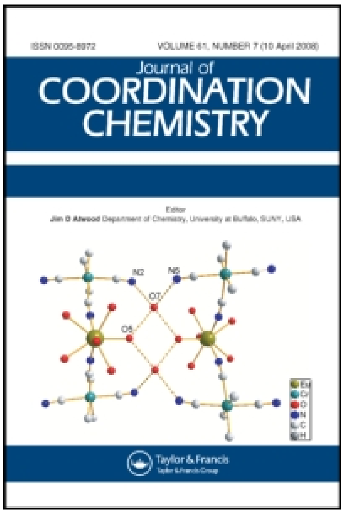

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Self-assembly and third-order nonlinear optical property (NLO) of one-dimensional silver(I) aggregation bridged by iodide

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SELF-ASSEMBLY AND THIRD-ORDER NONLINEAR OPTICAL PROPERTY (NLO) OF ONE-DIMENSIONAL SILVER(I) AGGREGATION BRIDGED BY IODIDE

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A new synthetic method was employed to prepare the silver(I) iodide polymer $\{[NEt_4]_3[Ag_6I_9]\}_n$ with a one-dimensional double-chain. A mixture of solid Et_4NI, AgI and $[NH_4]_2[MoO_2S_2]$ was heated gently and the reaction residue was extracted with MeCN. Orange-red monoclinic crystals were obtained at room temperature. The infinite chains of $[Ag_6I_9]_n^-$ consist of edge-shared square pyramids, in which iodides bridge silver atoms such that the geometry around the silver atoms is tetrahedral. A detailed study of its third-order nonlinear optical property *via* *Z*-scan is reported. The polymer $\{[NEt_4]_3[Ag_6I_9]\}_n$ shows a very strong self-focusing refractive effect with efficient third-order NLO susceptibility $\chi^{(3)}$ of 6.0×10^{-11} esu.

Keywords: Silver iodide; One-dimensional double chains; Tetragonal pyramid; Third-order NLO property

INTRODUCTION

Polyhalogen–metal complexes show a wide variety of solid-state structural features, including discrete geometries of varying nuclearity or polymeric extended systems [1]. Such coordination complexes are useful as magnets and solid conductors, and as liquid media for chemical reactions, catalysts and optical materials [2]. Interest in this field has produced several such species [3–5], among which Cu(I) complexes are prolific. Owing to the diversity of the Cu(I) coordination geometries and the ability of the halide ions to bridge between the diamagnetic metal ions, the structural chemistry of Cu(I) halides in the solid state is exceptionally diverse [6,7]. Subramanian and Hoffmann described some examples, including two-, three- or four-coordination with linear, trigonal planar and tetrahedral geometries [1].

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There are discrete or extended structures among copper(I) halide salts. In most cases, halide ions exist between Cu atoms as bridges, of which μ_2, μ_3, and tetrahedral μ_4 coordination of X (X = Cl, Br, I) are typical. Square pyramidal μ_4 coordination of X is atypical, and can be attributed to the different hybridization of the X ions [1]. The bridging ability and the hybridization mode of halide ions affect structures. For example, X = I prefers square pyramidal coordination. A secondary reason can be related to metal ions. Most reported ubiquitous structures contain Cu atoms. Comparatively, silver or gold(I) structures are much less common. The argentous halides AgF, AgCl and AgBr adopt the NaCl structure, while AgI prefers the wurtzite structure under normal conditions of temperature and pressure [8,9]. For gold(I) halides, structural information is available only for AuI, whose structure consists of bent chains made up of alternating Au and I atoms.

