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Combination of N-Arylstilbazolium Organic Nonlinear Optical Chromophores with Iodoargentates: Structural Diversities and Optical Properties

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ABSTRACT: Combination of N-arylstilbazolium organic nonlinear optical chromophores with iodoargentates results in five new hybrids, i. e., $[(DAST)(Ag_2I_3)]_n$ (1), $[(DMAQS)(Ag_2I_3)]_n$ (2), $[(DPAS)(Ag_2I_3)]_n$ (3), $[(DPTAS)_2(Ag_5I_7)]_n$ (4) and $[(CEMAS)_2(Ag_5I_7)]_n$ (5). Among them, the former four are centrosymmetric, and 5 is noncentrosymmetrical (space group *Pna2*₁) with the introduction of cyano group in organic chromophore. The $(Ag_5I_7)_n^{2h}$ chains in 4 and 5 are special, in which that of 4 is constructed from Ag_5I_{10} building blocks with a μ_6 -I σ -bonding to six Ag ions, and that in 5 is the connection of cubane-like Ag_4I_4 core with bridged AgI₄ tetrahedra. UV/Vis/near-IR adsorptions and near-IR photoluminescences have been observed. All the organic chromophores are stacked as head-to-tail arrangements, resulting in second harmonic generation (SHG) inactive in 1-4. But 5 is SHG active without J-aggregation of organic chromophore, whose symmetry break was driven by the formation of hydrogen bonds around cyano group. The SHG activity of 5 originates from the polarizations of the asymmetric contribution of $Ag_5I_9^{4^+}$ unit mixing with noncentrosymmetrical (CEMAS)₂²⁺ pair. Theoretical calculations were carried out to disclose their electronic structures.

INTRODUCTION

The discovery of new materials possessing photovoltaic conversion, stimuli-responsive chromism, magnetic or nonlinear optical (NLO) properties have attracted considerable interests in the last decade.¹⁻⁴ So far, great effort has been paid to the organic functional materials due to their

structural tenability and fascinating optical properties such as optical signal processing and THz generation.⁵⁻⁸ In this field, particularly interests were paid to the organic molecular crystalline materials due to advantages of high chromophore number density and excellent long-term orientational stability.⁹⁻¹¹ Stilbazolium-type π -delocalized molecules have exhibited the largest molecular hyperpolarizability (β) because of their unique structures with an electron acceptor linked to an electron donor group via a π -conjugated bridge.¹² A typical stilbazolium is 4-*N*,*N*-dimethylamino-4'-*N*'-methyl-stilbazolium tosylate (DAST), which has exhibited good second-order nonlinear optical activity (10³ times of the urea) owing to its outstanding NLO susceptibilities (d_{11} >1000 pm/V)), large electro-optic coefficients (r_{111} =77 pm/V), low dielectric constants (ϵ_1 =5.1).¹²⁻¹⁵ Hence, many stilbazolium derivatives with similar architectures such as DSTMS and DSNS have been investigated.¹⁶⁻¹⁷

However, the observation of bulk nonlinear susceptibility ($\chi^{(2)}$) using these chromophores depends on their parallel alignment with a noncentrosymmetric arrangement in the crystal. The control of alignment of the organic molecules in the solid state is still a big challenge,¹⁸ and great efforts have been devoted to the achievement of noncentrosymmetric arrangements of chromophores. Up to now, the most commonly used strategy is the introduction of various organic counter-anions to get noncentrosymmetric arrangements,^{8,16,19-27} such as tosylate derivatives (2-naphtalenesulfonate and 2,4,6-(trimethylbenzenesulfonate),^{16,19} tetracyanoquinodimethane.²⁰ In addition, recently, metal complexes were also utilized due to their large polarizability, which can be divided into following types: (a) mono-nuclear metal complexes, for example, [Ni(dmit)₂]^{-,28} [M^{III}₂M'^{II}(C₂O₄)₆]⁴⁻ (M =Rh, Fe, Cr; M' = Mn, Zn) mixed metal oxalates,²⁹ Au(CN)²⁻³⁰ and MPS₃ (M=Mn, Cd, Zn);³¹⁻³³ (b) polymeric metal halides;³⁴⁻³⁷ (c) polyoxometalates.³⁸ But these methods are also low efficiency in the control of chromophore aggregation modes, because they only modify the structure of one moiety.

Inorganic-organic hybrids pave a new way for the design of new nonlinear optical materials, because they can provide the modification method in both organic and inorganic moeities. In organic chromophore, different substituents can be introduced to induce their aggregation modes, and in inorganic moieties, high polarizability components can be incorporated. For example, iodoargentates polymers with high covalent feature of the Ag–I bond and possible existence of Ag…Ag interactions will give rise to high polarizability.³⁹ To the best of our knowledge, the study

about the combination of NLO-phore chromophores with iodoargentates is rare.³⁵ In this work, by introducing different substituents on NLO-phore chromophores, we obtain five chromophores and combine them with iodoargentates to afford five new NLO-phore chromophore/iodoargentates hybrids, namely, $[(DAST)(Ag_2I_3)]_n$ (1), $[(DMAQS)(Ag_2I_3)]_n$ (2), $[(DPAS)(Ag_2I_3)]_n$ (3), $[(DPTAS)_2(Ag_5I_7)]_n$ (4) and $[(CEMAS)_2(Ag_5I_7)]_n$ (5). Among them, 5 is second harmonic generation (SHG) active with a response as one time as that of KDP (potassium dihydrogen phosphate). This work provides an example of NLO active solid without J-aggregation of organic chromophore, in which the symmetry break was driven by the formation of hydrogen bonds around cyano group. Theoretical calculations were carried out to correlate the structure-property relationships.

EXPERIMENTAL SECTION

Materials and Methods All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. IR spectra were recorded on a Perkin-Elmer Spectrum-2000 FTIR spectrophotometer (4000-400 cm⁻¹) on powdered sample spread on KBr plate. Elemental analyses for C, H and N were performed on a Vario MICRO elemental analyzer. Purities of the grown crystals were confirmed by the X-ray powder diffraction (PXRD) performed on a Philips X'Pert-MPD diffractometer with CuK α radiation ($\lambda = 1.54056$ Å). Optical diffuse reflectance spectra were measured on a Aglient Carry 5000 UV/Vis/near-IR spectrophotometer equipped with an integrating sphere at 293 K and BaSO₄ plate used as a reference in the range of 200-2500 nm. The absorption spectra were calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1 - R)^2/(2R)$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.⁴⁰ Fluorescence spectra were characterized by a Edinburgh FL-FS 920 TCSPC spectrometer in solid state. ¹H NMR and ¹³C NMR spectra were recorded at a Bruker AVIII 400 spectrometer, whose chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane.

NLO Experiments Nonlinear optical properties were confirmed by the Kurtz and Perry technique,⁴¹ that is, the second-harmonic (SHG) powder test. The ground microcrystalline powdered samples were filtrated with different sizes and placed between two glass plates with a thickness of 2 mm. The measured SHG signals were converted into the measurable signal voltage with the fundamental beam being removed by appropriate filters. The collected digital signals

were then investigated by a photomultiplier and displayed with a DS1052E digital oscilloscope with respect to the corresponding powdered KDP with the same particle sizes of $300-350 \mu m$ as reference. A Q-switching laser with a wavelength of 2.0 μm was used as fundamental radiation to determine the SHG efficiency.

Computational Details The cif files of **1–5** were used to construct the calculated models. The electronic structure calculations were carried out using density functional theory (DFT) with the three non-local gradient-corrected exchange–correlation functions (GGA-PBE) and using CASTEP code,⁴² which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons.⁴³ The number of plane waves included in the basis was determined by a cutoff energy E_c of 550 eV. Pseudoatomic calculations were performed for Ag $4s^24p^64d^{10}5s^1$, I $5s^25p^5$, C $2s^22p^2$, N $2s^22p^3$, and H $1s^1$. The parameters used in the calculations and convergence criteria were according to the default values of the CASTEP program in Materials Studio 8.0.

