Ag(5)	67.90(6)	Ag(1)–I(4)–Ag(4)	95.36(7)
Ag(2)–I(1)–Ag(3)	67.03(6)	Ag(2)–I(5)–Ag(1)	64.11(5)
Ag(2)–I(5)–Ag(5)#1	65.49(5)	Ag(2)–I(6)–Ag(5)#1	66.66(6)
Ag(2)–I(7)–Ag(4)#1	61.98(6)	Ag(3)–I(4)–Ag(5)	103.71(7)
Ag(3)–I(4)–Ag(4)	67.66(6)	Ag(3)–I(7)–Ag(2)	67.05(6)
Ag(3)–I(7)–Ag(4)#1	126.93(7)	Ag(3)–I(4)–Ag(1)	63.52(5)
Ag(4)–I(2)–Ag(3)	73.86(6)	Ag(4)#1–I(6)–Ag(2)	64.48(7)
Ag(4)#1–I(6)–Ag(5)#1	67.11(7)	Ag(5)–I(3)–Ag(1)	72.26(6)
Ag(5)–I(4)–Ag(4)	62.53(6)	Ag(5)#1–I(5)–Ag(1)	126.38(6)
I(1)–Ag(1)–I(5)	110.94(6)	I(1)–Ag(1)–I(4)	107.63(7)
I(1)–Ag(1)–Ag(2)	57.43(5)	I(1)–Ag(1)–Ag(3)	57.43(5)
I(1)–Ag(2)–I(5)	113.02(7)	I(1)–Ag(2)–I(7)	105.71(7)
I(1)–Ag(3)–I(4)	107.10(6)	I(2)–Ag(3)–I(7)	113.48(7)
I(2)–Ag(3)–I(1)	110.02(7)	I(2)–Ag(3)–I(4)	97.83(6)
I(2)–Ag(4)–I(6)#2	125.83(9)	I(2)–Ag(4)–I(7)#2	103.16(7)
I(2)–Ag(4)–Ag(2)#2	153.07(9)	I(2)–Ag(4)–I(4)	96.31(7)
I(3)–Ag(1)–I(1)	119.02(8)	I(3)–Ag(1)–I(5)	106.24(7)
I(3)–Ag(1)–I(4)	98.48(6)	I(3)–Ag(5)–I(6)#2	114.42(8)
I(3)–Ag(5)–I(5)#2	114.64(7)	I(3)–Ag(5)–I(4)	97.75(6)
I(5)–Ag(1)–I(4)	114.22(7)	I(5)–Ag(2)–I(7)	111.57(8)
I(5)#2–Ag(5)–I(4)	111.91(7)	I(6)–Ag(2)–I(1)	103.37(7)
I(6)–Ag(2)–I(5)	109.02(7)	I(6)–Ag(2)–I(7)	113.92(7)
I(6)#2–Ag(4)–I(7)#2	111.00(7)	I(6)#2–Ag(4)–I(4)	109.35(8)
I(6)#2–Ag(5)–I(5)#2	107.27(7)	I(6)#2–Ag(5)–I(4)	110.70(7)
I(7)–Ag(3)–I(1)	105.99(7)	I(7)–Ag(3)–I(4)	121.97(8)
I(7)#2–Ag(4)–I(4)	109.80(8)		
Compound **2**[b]			
Ag(1)–I(4)	2.8115(12)	Ag(1)–I(2)	2.8121(14)
Ag(1)–I(2)#1	2.8630(14)	Ag(1)–I(1)	2.9108(14)
Ag(2A)–I(1)	2.779(3)	Ag(2A)–I(3)	2.872(3)
Ag(2A)–I(2)#2	2.792(3)	Ag(2A)–I(1)#3	2.928(3)
Ag(2A)#1–I(3)	2.872(3)	Ag(2A)#2–I(1)	2.928(3)
Ag(2A)#2–I(3)	2.872(3)	Ag(2A)#3–I(2)	2.792(3)
Ag(2A)#3–I(3)	2.872(3)	Ag(2A)#4–I(3)	2.872(3)
Ag(2A)#6–I(3)	2.872(3)	Ag(1)–Ag(2A)#2	2.915(3)
Ag(2A)–Ag(2A)#2	3.286(4)		
Ag(1)–I(2)–Ag(1)#4	116.60(5)	Ag(1)#5–I(4)–Ag(1)	131.01(6)
Ag(1)–I(1)–Ag(2A)#2	59.89(5)	Ag(1)#3–Ag(2A)–I(1)#3	59.76(6)
Ag(2A)–I(3)–Ag(2A)#1	110.21(5)	Ag(2A)–I(1)–Ag(1)	95.75(6)
Ag(2A)–I(1)–Ag(2A)#2	70.25(10)	Ag(2A)#2–I(3)–Ag(2A)#3	110.21(5)
Ag(2A)#2–I(3)–Ag(2A)#5	110.21(5)	Ag(2A)#2–I(3)–Ag(2A)#4	180.00(9)
Ag(2A)#2–I(3)–Ag(2A)	69.79(5)	Ag(2A)#2–I(3)–Ag(2A)#1	69.79(5)
Ag(2A)#3–I(2)–Ag(1)	97.91(7)	Ag(2A)#3–I(2)–Ag(1)#4	62.04(6)
Ag(2A)#3–I(3)–Ag(2A)#5	110.21(5)	Ag(2A)#3–I(3)–Ag(2A)#4	69.79(5)
Ag(2A)#3–I(3)–Ag(2A)	69.79(5)	Ag(2A)#3–I(3)–Ag(2A)#1	180.00(16)
Ag(2A)#4–I(3)–Ag(2A)	110.21(5)	Ag(2A)#4–I(3)–Ag(2A)#1	110.21(5)
Ag(2A)#5–I(3)–Ag(2A)#4	69.79(5)	Ag(2A)#5–I(3)–Ag(2A)	180.00(9)
Ag(2A)#5–I(3)–Ag(2A)#1	69.79(5)	I(1)–Ag(2A)–I(3)	107.44(8)
I(1)–Ag(2A)–I(1)#3	113.29(9)	I(2)–Ag(1)–I(2)#1	120.70(5)
I(2)–Ag(1)–I(1)	111.94(4)	I(2)#1–Ag(1)–I(1)	112.10(4)
I(2)#2–Ag(2A)–I(3)	105.89(9)	I(2)#2–Ag(2A)–I(1)#3	113.70(8)
I(3)–Ag(2A)–I(1)#3	103.52(9)	I(4)–Ag(1)–I(2)	108.06(4)
I(4)–Ag(1)–I(2)#1	98.05(4)	I(4)–Ag(1)–I(1)	103.47(4)