Our research work focuses on coordination polymers and polymeric transition metal chalcogenides. During synthesis of polymeric M–Ag–S (M = Mo, W) clusters, we serendipitously obtained the silver(I) iodide salt $\{[NEt_4]_3[Ag_6I_9]\}_n$, which has the same polymeric anion $[Ag_6I_9]_n^-$ as that in the reported salt $\{[NMe_4][Ag_2I_3]\}_n$ [10]. The structure is based on double chains comprising edge-shared square pyramids $[AgI_4]$. Previous studies on halogen metal salts have usually focused on structural description, seldom dealing with properties. In this paper, besides the structural description of the polymer $\{[NEt_4]_3[Ag_6I_9]\}_n$, we also study its third-order NLO property by *Z*-scan techniques. It exhibits excellent self-focusing effects with the third-order NLO susceptibility $\chi^{(3)}$ of 6.0×10^{-11} esu. This polymeric silver salt has a strong NLO capability, compared to many studied transition metal–sulfur clusters [11,12] and metal phenylacetylides [13], and it introduces a new candidate for NLO materials. In this article, the heavy atom effect has come into play in increasing its NLO properties.

EXPERIMENTAL

$(NH_4)_2MoO_2S_2$ was obtained by the procedure described in the literature [14]. The other chemicals were of A.R. grade and used without further purification. Elemental analyses were performed with a Perkin-Elmer 240C instrument.

Preparation

A thoroughly ground mixture of $(NH_4)_2MoO_2S_2$ (0.11 g, 0.5 mmol), AgI (0.24 g, 1 mmol) and Et_4NI (0.26 g, 1 mmol) was put into a reaction tube and heated at 90°C for 9 h in a pure nitrogen atmosphere. The orange MeCN (10 cm^3) extract from the brown solid product was obtained after filtration, and allowed to stand at room temperature. After two weeks, reddish-orange crystals (0.095 g) were obtained in an approximate yield of 30% based on AgI. Anal. Calcd. for $C_{24}H_{60}Ag_6I_9N_3$(%): C, 13.21; H, 2.75; N, 1.93. Found: C, 13.11; H, 2.90; N, 1.78.

Crystal Structure Determination

Crystallographic data for the compound were collected using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Rigaku RAXIS-IV image plate area detector. The data were corrected for Lorentz and polarization factors and for absorption using empirical

TABLE I Crystallographic data of $\{[NEt_4]_3[Ag_6I_9]\}_n$

Chemical formula	$C_{24}H_{60}Ag_6I_9N_3$
Formula weight	2180.07
Space group	*Pnma*
Unit cell dimensions (Å, °)	$a = 21.936(4)$, $\alpha = 90$ $b = 12.567(3)$, $\beta = 90$ $c = 18.231(4)$, $\gamma = 90$
V (Å^3)	5025.6 (17)
Z	4
T (K)	291(2)
λ (Å)	0.71073
Crystal size (mm)	0.20 × 0.20 × 0.20
μ (mm^{-1})	7.840
ρ_{calc} (mg cm^{-3})	2.881
$F(000)$	3936
θ range for data collection	1.45 to 25.00°
Reflections collected/unique	12309/4354 [R(int) = 0.0568]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4354/0/218
Goodness-of-fit on F^2	1.148
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0601$, $wR2 = 0.1240$
R indices (all data)	$R1 = 0.1109$, $wR2 = 0.1392$
Extinction coefficient	0.00031(2)
Largest diff. peak and hole (e Å^{-3})	1.130 and −0.963

scan data. The structure was solved with the SHELX program [15], and refined by full-matrix least-squares methods based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically and not refined. Crystal data are summarized in detail in Table I and bond distances and angles are given in Table II.

Nonlinear Optical Measurements

A dimethylformamide (DMF) solution of $\{[NEt_4]_3[Ag_6I_9]\}_n$ with concentration 1.4×10^{-4} mol dm^{-3} was placed in a 1-mm quartz cuvette for optical measurements. Its nonlinear refraction was measured with linearly polarized laser light ($\lambda = 532$ nm; pulse width = 7 ns) generated from a Q-switched and frequency-doubled Nd-YAG laser. The spatial profiles of the optical pulses were nearly Gaussian. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the beam waist was measured to be 30 ± 5 µm. Incident and transmitted pulse energies were measured simultaneously by two-energy detectors (Rjp-735 energy probes, Laser Precision) linked to a computer by an IEEE interface. The nonlinear optical property of the sample was determined by performing Z-scan measurements [16]. An aperture of 0.5-mm radius was placed in front of the detector to assist the measurement of the nonlinear optical self-focusing effect.