The gas structures of five organic chromophores were optimized at B3LPY/6-31g(d) level using Gaussian 09 program package.⁴⁴ Besides, DFT calculations were carried out to disclose the magnitude and direction of the dipole moments of the $Ag_5I_9^{4-}$ building block and $(CEMAS)_2^{2+}$ pair in the asymmetric unit using the Gaussian 09. During the calculations, $Ag_5I_9^{4-}$ building block constructed from Ag_4I_4 cubane and bridged AgI_4 tetrahedron was used to simulate the $(Ag_5I_7)_n^{2n-}$ chain of **5**. The calculations were performed by using spin restricted DFT wave functions B3LYP. The 6-31g(d) basis set was used for C, N and H atoms, while lanl2dz basis set was employed for the Ag and I atom.

Synthesis

Synthesis of organic chromophores: All organic chromophores, 4'-dimethylamino-N-methyl stilbazolium (DAST)·I, 4'-dimethylamino-N-methylquinolin stilbazolium (DMAQS)·I, 4'-diphenylamino-N-methyl stilbazolium (DPAS) I, 4'-(4-di-p-tolylamino)-N-methyl stilbazolium (DPTAS)·I, 4'-(4-(2-cyanoethyl)(methyl)amino)- N-methyl stilbazolium (CEMAS)·I were synthesized by Knoevenagel reaction methods using Dean-Stark apparatus (scheme 1), which have been recrystallized two times in order to obtain purer products.⁶ We set (DAST) I as example: 4-picoline (0.9300 g, 10 mmol), methyl iodide (1.4200 g, 10 mmol) were refluxed for 12 hours in methanol for producing 1,4-dimethylpyridin-1-ium iodide. solvent and then

4-*N*,*N*-dimethylamino-benzaldehyde (1.4900 g, 10 mmol) was added in the presence of piperidine (5 drops) as catalyst. The solution was continued refluxing for 12 hours to get final products. The ¹H NMR, ¹³C NMR spectra and their assignments of five chromophores can be seen in Fig. S1-5 (Supporting Information).



Scheme 1 The structure of N-Arylstilbazolium organic nonlinear optical chromophores

Crystal growth

[(DAST)(Ag₂I₃)]_{*n*} (1): 1 was prepared by solution low evaporation method. (DAST)·1 (0.0366 g, 0.1 mmol) was dissolved in 4 mL CH₃CN solvent. In another flask, AgI (0.0353 g, 0.15 mmol) and KI (0.0664 g, 0.4 mmol) were dissolved in 6 mL DMF and stirred for 30 min. The former solution was dropped into the latter slowly and kept stirring for another 30 min, afterwards the pH value of resultant solution was adjusted to 6.0 using 10% HI solution. The obtained solution was filtered and red filtrate liquor was kept at room temperature for slow evaporation. Block black crystals were obtained after the growth period of 1 week. Yield: 30.5% (0.0192 g, based on Ag). Anal. Cald. for C₁₆H₁₉Ag₂I₃N₂ (835.77): calcd. C 22.99, H 2.29, N 3.35 %; found C 22.85, H 2.20, N 2.26 %. IR (cm⁻¹): 3046(w), 2902(w), 1643(m), 1566(s), 1506(s), 1370(m), 1154(s), 1038(m), 939(m), 864(m), 800(m), 721(m).

 $[(DMAQS)(Ag_2I_3)]_n$ (2): 2 was prepared by solvothermal method. ((DMAQS)·I (0.0418g, 0.1 mmol), AgI (0.0235 g, 0.10 mmol) and KI (0.0332 g, 0.2 mmol) were dissolved in 10 mL CH₃CN

and then transferred them to a Teflon jar (25 mL). The solution was stirred for 30 min at room temperature to become homogeneous, and the Teflon jar with the reactant was put into the steel sleeve and tightened the cover. The autoclave was heated to 120°C at a rate of 30°C per hour and held at this temperature for 72 h, afterwards the autoclave was cooled to room temperature with cooling rate of 2 °C per hour. The black crystals were washed three times with ethanol and dried at room temperature. Yield: 33.2% (0.0147 g based on Ag). Anal. Cald. for $C_{20}H_{21}Ag_2I_3N_2$ (885.83): calcd. C 28.47, H 2.39, N 3.16 %; found C 28.60, H 2.24, N 3.09 %. IR (cm⁻¹): 3076(s), 2899(w), 1523(s), 1324(m), 1165(m), 1104(m), 966(s), 819(s), 751(s), 512(s).

[(DPAS)(Ag₂I₃)]_n (3): The synthesis process of 3 was similar to that of 1, except that (DPAS)·I (0.0490 g, 0.1mmol) was used as starting organic chromophore. Block black crystals were obtained after one week. Yield: 28.4% (0.0204 g, based on Ag). Anal. Cald. for $C_{26}H_{26}N_2Ag_2I_3$ (959.90): calcd. C 32.53, H 2.71, N 2.92%; found C 32.45, H 2.73, N 2.94 %. IR (cm⁻¹): 3056(w), 1569(s), 1485(s), 1292(m), 1164 (s), 967(m), 830(s), 750(s), 693(s), 535(s).

[(DPTAS)₂(**Ag**₅**I**₇)]_{*n*} (**4)**: The synthesis of **4** was the same with that of **2**, except that the type and amount of starting materials differ to some extent. (DPTAS)·I (0.0518g, 0.1 mmol) and AgI (0.0352 g, 0.15 mmol) were dissolved in 10 mL CH₃CN. The autoclave was cooled to room temperature within 24 hour. The obtained black crystals were washed three times with ethanol and dried at room temperature. Yield: 27.3% (0.0181 g based on Ag). Anal. Cald. for $C_{56}H_{54}Ag_5I_7N_4$ (2210.68): calcd. C 30.42, H 2.55, N 2.53%; found C 30.60, H 2.44, N 2.69%. IR (cm⁻¹): 3027(w), 2919(w), 2250(w), 1896(w), 1582(s), 1500(s), 1320(s), 1265(s), 1175(s), 963(s), 815(s), 714(s), 532(s).

[(CEMAS)₂(Ag₅I₇)]_{*n*} (5): The synthesis details of 5 was similar to that of 2, in which (CEMAS)·I (0.0418g, 0.1 mmol) was used as starting organic chromophore. The autoclave was heated to 160 °C at a rate of 40°C per hour and held at this temperature for 72 h, afterwards the autoclave was cooled to room temperature in 48 h. The dark red stick crystals were washed three times with ethanol and dried at room temperature. The sizes, sharps and colors of as-synthesized crystals were shown in Fig. S6 (Supporting Information). Yield: 35.7% (0.0142 g based on Ag). Anal. Cald. for $C_{36}H_{40}Ag_5I_7N_6$ (1984.39): calcd. C 21.79, H 2.03, N 4.23 %; found C 21.72, H 2.20, N 4.33 %. IR (cm⁻¹): 3035(s), 2902(w), 2242(m), 1641(s), 1572(s), 1518(s), 1379(m), 1312(m), 1248(m), 1161(s), 1112(s), 1037(s), 966(m), 827(m).

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X-ray crystallography The intensities of five crystals were all collected on a Bruker APEX II diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature by using $\omega/2\theta$ scan mode. The empirical absorption corrections were based on equivalent reflections. Structures were solved by direct method followed by successive difference Fourier methods. Computations were performed using SHELXTL and final full-matrix refinements were against F^{2.45,46} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of C-H were generated geometrically. The relative high residual peaks of **5** locate at around Ag atoms (1.36 and 0.43 Å from Ag(3)), suggest that they are dummy peaks. Crystallographic data and refinement details are listed in Table 1. Selected bond distances and angles of **1-5** are given in Table S1 and S2, hydrogen bond parameters are shown in Table S3, π – π stacking interactions are summarized in Table S4 (Supporting Information). Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary publications.