[a] Symmetry transformations used to generate equivalent atoms: #1: *x* + 1, *y*, *z*; #2: *x* – 1, *y*, *z*; #3: –*x*, –*y*, –*z* + 1; #4: –*x*, –*y*, –*z*. [b] Symmetry transformations used to generate equivalent atoms: #1: –*y*, *x* – *y*, *z*; #2: *x* – *y*, *x*, –*z*; #3: *y*, –*x* + *y*, –*z*; #4: –*x* + *y*, –*x*, *z*; #5: –*x*, –*y*, –*z*.

Synthesis of [(bmph)(Ag_5I_7)]$_n$ (1): A suspension of AgI (0.234 g, 1.0 mmol), NaI (0.225 g. 1.5 mmol), and bmph·I_2 (0.262 g, 0.5 mmol) in DMF (10 mL) was stirred at 60 °C for 40 min. During the course of stirring, a small amount of NaI was added until the solution became colorless and clear. The resultant solution was adjusted to pH = 5.0 with 10% HI solution. After filtration, diethyl ether (10 mL) was slowly condensed into the solution. Colorless block crystals of **1** were isolated with a yield of 0.132 g (38.9%, based on Ag) after 4 d. $C_{18}H_{26}Ag_5I_7N_2$ (1698.1): calcd. C 12.73, H 1.54, N 1.64; found C 12.75, H 1.52, N 1.65. IR: $\tilde{\nu}$ = 3049 (m), 2932 (s), 2854 (m), 2445 (s), 1790 (s), 1637 (s), 1571 (m), 1510 (m), 1465 (s), 1384 (s), 1365 (s),1304 (w), 1256 (m), 1177 (s), 1115 (w), 1031 (m), 835 (s), 811 (s), 731 (m), 700 (m) cm^{-1}.

Synthesis of [(Hteda)$_4$($Ag_{12}I_{16}$)]$_n$ (2): A mixture of AgI (0.117 g, 0.5 mmol), NaI (0.225 g. 1.5 mmol), and teda (0.247 g, 2.2 mmol) in 10 mL of DMF was stirred until it became colorless and clear and was then adjusted to pH = 5.0 with 10% HI solution. Colorless crystals of **2** were isolated with a yield of 54.3% after 5 d. $C_{12}H_{26}Ag_6I_8N_4$ (1888.8): calcd. C 7.63, H 1.39, N 2.97; found C 7.69, H 1.35, N 2.80. IR: $\tilde{\nu}$ = 3437 (s), 2968 (m), 2890 (w), 2788 (m), 2637 (m), 1685 (w), 1637 (s), 1459 (s), 1177 (s), 1051 (m), 983 (s), 897 (s), 844 (s), 788 (s), 599 (s) cm^{-1}.

X-ray Crystallography: X-ray data for both complexes were collected at 293(2) K with a Rigaku Weissenbery IP diffractometer using graphite-monochromated Mo-K_α radiation [λ = 0.71069 Å]. Correction for Lp factors and multi-scan absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.[18] All non-hydrogen atoms of **1** and **2** were treated anisotropically. CH hydrogen atoms were generated geometrically. Experimental X-ray data are listed in Table 2, and selected bond lengths and angles are given in Table 3. CCDC-289211 (**1**) and -280903 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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