RESULTS AND DISCUSSION

Synthesis

Several synthetic strategies have been employed to obtain polyhalogenometal networks. Most conventional methods for synthesizing such complexes involve the reaction of the

TABLE II Selected bond lengths (Å) and bond angles (°) of $\{[NEt_4]_3[Ag_6I_9]\}_n$

Ag(1)–I(1)	2.7947(12)	I(1)–Ag(3)#3	2.8008(12)
Ag(1)–I(4)	2.8080(13)	I(2)–Ag(1)#1	2.9454(14)
Ag(1)–I(3)	2.9155(14)	I(2)–Ag(3)#3	2.9545(13)
Ag(1)–I(2)	2.9453(14)	I(2)–Ag(3)#4	2.9545(13)
Ag(1)–Ag(1)#1	3.372(2)	I(3)–Ag(1)#1	2.9155(14)
Ag(2)–I(4)	2.7957(13)	I(3)–Ag(2)#1	2.9406(13)
Ag(2)–I(5)	2.7972(12)	I(6)–Ag(3)#1	2.9305(13)
Ag(2)–I(3)	2.9406(13)	I(6)–Ag(2)#1	2.9747(13)
Ag(2)–I(6)	2.9747(13)	Ag(3)–I(5)	2.8038(12)
Ag(2)–Ag(2)#1	3.169(2)	Ag(3)–I(6)	2.9305(13)
Ag(3)–I(1)#2	2.8008(12)	Ag(3)–I(2)#2	2.9545(13)
Ag(3)–Ag(3)#1	3.198(2)		
		I(4)–Ag(1)–Ag(1)#1	119.74(3)
I(1)–Ag(1)–I(4)	116.61(5)	I(3)–Ag(1)–Ag(1)#1	54.67(2)
I(1)–Ag(1)–I(3)	116.20(5)	I(2)–Ag(1)–Ag(1)#1	55.08(2)
I(4)–Ag(1)–I(3)	101.43(4)	I(4)–Ag(2)–I(5)	119.45(4)
I(1)–Ag(1)–I(2)	101.50(4)	I(4)–Ag(2)–I(3)	101.10(4)
I(4)–Ag(1)–I(2)	111.58(5)	I(5)–Ag(2)–I(3)	107.27(4)
I(3)–Ag(1)–I(2)	109.75(4)	I(4)–Ag(2)–I(6)	115.47(4)
I(1)–Ag(1)–Ag(1)#1	123.58(3)	I(5)–Ag(2)–I(6)	98.94(4)
I(1)#2–Ag(3)–I(6)	112.09(4)	I(3)–Ag(2)–I(6)	115.10(4)
I(5)–Ag(3)–I(6)	99.85(4)	I(4)–Ag(2)–Ag(2)#1	122.31(3)
I(1)#2–Ag(3)–I(2)#2	101.13(4)	I(5)–Ag(2)–Ag(2)#1	118.10(3)
I(5)–Ag(3)–I(2)#2	113.83(4)	I(3)–Ag(2)–Ag(2)#1	57.40(2)
I(6)–Ag(3)–I(2)#2	113.96(4)	I(6)–Ag(2)–Ag(2)#1	57.82(2)
I(1)#2–Ag(3)–Ag(3)#1	125.65(3)	I(1)#2–Ag(3)–I(5)	116.65(4)
I(5)–Ag(3)–Ag(3)#1	117.68(3)	Ag(1)–I(2)–Ag(3)#4	112.34(4)
I(6)–Ag(3)–Ag(3)#1	56.93(2)	Ag(3)#3–I(2)–Ag(3)#4	65.54(4)
I(2)#2–Ag(3)–Ag(3)#1	57.23(2)	Ag(1)–I(3)–Ag(1)#1	70.66(5)
Ag(1)–I(1)–Ag(3)#3	81.11(4)	Ag(1)–I(3)–Ag(2)	76.62(4)
Ag(1)#1–I(2)–Ag(1)	69.84(5)	Ag(1)#1–I(3)–Ag(2)	113.06(5)
Ag(1)#1–I(2)–Ag(3)#3	112.34(4)	Ag(1)–I(3)–Ag(2)#1	113.06(5)
Ag(1)–I(2)–Ag(3)#3	76.14(3)	Ag(1)#1–I(3)–Ag(2)#1	76.62(4)
Ag(1)#1–I(2)–Ag(3)#4	76.14(3)	Ag(3)#1–I(6)–Ag(2)#1	77.90(3)
Ag(2)–I(3)–Ag(2)#1	65.20(5)	Ag(3)–I(6)–Ag(2)#1	111.82(4)
Ag(2)–I(4)–Ag(1)	80.76(4)	Ag(3)#1–I(6)–Ag(2)	111.82(4)
Ag(2)–I(5)–Ag(3)	83.03(4)	Ag(3)–I(6)–Ag(2)	77.90(3)
Ag(3)#1–I(6)–Ag(3)	66.14(4)	Ag(2)#1–I(6)–Ag(2)	64.37(4)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1/2, z$; #2 $x+1/2, y, -z+3/2$; #3 $x-1/2, y, -z+3/2$; #4 $x-1/2, -y+1/2, -z+3/2$.