RESULTS AND DISCUSSION

Description of structures

Compound 1-3 all contain 1-D anionic chains with formula of $(Ag_2I_3)_n^{n-}$ and corresponding N-arylstilbazolium organic nonlinear optical chromophores. The formula of $(Ag_2I_3)_n^{n-}$ chains in iodoargentate system are commonly observed, for example, $(Habtz)(Ag_2I_3)$, $(HCP)(Ag_2I_3)$, (MC)(Ag₂I₃).^{3,35,47-49} But their structures differ to some extent due to the different linkage modes of AgI4 tetrahedra. The asymmetric units of 1-3 contain two Ag atoms, three I atoms and one N-arylstilbazolium cation. All Ag centers are in distorted tetrahedral geometries with four I donors without taking Ag-Ag bond into account. For 1, each Ag center is bound to two μ_2 -I and two μ_4 -I atoms, and in 2 and 3, Ag ions are coordinated by one μ_2 -I and three μ_3 -I atoms. The Ag-(μ_2 -I) (2.7629(11)-2.8482(12) Å), Ag-(µ3-I) (2.8217(22)-3.1979(13) Å) and Ag-(µ4-I) (2.9240(15)-3.0399(17) Å) bond lengths, and their corresponding I-Ag-I bond angles (91.72(2)-130.13(3)°) are consistent with those of the other reported $(Ag_2I_3)_n^{n-}$ chains (Table S1, S2).³⁵ The $(Ag_2I_3)_n^{n-}$ chain in 1 can be discussed in terms of Ag_2I_6 unit, which is constructed from two edge-sharing AgI₄ tetrahedra. In this Ag_2I_6 unit, argentophilic interaction is present judged from the Ag. Ag separation (3.148(2) Å, shorter than the sum of van der Waals radius of silver 3.44 Å). Adjacent Ag₂I₆ units are linked into a 1-D straight line chain along *c*-axis via sharing four edges (Fig. 1a), which is structural similar to $\{[Er(DMF)_8][Ag_6I_9]\}_n$.⁴⁹

The $(Ag_2I_3)_n^{n-}$ chain in 2 and 3 are isostructures build from Ag_4I_8 units, which are defined by four edge-sharing AgI₄ tetrahedra. Here only we set 2 as example. Versatile argentophilic interactions can be observed with Ag···Ag separations of 3.0004(18)–3.1294(13) Å, upon which a planar Ag₄ rhomboid is given. The bridged I atoms locate at two sides of the Ag₄ rhomboid. Furthermore, neighboring Ag₄I₈ units are connected into a 1-D straight chain along *a*-axis by sharing the same edges (Fig. 2a and Fig. S7(a)).

Compound 4 and 5 are composed by a 1-D $(Ag_5I_7)_n^{2n}$ chains and two crystallographically independent organic $(DPTAS)^+/(CEMAS)^+$ chromophores. The formula of $(Ag_5I_7)_n^{2n-}$ chains have also been frequently documented, for example, $[Mn(phen)_3](Ag_5I_7)$ and ${[Et_3N(CH_2)_6NEt_3][Ag_5I_7]}_n^{50,51}$ But their real structures also differ with each other greatly. The $(Ag_5I_7)_n^{2n}$ chain in 4 is unique due to the presence of interesting 2+2 AgI₄ planar square geometries. In detail, the building block of **4** is termed as Ag_5I_{10} unit (Fig. 3a). In this Ag_5I_{10} unit, Ag(2), Ag(2)#2, Ag(3), Ag(3)#2 (#2: -x+1/2, y,-z+1/2) are in tetrahedral environments with four I donors, and the Ag-I bond lengths and angles are comparable to those of AgI₄ tetrahedra in other hybrid iodoargentates.^{50,51} But coordinated environment of Ag(1) is unique with two short (2.7954(9) Å) and two long (3.2748(3), 3.3944(3) Å) Ag-I bonds. If two long Ag-I bonds are not considered, the Ag(1) center is in linear geometry. But when two weak Ag-I bonds (semi-bonds) are taken into account, Ag(1) center is in planar square environment. Therefore, the coordinated environment of Ag(1) can be treated as a 2+2 planar square environment. Abundant Ag. Ag interactions can be observed with distances of 3.041(2)-3.183(2) Å (Table S2). Based on these Ag...Ag interactions, five Ag atoms and six I atoms are generally co-planar with deviation less than 0.0012 Å. I(1), I(4) locate at both sides of this plane. In addition, the relatively higher thermal parameter of Ag(1) (0.23913) also suggests its relaxed coordinated environment, where Ag(1) is encapsulated in the cavity defined by Ag_4I_{10} unit. Neighboring Ag_5I_{10} units are connected into a 1-D straight line chain along *b*-axis via edge-sharing fashion (Fig. 3b). Consequently, a μ_6 -I(2) is observed locating at the center of the hexagonal and σ -bonding to six Ag atoms. This kind of condensation modes has not been reported in hybrid iodoargentates until now.

The $(Ag_5I_7)_n^{2n}$ of **5** is a zigzag-like chain built from cubane-like Ag_4I_4 nodes. The distorted cubane-like Ag_4I_4 core is similar with typical Mo–S cubane, which have been commonly observed in iodoargentates system. Based on Ag_4I_4 cubane, 0-D clusters (for instances,

 $(Y(DMSO)_7)(Ag_4I_8)_3)$,⁵² 1-D chains $([(APHEN-H)_2(Ag_4I_6)]_n)$,⁵³ 2-D layers (such as $\{[PC]_2[Ag_4I_6]\}_n)$,⁴⁸ and 3-D open frameworks $(\{[BCP]_2[Ag_4I_6]\}_n)$,^{48,54} of iodoargentate hybrids have been documented. But the linkage mode of cubane-like Ag_4I_4 core in the $(Ag_5I_7)_n^{2n}$ chain of 5 differs greatly. In detail, each Ag_4I_8 unit containing cubane-like Ag_4I_4 core connects with neighboring units via bridged AgI_4 tetrahedra and I atoms to give a 1-D zigzag-like chain along *a*-axis (Fig. 4a). Consequently, abundant $Ag\cdots Ag$ interactions with separations among 2.978(2)–3.318(2) Å are observed, indicating the presence of strong argentophilic interactions.

The structural parameters of organic chromophores are summarized in Table 2 (DAST⁺ was set as example and shown in Fig. 1b). The least-squares analysis showed that the dihedral angles between pyridine ring and benzene ring are $1.78-13.28^{\circ}$, indicating that two planes (pyridine and benzene rings) are approximately coplanar. Among them DMAQS⁺ in **5** exhibits the largest dihedral angle of 13.28° , which might be driven by the formation of hydrogen bonds. The sum of the three C–N–C angles taking N atoms as centers are all close to 360.0° , suggesting that outstretched methyl and carbon atoms of N-substituents are generally co-planar. These coplanar natures illustrate that the π -electrons in the organic chromophores are delocalized. The bond lengths of C–C based on the benzene and pyridine rings range between the C–C single bond (1.524 Å) and C–C double bond (1.317 Å), indicating that the bond lengths are even. All the organic chromophore exists in the trans *E*-configuration with respect to the ethenyl double bonds (bond distances: 1.30(2)-1.339(14) Å) with the torsion angle of $175.1(4)-178.9(6)^{\circ}$. Compared with the free organic chromophores (optimized at B3LYP/6-31g(d) level), only slight structural adjustments on dihedral angles between pyridine ring and benzene ring have happened, which might be led by weak interactions with iodoargentates.

There are no classic hydrogen bonds and $\pi \cdots \pi$ stacking can be found in **1** and **3**, and only electrostatic interactions contribute to the structural stabilization (Fig.1c, Fig. S7b). But in **2**, strong face-to-face $\pi \cdots \pi$ stacking interactions among head-to-tail arranged DMAQS⁺ are observed (Fig. 2b, Table S4). Interestingly, intermolecular C-H \cdots N and C-H \cdots I hydrogen bonds are present in **4** and **5**, which contribute to the structural stabilization. The H \cdots I distance in the range of 2.94–2.96 Å and C–H \cdots I angles in the range of 150–151° are in agreement with the values reported in the literature (Table S3, Supporting Information).³ In detail, in **4**, C(6)-H(6) \cdots I(2) hydrogen bond can be found between pyridine ring and μ_6 -I(2), which extends the 1-D chain to be

a 2-D layer along *ab*-plane (Fig. 3c). And in **5**, two C-H···N intermolecular hydrogen bonds are given. The first is between methyl C-H on pyridine in one crystallographically independent $(CEMAS)^+-1$ cation (defined by N(4)-N(5)-N(6)) and the cyano group on the other $(CEMAS)^+-2$ cation (defined by N(1)-N(2)-N(3)), upon which an un-symmetric $(CEMAS)_2^{2+}$ pair with head-to-tail arrangement is generated. In this $(CEMAS)_2^{2+}$ pair, $\pi \cdots \pi$ stacking interactions between pyridine and benzene rings are observed (Fig. 4b). Furthermore, un-symmetric $(CEMAS)_2^{2+}$ pairs interact with each other via C-H(benzene)-cyano group hydrogen bond to give a 1-D $(CEMAS)_{2n}^{2n+}$ chain along c-axis (Fig. 4b). Finally, C(29)–H(29)…I(2) hydrogen bond between $(Ag_5I_7)_n^{2n-}$ and $(CEMAS)_{2n}^{2n+}$ chains gives rise to the so-called hybrid structure (Fig. 4c).