corresponding metal halides with Q^+X^- ($Q = Na$, $[NR_4]$; $X = Cl$, Br, I). Redox processes, heating solutions and hydrothermal reactions have been used to prepare such species. However, under normal conditions, such complexes can only be obtained when CuX exists. Polyhalogenosilver complexes are seldom obtained because of the poor solubility of AgI in common organic solvents and water. Here, we prepared polymer $\{[NEt_4]_3[Ag_6I_9]\}_n$ by solid-state reaction at low temperature. The solid-state method removes the disadvantage of the low solubility of AgI; an organic solvent is used to extract the product when the reaction is finished.

Structure Description

The structure is composed of polymeric $[Ag_6I_9]_n^-$ anions and countercations $[NEt_4]^+$ (Fig. 1). All the Ag and I atoms arrange in pyramidal geometry with Ag atoms as the bases. In Fig. 2, we can see an extended double-chain, bridged by iodine atoms. Ag atoms adopt distorted tetrahedral geometry. The distortions of the polyhedron

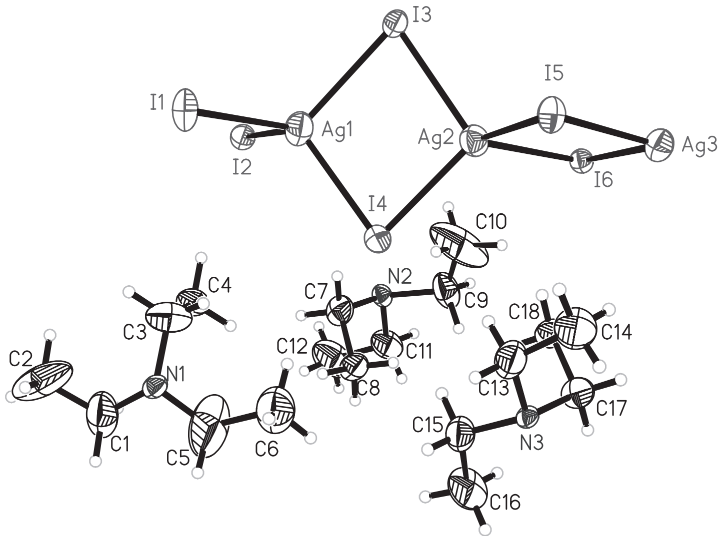

FIGURE 1 The ORTEP diagram of the {$[NEt_4]_3[Ag_6I_9]$} structure.

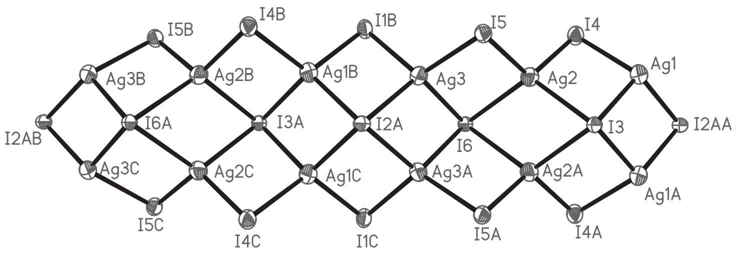

FIGURE 2 The polymeric chain of $[Ag_6I_9]_n^-$, which is based on the edge-shared pyramids [μ_4-IAg_4].

around Ag are slight. Ag–I distances range from 2.7947(12) to 2.9747(13) Å. The I–Ag–I angles are in the range 98.94(4)–116.65(4)°.

I ions bridge in two ways. I(2), I(3) and I(6) are involved in μ_4 square pyramidal geometry, surrounded by four Ag atoms. Each μ_4-I atom occupies the apex of a square pyramid. I(1), I(4) and I(5) have a μ_2-bridging mode. In Fig. 2, the μ_4-I atoms are alternately above and below the plane of the Ag atoms, and μ_2-I atoms also alternate with the μ_4-I atoms. The μ_4-I–Ag distances vary from 2.9155(14) to 2.9747(13) Å, while those of μ_2-I–Ag are from 2.7947(12) to 2.8080(13) Å. An obvious feature of the polymeric chain $[Ag_6I_9]_n^-$ is the existence of acute Ag–I–Ag bridging bond angles, which leads to short Ag···Ag distances. This effect is always apparent when $X = I$, as has been previously stated in the literature [17]. The '*cis*' Ag–I–Ag angles in the bridges are typically in the range 64.37(4) to 83.03(4)°. The acute angles present in μ_4 bridges are in the range 64.37(4)–77.90(3)°, and lead to short Ag···Ag distances within the chains. In this system, the Ag···Ag distances are 3.679 Å (average) along the chain direction and 3.661 Å (average) perpendicular to the chain direction. The distances are much longer than those found in $[Ag_2Cl_3]_n^-$ (3.348 Å) and $[Ag_2Br_3]^-$ (3.078 Å) [18].

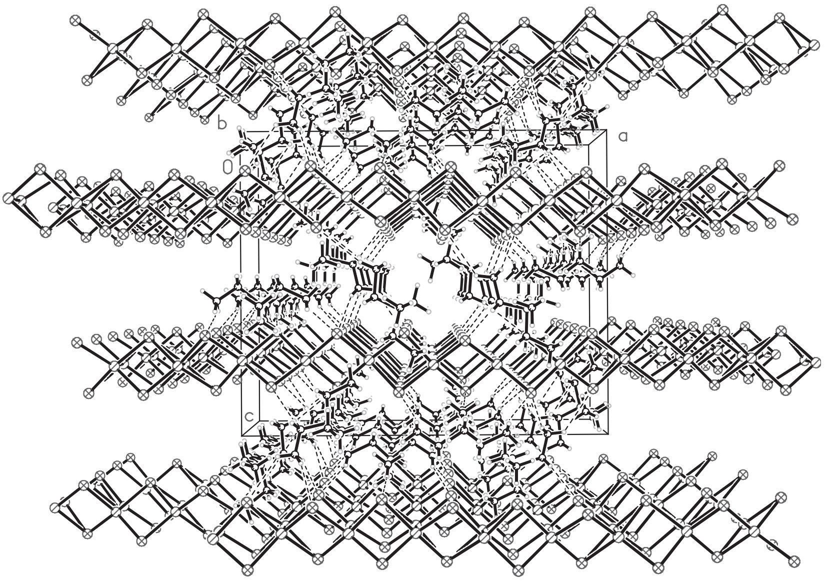

FIGURE 3 Packing feature of $\{[NEt_4]_3[Ag_6I_9]\}_n$ along the crystallographic *a* direction.