All the π -conjugated organic chromophores are arranged themselves in head-to-tail fashion (the pyridinium as head and trimethylammonium as tail) with alternating directionality due to the strong 'push–pull' electron nature.³⁶ Consequently, **1-4** crystallize in centrosymmetric space groups. But in **5**, due to the presence of cyano group as a strong hydrogen acceptor, the head-to-tail arrangement is broken, leading to the generation of noncentrosymmetric space groups *Pna2*₁. In other words, without the J-aggregation of organic chromophores, the solid is still SHG active, in which the cyano group controls the segregation of (CEMAS)⁺ NLO-phore layer. The large SHG of **5** stems from this macroscopic polarity.

Optical diffuse-reflection spectra

The phase purities of crystals of **1–5** for physical property measurements have been verified by powder X-ray diffraction (PXRD) (Fig. S8). The experimental PXRD patterns are in good agreement with the simulated patterns from the single-crystal structures, suggesting the good phase purities of the bulk crystalline materials. Solid-state unpolarized visible/near-IR absorption spectra of **1-5** and their corresponding organic chromophores with the thickness of 0.6–0.8 mm were recorded from powder samples at room temperature (Fig. 5a). Organic chromophores and their hybrids **1-5** exhibit broad adsorption zones from ultra-violet (260–600 nm) to near-infrared (650-800nm) and IR. The optical diffuse-reflection spectra of hybrids **1-5** (imaginary line) are generally the same with their corresponding organic chromophores (solid line), suggesting that the optical adsorptions stem from the organic chromophores (from 270 to 650 nm centered at about 440 nm). ^{35,55,56} Among them, (DPAS)·I and **3** illustrate the narrowest adsorption, and due to the presence of larger conjugated moiety naphthalene in (DMAQS)·I and **2**, the widest adsorption

zone can be found. Bathochromic shifts about 35-60nm of hybrids **1-5** compared with their corresponding organic chromophores can be obtained, which should be attributed to the lower polarity in the hybrids because the organic functional molecules are highly sensitive to the polarity of the environment.^{57,58} In addition, no obvious narrow absorption bands are observed for **1-4**, so organic chromophores do not tend to form J-aggregates in the hybrids because of the hindrance of iodoargentates. Specially, the adsorptions in near-infrared zone (650-800nm) might also originate from the charge-transfer between iodoargentates and organic chromophores.⁸ Such a charge transfer between organic molecules and inorganic metal halides has already been reported.³⁹ All samples are transparent among 900-2100 nm with weak absorptions around 1700 and 1950 nm, which might be assigned to the overtones of the C–H stretching vibrations.⁸

Solid-state UV–Vis diffuse spectra of **1-5** calculated from the diffuse reflectance data by using the Kubelka–Munk function is plotted in Fig. 5b. The band gaps can be estimated as 1.67, 1.42, 1.91, 1.75 and 1.60 eV for **1–5** respectively, indicating that all compounds are semi-conductors with narrow gaps. These gaps are greatly lower than other iodoargentate-based hybrids (for example, 2.95 eV in (Etbtz)(AgI₂)), ³ which might be explained as the introduction of large π -conjugated organic chromophores. It's universally accepted that the band gaps increase as the dimensionality decreases. ³⁹ Therefore, the gaps of five compounds exhibit obvious blue shifts compared with the measured value of 2.75 eV for bulk AgI. The optical gap of **3** (1.91 eV) and **4** (1.75 eV) are obviously higher than others, which might be assigned to the hindrance of larger groups (phenyl) to inhibit the organic-inorganic charge-transfers. According to literature, a high M (M = Cu or Ag) content will lead to the low electronic band gap.⁵⁹ So the slight blue shift of the band gap of **4** compared to that of **3** can be ascribed to its relatively higher Ag/I ratio.

Photoluminescent emissions and second-order non-linear optical property

One-photon photoluminescence spectra of 1, 3, 4, 5 and their organic chromophores measured at room temperature in the solid state are shown in Fig. 6. And 2 shows no luminescence compared with (DMAQS)·I (emissions at 678, 778nm). Upon excitation, broad red emissions at 662, 731nm (for (DAST)·I and 1), 625, 661 nm (for (DPAS)·I and 3), 675, 716 nm (for (DPTAS)·I and 4), 695, 701 nm (for (CEMAS)·I and 5) can be detected (exited, emission peaks and red-shift are summarized in Table 3). The luminescence of iodoargentates were commonly observed at about 450-500nm,⁵¹ So the intense luminescence in this work all stem from the organic

chromophores. Upon comparison the emissions of organic chromophores and their hybrids, enhanced and slightly red-shifted emissions can be observed, which have been documented in other N-Arylstilbazolium organic nonlinear optical chromophores and their metal complexes.³⁷ Among them, **1** exhibits the largest enhanced amount (two times augment) and red-shift (69nm). The luminescence quenching in the solid state of π -delocalized molecules-containing systems has been explained as the intermolecular interactions such as $\pi \cdots \pi$ stacking.⁶⁰ In **2**, strong $\pi \cdots \pi$ stacking interactions with centroidal distance of 3.548(5) Å, which may leads to the mixing of HOMO and LUMO orbitals of π system, and consequently, produces excited states with low reduced efficiency.⁶⁰ But strong $\pi \cdots \pi$ stacking interaction is also present in **5**, the emission quenching process didn't take place. This might be ascribed to the strong H-bond with iodoargentate and worse overlap of two planes compared with that in **2**.

Herein, considered that 5 crystallizes in noncentrosymmetric (NCS) space group $Pna2_1$, its second-order non-linear optical effect was investigated. The experimental SHG intensities under 2.0 um radiation as a function of particle sizes for crystalline 5 is given in Fig. 7. As shown by Fig. 7, the SHG intensities of 5 increases with particle sizes and approach almost saturated, indicating its phasematchable property of Type I.⁶¹ In addition, SHG intensity of **5** is equal to that of KDP with the same particle size of 300-350 µm (Fig. 7). The SHG result reveals that the combination of N-arylstilbazolium organic nonlinear optical chromophores with iodoargentates can generate a favorable NCS packing and excellent optical second-order nonlinearity. It is universally accepted that the SHG behavior is determined by the size and the orientation of the dipole moments of the SHG active units in the NCS structure. To make clear the SHG resource of 5, the magnitude and direction of the dipole moments of the $Ag_{5}I_{9}^{4-}$ building block (constructed from $Ag_{4}I_{4}$ cubane and bridged AgI₄ tetrahedron) and $(CEMAS)_2^{2+}$ pair in the asymmetric unit were calculated using a G09 program (Table S5). The dipole moment of the $Ag_5I_9^{4-}$ unit is 6.5147 D, while that of $(CEMAS)_2^{2^+}$ pair is relative small with amount of 2.6685 D (the dipole moment of a water molecular is known as 2.16 D). Thus the direction of the net dipole moment of a unit cell of 5 mainly derives from the polarizations of the asymmetric contribution of $Ag_5I_9^{4-}$ unit mixing with smaller contributions from CEMAS⁺ chromophore. The SHG behavior can also be achieved without the J-aggregates of organic chromophores. In 5, the introduction of cyano group results in the un-symmetric $(CEMAS)_2^{2+}$ pair, and consequently, in the polarizations of iodoargentate. It's

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worth noting that the spatial arrangements of the SHG-active units $(Ag_5I_9)^{4-}$ and $(CEMAS)_2^{2+}$ pair are not in complete alignment, which inhibits the theoretical enhancement of macroscopic polarizabilities. Therefore, a higher SHG response can be expected if the dipole moments of SHG-active units are aligned more effectively in a new NCS hybrid. How to control the aggregations of organic chromophore via crystal engineering method to improve its NLO property is still a big challenge.

Electronic Structure Calculations

In order to look further insight into the linear optical properties of 1-5, DFT calculations illustrated by band structures along with high symmetry points of the first Brillouin zone and density of states (DOS) were executed using the CASTEP code in Materials Studio 8.0. The band structures, total and partial DOS of 1-5 along certain symmetry directions are given in Fig. 8, Fig. S9 and Fig. S10, respectively. The calculated band gaps of 1-5 using the GGA-PBE are 1.43, 1.05, 1.49, 1.22 and 1.38 eV, which are slightly smaller than their corresponding experimental values of 1.67, 1.42, 1.91, 1.75 and 1.60 eV, respectively. But the trend is right with largest gap observed in 3 and lowest one in 2. This discrepancy is contributed to the band gap underestimation of DFT method.⁶² Besides, 1 and 2 exhibit indirect band gaps, but 3, 4, 5 are direct band gaps. The bands can be explained by PDOS (Fig. 8, Fig. S10). As shown by the total and partial DOS diagrams, 1-5 possess similar electronic structures, in which the contributions of organic chromophores are dominated mixing by iodoargentates in the frontier orbitals. In detail, the top of the VBs between -5 and Fermi energy originate from the π bonding orbitials of organic chromophores mixed with small amount of Ag-4d, I-5p states. And the bottom of the CBs are almost the contribution of the $p-\pi^*$ antibonding orbitals of organic chromophores. So both HOMO and LUMO of crystal orbitals in this work are the components of organic chromophores. These orbital components support the fluorescence assignments that the intense luminescences of four compounds all stem from the organic chromophores, i. e., the emissions are the transitions from HOMO (π bonding orbitials) to LUMO ($p-\pi^*$ antibonding orbitals) of organic chromophores. In the band structure of β -AgI, its CBs stem form Ag-5s, I-5p orbitals. So conclusion could be drawn that organic chromophores adopt a direct way to modify the band gaps of iodoargentate hybrids, which have been reported in other metal halide-based hybrids containing aromatic organic molecules.^{48,63} Consequently, the intrinsic absorption of 1-5 can be mainly ascribed to the π - π * transfer of

charge organic chromophores assisted by transitions from I-5p state to $p-\pi^*$ orbitals of the organic chromophores.

CONCLUSIONS

In summary, combination of N-arylstilbazolium organic nonlinear optical chromophores with iodoargentates results in series of new hybrids, whose single crystals were grown from solutions or solvothermal methods. The stilbazoliums vary from their electron donating -NR₂ substituents, i. e. R=-Me, -Ph, p-CH₃-Ph, -CH₂CH₂CN, among which -CH₂CH₂CN containing hybrid $[(CEMAS)_2(Ag_5I_7)]_n$ (5, space group *Pna*2₁) is noncentrosymmetrical, however, other four hybrids $[(DAST)(Ag_2I_3)]_n$ (1), $[(DMAQS)(Ag_2I_3)]_n$ (2), $[(DPAS)(Ag_2I_3)]_n$ (3), $[(DPTAS)_2(Ag_5I_7)]_n$ (4) are centrosymmetric structures. The $(Ag_5I_7)_n^{2n}$ chain in 4 and 5 are new kinds of condensation modes in hybrid iodoargentates. UV/Vis/near-IR adsorptions and near-IR photoluminescences have been observed. All the organic chromophores are stacked as head-to-tail arrangements, resulting in second harmonic generation (SHG) inactive in 1-4. But 5 is SHG active without J-aggregation of organic chromophore, whose symmetry break was driven by the formation of hydrogen bonds around cyano group. This work provides a theoretical guide for the design of new NLO materials.

ASSOCIATED CONTENT

Supporting Information The Supporting Information including the selected bond lengths and angles, hydrogen bond details, π - π stacking interactions, ¹H NMR and ¹³C NMR spectra, the photographs of as-grown crystals, additional structural figures, PXRD patterns, band structures and PDOS are available free of charge on the ACS Publications website.

Accession Codes CCDC 1567096 (for 1), 1582739 (for 2), 1583256 (for 3), 1582759 (for 4), 1582820 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The CambridgeCrystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

Marinotto, D.; Danelli, S. G. Giaretta, A.; Lucenti, E.; Stadler, P.; Tordin, E.; G. Mattei, Scavia,
 G.; Ugo, R.; Cariati, E. Thermal Layer-by-layer Preparation of Oriented Films of a Cu(I) Ionic
 Inorganic–organic Hybrid material Showing Semiconducting and SHG Properties. *J. Mater. Chem. C*,
 2016, *4*, 7077–7082.

(2) Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) Hybrid Inorganic–organic Materials with Intriguing Stimuli Responsive and Optoelectronic Properties. *Coord. Chem. Rev.* **2016**, *306*, 566–614.

(3) Liu, G. N.; Jiang, X. M.; Fan, Q. S.; Hussain, M. B.; Li, K.; Sun, H.; Li, X. Y.; Liu, W. Q.; Li,
C. C. Water Stability Studies of Hybrid Iodoargentates Containing N-Alkylated or N-Protonated
Structure Directing Agents: Exploring Noncentrosymmetric Hybrid Structures. *Inorg. Chem.* 2017, 56, 1906–1918.

(4) He, Y. D.; Zhang, Z. L.; Xue, J.; Wang, X. H.; Song, F.; Wang, X. L.; Zhu, L. L.; Wang, Y. Z. Biomimetic Optical Cellulose Nanocrystal Films with Controllable Iridescent Color and Environmental Stimuli-Responsive Chromism. *ACS Appl. Mater. Interfaces*, 2018, *10*, 5805-5811.
(5) Sun, Z. H.; Luo, J. H.; Chen, T. L.; Li, L. N.; Xiong, R. G.; Tong, M. L.; Hong, M. C. Distinct Molecular Motions in a Switchable Chromophore Dielectric 4-N,N-Dimethylamino-4'-N'-methylstilbazolium Trifluoromethanesulfonate. *Adv. Funct. Mater.* 2012, *22*, 4855–4861.

(6) Lee, S. H.; Kang, B. J.; Yoo, B. W.; Lee, S. C.; Lee, S. J.; Jazbinsek, M.; Yun, H.; Rotermund,
B.; Kwon, O. Terahertz Phonon Mode Engineering of Highly Efficient Organic Terahertz
Generators. *Adv. Funct. Mater.* 2017, *27*, 1605583.

(7) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Clays, A. K.; Olbrechts, G.; Persoons, A.; Hupp, J. T.; Johnson, R. C.; Coles, S. J.; Hursthouse, M. B.; Nakatani, K. Quadratic Optical Nonlinearities of

N Methyl and N Aryl Pyridinium Salts. Adv. Funct. Mater. 2003, 13, 347–357.

(8) Sun, Z. H.; Liu, X. T.; Wang, X. Q.; Li, L. N.; Shi, X. J.; Li, S. G.; Ji, C. J.; Luo, J. H.; Hong,

M. C. Engineering of Acentric Stilbazolium Salts with Large Second-Order Optical Nonlinearity and Enhanced Environmental Stability. *Cryst. Growth&Des.* **2012**, *12*, 6181–6187.

(9) Marder, S. R.; Perry, J. W.; Schaefer, W. P. Organic Salts with Large Second-Order Optical Nonlinearities. *Chem. Mater.* **1994**, *6*, 1137–1147.

(10) Coe, B. J.; Harris, J. A.; Clays, A. K.; Olbrechts, G.; Persoons, A.; Hupp, J. T.; Johnson, R.

C.; Coles, S. J.; Hursthouse, M. B.; Nakatani, K. Quadratic Nonlinear Optical Properties of N-Aryl Stilbazolium Dyes. *Adv. Funct. Mater.* **2002**, *12*, 110–116.

(11) Wolf, T.; Niazov-Elkan, A..; Sui, X. M.; Weissman, H.; Bronshtein, I.; Raphael, M.; Wagner, H. D.; Rybtchinski, B. Free-Standing Nanocrystalline Materials Assembled from Small Molecules *J. Am. Chem. Soc.* 2018, *140*, 4761–4764.