The polymeric $[Ag_6I_9]_n^-$ anion is a double chain running parallel to the *a* axis. The chain consists of edge-sharing AgI_4 tetrahedra, and the $[Ag_6I_9]^-$ unit can be a unit synthon for developing extended structures. Parallel chains form layers in the *c* direction. $[NEt_4]^+$ cations spread over the space between two neighboring layers to make up the electronic balance. A view from the crystallographic *b* direction shows a layered arrangement (Fig. 3). Additionally, hydrogen bonding exists among different infinite chains. Hydrogen atoms from CH_3 interact with I, the interacting distances being about 3.1 Å.

NLO Property

The NLO property of $\{[NEt_4]_3[Ag_6I_9]\}_n$ was investigated *via* *Z*-scan techniques [16]. Dividing the normalized *Z*-scan data obtained under the closed aperture configuration allowed assessment of the data. The refractive index n_2 can be derived by Eq. (1):

$$n_2^{\mathrm{eff}} = \frac{\lambda a_0}{0.812\pi I(1 - e^{-a_0 L})} \cdot \Delta T_{V-P} \tag{1}$$

where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak positions.

Figure 4 describes the normalized NLO refractive curve in DMF solution with concentration of $1.4 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, and shows that the compound has a very strong nonlinear self-focusing effect. The difference between normalized transmittance values at valley and peak positions, ΔT_{V-P}, is 0.81, and the difference along the *Z*-axis at valley and peak positions, ΔZ, is about 12. In accordance with Eq. (1), n_2 can be calculated to be $4.34 \times 10^{-17}\,\mathrm{m^2\,W^{-1}}$.

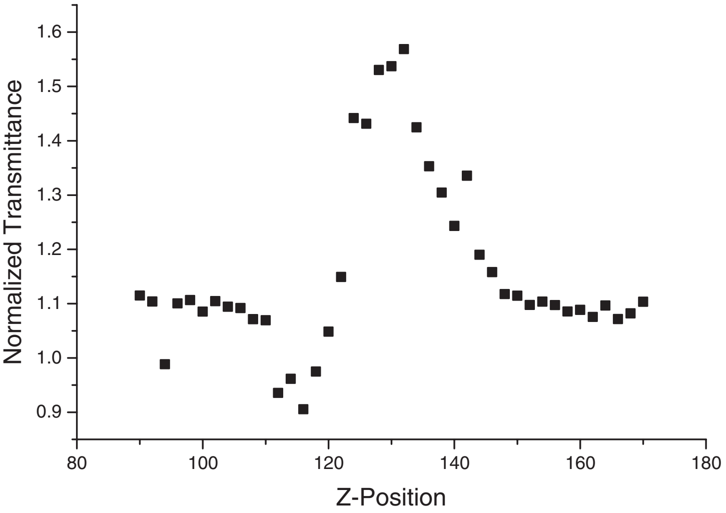

FIGURE 4 Z-scan data of $\{[NEt_4]_3[Ag_6I_9]\}_n$ in 1.4×10^{-4} mol dm^{-3} DMF solution, obtained by dividing the normalized Z-scan measured under a closed aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration, showing a strong self-focusing effect.

From the n_2 value, the modulus of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by Eq. (2):

$$|\chi^{(3)}| = \left|\frac{cn_0^2}{80\pi}\, n_2\right| \tag{2}$$

where n_0 is the linear refractive index of the sample. $\chi^{(3)}$ is calculated to be 6.0×10^{-11} esu. We can use the hyperpolarizability γ to represent the NLO properties of neat materials. $|\chi^{(3)}| = |\gamma| \times NF^4$, where N is the number density of the investigated sample and $F^4 = 3$ is the local field correction factor. The γ value can be derived as 3.24×10^{-27} esu.