(12) Meier, H. The Photochemistry of Stilbenoid Compounds and Their Role in Materials Technology. *Angew. Chem., Int. Ed. Engl.*, **1992**, *31*, 1399–1540.

(13) Marder, S. R.; Perry, J. W.; Schaefer, W. P. Synthesis of Organic Salts with Large Second-order Optical Nonlinearities. *Science*, **1989**, *245*, 626–628.

(14) Pan, F.; Wong, M. S.; Bosshard, C.; Gunter, P. Crystal Growth and Characterization of the Organic salt 4-N, N-dimethylamino-4'-N-methyl-stilbazolium Tosylate (dast). *Adv. Mater.* **1996**, *8*, 592–595.

(15) Karuppanan, N.; Kalainathan, S. A New Nonlinear Optical Stilbazolium Family Crystal of
(E)-1-Ethyl-2-(4-nitrostyryl) Pyridin-1-ium Iodide: Synthesis, Crystal Structure, and Its
Third-Order Nonlinear Optical Properties. *J. Phys. Chem. C.* 2018, *122*, 4572–4582.

(16) Yang, Z.; Mutter, L.; Stillhart, M.; Ruiz, B.; Aravazhi, S.;Jazbinsek, M.; Schneider, A.; Gramlich, V.; Günter, P. Large-Size Bulk and Thin-Film Stilbazolium-Salt Single Crystals for Nonlinear Optics and THz Generation. *Adv. Funct. Mater.* **2007**, *17*, 2018–2023.

(17) Ruiz, B.; Yang, Z.; Gramlich, V.; Jazbinsek, M.; Günter, P. Synthesis and Crystal Structure of a New Stilbazolium Salt with Large Second-order Optical Nonlinearity. *J. Mater. Chem.* **2006**, *16*, 2839–2842.

(18) Song, T.; Yu, J. C.; Cui, Y. J.; Yang, Y.; Qian, G. D. Encapsulation of Dyes in Metal–Organic Frameworks and Their Tunable Nonlinear Optical Properties. Dalton Trans., **2016**, *45*, 4218–4223

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(19) Ruiz, B.; Yang, Z.; Gramlich, V.; Jazbinsek, M.; Gunter, P. Synthesis and Crystal Structure of a New Stilbazolium Salt with Large Second-order Optical Nonlinearity. J. *Mater.Chem.* **2006**, *16*, 2389–2842.

(20) Andreu, R.; Malfant, I.; Lacroix, P. G.; Gornitzka, H.; Nakatani, K. Chiral Stilbazolium Chromophores: An Approach toward Multiproperty Materials Combining Conductivity and Second-Order Optical Nonlinearities. *Chem. Mater.* **1999**, *11*, 840–848.

(21) Kim, P. J.; Jeong, J. H.; Jazbinsek, M.; Kwon, S. J.; Yun, H.; Kim, J. T.; Lee, Y. S.; Baek, I. H.; Rotermund, F.; Kwon, O. P. Acentric Nonlinear Optical N-benzyl Stilbazolium Crystals with High Environmental Stability and Enhanced Molecular Nonlinearity in Solid State. *CrystEngComm*, **2011**, *13*, 444–451.

(22) Nunzi, F.; Fantacci, S.; Cariati, E.; Tordin, E.; Casatid, N.; Macchi, P. Stabilization through p-dimethylaminobenzaldehyde of a New NLO-active Phase of [E-4-(4-dimethylaminostyryl)-1-methylpyridinium] Iodide: Synthesis, Structural Characterization and Theoretical Investigation of its Electronic Properties. J. Mater. Chem. 2010, 20, 7652–7660.

(23) Matsukawa, T.; Yoshida, Y.; Hoshikawa, A.; Okadab, S.; Ishigaki,T. Neutron Crystal Structure Analysis of Stilbazolium Derivatives for Terahertz-wave Generation. *CrystEngComm*, 2015, *17*, 2616–2619.

(24) Nivetha, K.; Kalainathan, S.; Yamada, M.; Kondoc, Y.; Hamada, F. Investigation on the Growth, Structural, HOMO-LUMO and Optical Studies of 1-Ethyl -2-[2-(4-hydroxy-phenyl)-vinyl]-pyridinium iodide (HSPI)-A new Stilbazolium Derivative for Third-order NLO Applications. *RSC Adv.* **2016**, *6*, 35977–35990.

(25) Kim, P. J.; Jazbinsek, M.; Kwon, O. P. Selective Growth of Highly Efficient Electrooptic Stilbazolium Crystals by Sequential Crystal Growth in Different Solvents. *Cryst. Growth&Des.*2011, 11, 3060–3064.

(26) Yang, Z.; Wörle, M.; Mutter, L.; Jazbinsek, M.; Günter, P. Synthesis, Crystal Structure, and Second-Order Nonlinear Optical Properties of New Stilbazolium Salts. *Cryst. Growth&Des.* 2007, 7, 83–86.

(27) Yang, Z.; Aravazhi, S.; Schneider, A.; Seiler, P.; Jazbinsek, M.; Günter, P. Synthesis and Crystal Growth of Stilbazolium Derivatives for Second–Order Nonlinear Optics. *Adv. Funct. Mater.* **2005**, *15*, 1072–1076.

(28) Malfant, I.; Andreu, R.; Lacroix, P. G.; Faulmann, C.; Cassoux, P. Synthesis, Structure, and Physical Properties of Nickel Bis(dithiolene) Metal Complexes, [Ni(dmit)₂], with Highly Polar Cyanine Dyes. *Inorg. Chem.* **1998**, *37*, 3361–3370.

(29) Cariati, E.; Macchi, R.; Roberto, D.; Ugo, R.; Galli, S.; Casati, N.; Macchi, P.; Sironi, A.; Bogani, L.; Caneshi, A.; Gatteschi, D. Polyfunctional Inorganic-organic Hybrid Materials: an Unusual Kind of NLO Active Layered Mixed Metal Oxalates with Tunable Magnetic Properties and very large second harmonic generation. *J. Am. Chem.Soc.* **2007**, *129*, 9410–9420.

(30) Lacroix, P. G.; Munoz, M. C.; Gaspar, A. B.; Real, J. A.; Bonhommeau, S.; Rodriguez, V.; Nakatani, K. Synthesis, Crystal Structures, and Solid State Quadratic Nonlinear Optical Properties of a Series of Stilbazolium Cations Combined with Gold Cyanide Counter-ion. *J. Mater. Chem.* 2011, *21*, 15940–15949.

(31) Coradin, T.; Clement, R.; Lacroix, P. G.; Nakatani, K. From Intercalation to Aggregation: Nonlinear Optical Properties of Stilbazolium Chromophores–MPS₃ Layered Hybrid Materials *Chem. Mater.* **1996**, *8*, 2153–2158.

(32) Lacroix, P. G.; Ement, R. C.; Nakatani, K.; Zyss, J.; Ledoux, I. Stilbazolium-MPS₃ Nanocomposites with Large Second-order Optical Nonlinearity and Permanent Magnetization. *Science*, **1994**, *263*, 658–660.

(33) Möbius, D. Scheibe Aggregates. Adv. Mater. 1995, 7, 437-444.

(34) Cariati, E.; Ugo, R.; Cariati, F.; Roberto, D.; Masciocchi, M.; Galli, S.; Sironi, A.
 J□Aggregates Granting Giant Second-Order NLO Responses in Self□Assembled Hybrid Inorganic–Organic Materials. *Adv. Mater.* 2001, *13*, 1665–1668.

(35) Cariati, E.; Macchi, R.; Roberto, D.; Ugo, R.; Galli, S.; Masciocchi, N.; Sironi, A. Sequential Self-Organization of Silver(I) Layered Materials with Strong SHG by J Aggregation and Intercalation of Organic Nonlinear Optical Chromophores through Mechanochemical Synthesis. *Chem. Mater.* **2007**, *19*, 3704–3711.

(36) Xu, G.; Li, Y.; Zhou, W. W.; Wang, G. J.; Long, X. F.; Cai, L. Z.; Wang, M. S.; Guo, G. C.; Huang, J. S.; Bator, G.; Jakubas, R. A Ferroelectric Inorganic–organic Hybrid Based on NLO-phore Stilbazolium. *J. Mater. Chem.* **2009**, *19*, 2179–2183.

(37) Guloy, A. M.; Tang, Z.; Miranda, P. B.; Srdanov, V. I. A New Luminescent Organic–Inorganic Hybrid Compound with Large Optical Nonlinearity. *Adv. Mater.* 2001, *13*,

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833-837.

(38) Compain, J. D.; Mialane, P.; Dolbecq, A.; Marrot, J.; Proust, A.; Nakatani, K.; Yu, P.; Secheresse, F. Second-order Nonlinear Optical Properties of Polyoxometalate Salts of a Chiral Stilbazolium Derivative. *Inorg. Chem.* **2009**, *48*, 6222–6228.

(39) Zhang, R. C.; Wang, J. J.; Zhang, J. C.; Wang, M. Q.; Sun, M.; Ding, F.; Zhang, D. J.; An, Y.

L. Coordination-Induced Syntheses of Two Hybrid Framework Iodides: A Thermochromic Luminescent Thermometer. *Inorg. Chem.* **2016**, *55*, 7556–7563.

(40) Wendlandt, W. M.; Hecht, H. G. Reflectance Spectroscopy; Interscience: New York, 1966.

(41) Kurtz, S. K.; Perry, T. T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798–3813.

(42) Segall, M.; Lindan, P.; Probert, M.; C. Pickard, C. et al (2012), Materials Studio CASTEP version 8.0.

(43) Hamann, D. R.; Schlüter, M.; Chiang, C. Norm-Conserving Pseudopotentials. *Phys. Rev. Lett.*1979, 43, 1494–1497.

(44) Frisch, 1 M. J.; Trucks, G. W.; Schlegel, H. B.; et al. Gaussian 09, Revision A01, Gaussian, Inc., Wallingford, CT, 2009.

(45) Sheldrick, G. M. SHELXS-97: Program for Crystal StructureSolution; Göttingen University: Göttingen, Germany, 1997.

(46) Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures; Göttingen University: Göttingen, Germany, 1997.

(47) Yu, T. L.; An, L.; Zhang, L.; Shen, J. J.; Fu, Y. B.; Fu, Y. L. Two Thermochromic Layered Iodoargentate Hybrids Directed by 4- and 3-Cyanopyridinium Cations. *Cryst. Growth&Des.* **2014**, *14*, 3875–3879.

(48) Shen, J. J.; Zhang, C. F.; Yu, T. L.; An, L.; Fu, Y. L. Structural and Functional Modulation of Five 4-Cyanopyridinium Iodoargentates Built Up from Cubane-like Ag₄I₄ Nodes. *Cryst.Growth&Des.* 2014, *14*, 6337–6342.

(49) Li, H. H.; Huang, S. W.; Lian, Z. X.; Liu, J. B.; Wang, M.; Chen, Z. R. Incorporating Rare Earth Metal Complexes and Conjugated Organic Cations into Polymeric Iodoargentate: Structures and Properties of Two Hybrid Iodoargentates. *Z. Anorg. Allg. Chem.* **2012**, *638*, 851–855.

(50) Lei, X. W.; Yue, C. Y.; Feng, L. J.; Han, Y. F.; Meng, R. R.; Yang, J. T.; Ding, H.; Gao, C.

S.; Wang, C. Y. Syntheses, Crystal sStructures and Photocatalytic Properties of Four Hybrid Iodoargentates with Zero-and Two-dimensional Structures. *CrystEngComm*, **2016**, *18*, 427–436.

(51) Li, H. H.; Chen, Z. R.; Li, J. Q.; Huang, C. C. ; Zhang, Y. F.; Jia, G. X. Role of Spacers and Substituents in the Self-assembly Process: Syntheses and Characterization of Three Novel Silver (I)/iodine Polymers. *Cryst. Growth Des.* **2006**, *6*, 1813–1820.

(52) Mishra, S.; Jeanneau, E.; Daniele, S.; Ledouxc, G. Reactions of Metal Iodides as a Simple Route to Heterometallics: Synthesis, Structural Transformations, Thermal and Luminescent Properties of Novel Hybrid Iodoargentate Derivatives Templated by $[YL_8]^{3+}$ or $[YL_7]^{3+}$ Cations (L = DMF or DMSO). *DaltonTrans.* **2008**, 6296–6304.

(53) Li, H. H.; Wu, J. X.; Dong, H. J.; Wu, Y. L.; Chen, Z. R. A Combined Experimental and Theoretical Study of an Semi-conductive Iodoargentate Hybrid Induced by Large Conjugate Cation. *J. Mole. Struct.* **2011**, *987*, 180–185.

(54) Hao, P. F.; Qiao, Y. R.; Yu, T. L.; Shen, J. J.; Dai, D. T.; Fu, Y. L. Three Iodocuprate Hybrids Symmetrically Modulated by Positional Isomers and the Chiral Conformation of N-benzyl-methylpyridinium. *RSC Adv.* **2016**, *6*, 53566–53572.

(55) Zhang, X. J.; Tian, Y. P.; Jin, F.;Wu, J. Y.; Xie, Y.; Tao, X. T.; Jiang, M. H. Self-Assembly of an Organic Chromophore with Cd–S Nanoclusters: Supramolecular Structures and Enhanced Emissions. *Cryst. Growth&Des.* **2005**, *5*, 565–570.

(56) Ren, Y.; Fang, Q.; Yu, W. T.; Lei, H.; Tian, Y. P.; Jiang, M. H.; Yang, Q. C.; Mak, T. C. W. Synthesis, Structures and Two-photon Pumped up-conversion Lasing Properties of Two New Organic salts. *J. Mater. Chem.* **2000**, *10*, 2025–2030.

(57) Shiraishi, Y.; Miyarnoto, R.; Hirai, T. A Hemicyanine-conjugated Copolymer as a Highly Sensitive Fluorescent Thermometer. *Langmuir*, **2008**, *24*, 4273–4279.

(58) Cao, X.; Tolbert, R. W.; McHale, J. L.; Edwards. W. D. Theoretical Study of Solvent Effects on the Intramolecular Charge Transfer of a Hemicyanine Dye. *J. Phys. Chem. A*, **1998**, *102*, 2739–2748.

(59) Wu, L. M.; Wu, X. T.; Chen, L. Structural Overview and Structure–property Relationships of Iodoplumbate and Iodobismuthate. *Coord. Chem. Rev.* **2009**, *253*, 2787–2804.

(60) Cariati, E.; Roberto, D.; Ugo, R.; Ford, P. C.; Galli, S.; Sironi, A. New Structural Motifs, Unusual Quenching of the Emission, and Second Harmonic Generation of Copper(I) Iodide

Polymeric or Oligomeric Adducts with Para-Substituted Pyridines or trans-Stilbazoles. *Inorg. Chem.* **2005**, *44*, 4077–4085.

(61) Zhang, J.; Zhang, Z.; Zhang, W.; Zheng, Q.; Sun, Y.; Zhang, C.;Tao, X. Polymorphism of BaTeMo₂O₉: A New Polar Polymorph and the Phase Transformation. *Chem. Mater.* **2011**, *23*, 3752–3761.

(62) Okoye, C. M. I. Theoretical Study of the Electronic Structure, Chemical Bonding and Optical Properties of KNbO₃ in the Paraelectric Cubic Phase. *J. Phys. Condens. Matter*, **2003**, *15*, 5945–5958.