Comparing the NLO data to those of previously reported clusters, we find that the title polymer $\{[NEt_4]_3[Ag_6I_9]\}_n$ possesses a good NLO property (Table III). Investigating its components and structural type, we can deduce some reasons: (1) The constituent elements of this polymer are heavy. The incorporation of Ag(I) and I into a polymeric framework introduces more sublevels into the energy hierarchy as compared to carbon-based molecules with the same number of skeleton atoms, permitting more spin-allowed exited state–excited state transitions to take place and hence larger σ_∞ values [11]. (2) Since high polarizability is crucial to nonlinear optical responses, it is advantageous to choose metals with a completely filled d shell. Ag(I) satisfies this, and many examples verified that $\chi^{(3)}$ values for Ag(I)-containing polymers were larger than those of the other metal polymers. (3) Previous work on the NLO properties of organic polymers and clusters suggests that $\chi^{(3)}$ or γ increase with the degree of oligomerization. In this work, the chain is polymerized. The effective conjugation length increases and excitation energies (ΔE) of the MICT bands decrease, resulting in significant enhancement of the third-order NLO responses. (4) The asymmetric arrangement of the ligands around the metal atoms produces an asymmetric

TABLE III Comparison of NLO hyperpolarizability γ values between the title complex $\{[NEt_4]_3[Ag_6I_9]\}_n$ and some other compounds

Compounds	γ(esu)	*Ref.*
$\{[NEt_4]_2[MoS_4Cu_4(CN)_4]\}_n$	1.15×10^{-29}	[12]
$\{[NEt_4]_2[WS_4Cu_4(CN)_4]\}_n$	1.26×10^{-29}	[12]
$\{[Et_4N]_2[WS_4Cu_4(SCN)_4(2\text{-pic})_4]$	9.42×10^{-32}	[18]
$\{[Et_4N]_2[MoS_4Cu_4(SCN)_4(2\text{-pic})_4]$	1.29×10^{-31}	[18]
$[Ru(dmb)_2(PNOPH)][ClO_4]_2 \cdot 2H_2O$	6.46×10^{-29}	[19]
$[Ru(dmb)_2(MNOPH)][ClO_4]_2 \cdot H_2O$	3.99×10^{-29}	[19]
$[Ru(dmb)_2(ONOPH)][ClO_4]_2 \cdot H_2O$	5.09×10^{-29}	[19]
$[Ru(dmb)_2(PNOP)][ClO_4] \cdot H_2O$	4.87×10^{-29}	[19]
$[Ru(dmb)_2(MNOP)][ClO_4] \cdot H_2O$	3.65×10^{-29}	[19]
$[Ru(dmb)_2(ONOP)][ClO_4] \cdot 3H_2O$	4.77×10^{-29}	[19]
$[MoOS_3Cu_2(PPh_3)_3]$	9.8×10^{-28}	[20]
$[WOS_3Cu_2(PPh_3)_4]$	9×10^{-29}	[20]
$[Ru(bpy)_2(fmp)][ClO_4]_2$	7.34×10^{-29}	[21]
$[Ru(bpy)_2(H_2bplb)][ClO_4]_2$	13.86×10^{-29}	[21]
$[(bpy)_2Ru(H_2bplb)Ru(bpy)_2][ClO_4]_2$	26.85×10^{-29}	[21]
$[(n\text{-}Bu)_4N]_2[MoOS_3(CuSCN)_3]$	4.8×10^{-29}	[22]
trans-$[Mo(CO)_4(PPh_3)_2]$	3.3×10^{-32}	[23]
cis-$[Mo(CO)_4(PPh_3)_2]$	1.7×10^{-31}	[23]
C_{60}	7.5×10^{-34}	[24]
C_{70}	1.3×10^{-33}	[24]
$\{[NMe_4]_2[MoOS_3Cu_3(\mu_2\text{-}I)_3]\}_n$	3.39×10^{-28}	[25]
$\{[NMe_4]_2[WOS_3Cu_3(\mu_2\text{-}I)_3]\}_n$	1.02×10^{-26}	[25]
$\{[NEt_4]_3[Ag_6I_9]\}_n$	3.24×10^{-27}	This work

electronic distribution, which is desirable for NLO properties. Though all Ag–I bonds are all σ-bonds, the bond lengths around one Ag(I) atom are unequal, giving rise to third-order NLO responses. (5) Metal–metal bonding may contribute to electron delocalization in the cluster or polymers. The Ag···Ag interaction of approximately 3.2 Å is weak, but may function to enhance the third-order NLO effect. Metal–metal bonding is important if a strong M–M bond exists.

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