(63) Liu, G. N.; Liu, L. L.; Chu, Y. N.; Sun, Y. Q.; Zhang, Z. W.; Li, C. C. Different Contributions of Aliphatic and Conjugated Organic Cations to Both the Crystal and Electronic Structures: Three Hybrid Iodoargentates Showing Two Isomers of the (AgI₂)⁻ Chain. *Eur. J. Inorg. Chem.* **2015**, *2015*, 478–487.

| Compound | 1 | 2 | 3 | 4 | 5 |
|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---|
| Empirical formula | $C_{16}H_{19}N_2Ag_2I_3$ | $C_{20}H_{21}N_2Ag_2I_3$ | $C_{26}H_{26}N_2Ag_2I_3$ | $C_{56}H_{54}N_4Ag_5I_7$ | C ₃₆ H ₄₀ Ag ₅ I ₇ N ₆ |
| Formula mass | 835.77 | 885.83 | 959.90 | 2210.68 | 1984.39 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P2_{1}/c$ | <i>P</i> -1 | <i>P</i> -1 | P2/n | $Pna2_1$ |
| a[Å] | 18.92 (1) | 8.203 (3) | 8.3233 (9) | 20.836 (4) | 14.3136 (12) |
| $b[\text{\AA}]$ | 15.679 (8) | 11.936 (4) | 10.2502 (9) | 6.6692 (11) | 15.5748 (13) |
| <i>c</i> [Å] | 7.237 (4) | 13.473 (4) | 16.8379 (16) | 22.920 (4) | 22.2132 (19) |
| α[°] | 90.00 | 110.823 (4)° | 105.111 (2)° | 90.00 | 90.00 |
| β[°] | 95.993 (8) | 90.663 (5)° | 90.701 (2)° | 103.374 (2) | 90.00 |
| γ[°] | 90.00 | 106.013 (5)° | 90.708 (2)° | 90.00 | 90.00 |
| <i>V</i> [Å] | 2135(2) | 1176.3 (7) | 1386.6 (2) | 3098.6 (10) | 4952.0 (7) |
| Z | 4 | 2 | 2 | 2 | 4 |
| $D_{\rm c}[g/{\rm cm}^3]$ | 2.600 | 2.501 | 2.299 | 2.369 | 2.662 |
| $\mu[\mathrm{mm}^{-1}]$ | 6.172 | 5.610 | 4.769 | 5.078 | 6.338 |
| F(000) | 1528 | 816 | 892 | 2048 | 3616 |
| Reflections, total | 7040 | 6068 | 8056 | 9937 | 18153 |
| Reflections, unique | 3671 | 3412 | 4668 | 5293 | 6191 |
| | $(R_{int} = 0.0297)$ | $(R_{int}=0.0237)$ | $(R_{\rm int} = 0.0168)$ | $(R_{int}=0.0306)$ | $(R_{int}=0.0276)$ |
| Reflections, observed | 2991 | 3086 | 4174 | 3729 | 5704 |
| Goodness-of-fit on $F^2/$ | 1.082 | 1.021 | 1.047 | 1.035 | 1.054 / 0.05(5) |
| Flack factor | | | | | |

Table 1. Summary of the crystal data and structure determination

| No. of parameters refine | d 211 | | 247 | | 299 | 329 | 491 |
|---|--|--|----------------------------------|---|---------------------|---|-------------------|
| $R_1[I \ge 2\sigma(I)]^a$ | 0.0484 | | 0.0377 | | 0.033 | 0.0611 | 0.0476 |
| $wR_2 [I \ge 2\sigma(I)]$ | 0.1574 | | 0.0918 | | 0.0829 | 0.1517 | 0.1272 |
| Residual extremes(e/Å ³) | 1.249, - | 1.669 | 1.501, - | 1.504 | 2.296, -1.522 | 1.808, -2.120 | 4.460, -2.887 |
| ${}^{a}R_{1} = \sum F_{0} - F_{0} $ | $ /\Sigma F_0 , wR_2$ | $= \{\sum [w(F_0)]$ | $(2^{2}-F_{c}^{2})^{2}]/\sum[w]$ | $v(F_0^2)^2]\}^{1/2}$ | 2 | | |
| | Table 2 St | ructural | parameters | s of organ | ic chromophores in | solids and in gas | |
| Organic | Dihedral | angle | Sum of | C-N-C | Sum of C-N-C | Bond length of | Torsion angle (°) |
| chromophores | between | | angles | around | angles around | ethenyl double | |
| | pyridine | and | pyridine l | N (°) | amido N(°) | bond (Å) | |
| | benzene | rings (°) | | | | | |
| DAST ⁺ in 1 | 11.13 | | 360.0(3) | | 359.0(3) | 1.302(17) | 178.9(6) |
| Free DAST ⁺ | 10.93 | | 359.9(9) | | 358.9(3) | 1.3005(2) | 178.9(6) |
| $DMAQS^+$ in 2 | 1.78 | | 360.2(0) | | 358.0(8) | 1.333(10) | 177.6(8) |
| Free DMAQS ⁺ | 1.77 | | 360.0(0) | | 357.9(3) | 1.3333(9) | 177.6(9) |
| DPAS ⁺ in 3 | 8.12 | | 360.1(6) | | 360.0(2) | 1.337(8) | 175.1(4) |
| Free DPAS ⁺ | 7.89 | | 359.9(7) | | 360.0(0) | 1.3364(1) | 175.1(4) |
| DPTAS ⁺ in 4 | 9.05 | | 360.2(4) | | 358.7(2) | 1.339(14) | 177.4(3) |
| Free DPTAS ⁺ | 9.02 | | 358.0(0) | | 358.4(9) | 1.3382(2) | 177.4(2) |
| CEMAS ⁺ in 5 | 6.87/13.2 | 28 | 360.7(0)/. | 359.8(3) | 359.9(1)/358.7(3) | 1.31(3)/ 1.30(2) | 177.9(0)/178.5(8) |
| Free CEMAS ⁺ | 5.99 | | 360.0(0) | | 359.9(9) | 1.311(5) | 177.9(0) |
| Т | ble 3 The ex | cited and | emission r | neaks for | hybrids and their o | rganic chromopho | ores |
| | able 5 The ex | enteu unu | | Jeaks 101 | | 8 | |
| Compo | und Ex | cited pea | ks (nm) | Emissio | n maxima (nm) | Amount of red-sh | ift (nm) |
| Compo (DAST | und Ex)·I 34 | cited pea 4 | ks (nm) | Emissio 662 | n maxima (nm) | Amount of red-sh | ift (nm) |
| Compo (DAST 1 | und Ex ∑)·I 344 423 | cited pea 4 8 | ks (nm) | Emissio 662 731 | n maxima (nm) | Amount of red-sh | ift (nm) |
| Compo (DAST 1 (DPAS | Ind Ex Ind Ex `)·I 34 42: | cited pea 4 8 0 | ks (nm) | Emissio 662 731 625 | n maxima (nm) | Amount of red-sh 69 36 | ift (nm) |
| Compo (DAST 1 (DPAS 3 | and Ex and Ex ()·I 34 42: ()·I ()·I 300 43: (43) | cited pea 4 8 0 8 | ks (nm) | Emissio 662 731 625 661 | n maxima (nm) | Amount of red-sh 69 36 | ift (nm) |
| Compo (DAST 1 (DPAS 3 (DPTA | Int S The Cx und Ex T)·I 34. 42: 42.)·I 30. 43: 43. S)·I 35. | cited pea 4 8 0 8 2 | ks (nm) | Emissio 662 731 625 661 675 | n maxima (nm) | Amount of red-sh 69 36 41 | ift (nm) |
| Compo (DAST 1 (DPAS 3 (DPTA 4 | Ind Ex Ind Ex ')·I 34 42: 42:)·I 30: 43: 43: S)·I 35: 44 | cited pea 4 8 0 8 2 1 | ks (nm) | Emissio 662 731 625 661 675 716 | n maxima (nm) | Amount of red-sh 69 36 41 | ift (nm) |
| Compo (DAST 1 (DPAS 3 (DPTA 4 (CEMA | and Ex and Ex ()·I 34. 42: 42. ()·I 30. 43: 43. S)·I 35. 44 45)·I 43. | cited pea 4 8 0 8 2 1 0 0 | ks (nm) | Emissio 662 731 625 661 675 716 695 | n maxima (nm) | Amount of red-sh 69 36 41 6 | ift (nm) |
| Compo (DAST 1 (DPAS 3 (DPTA 4 (CEMA 5 | and Ex and Ex (1) · I 34 42: 42: (1) · I 30: 43: 43: S) · I 35: 44 43: AS) · I 43: | cited pea 4 8 0 8 2 1 0 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 | ks (nm) | Emissio 662 731 625 661 675 716 695 701 | n maxima (nm) | Amount of red-sh 69 36 41 6 | ift (nm) |

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(c)

Fig. 1 (a) Structure of $(Ag_2I_3)_n^{n-}$ chain constructed from edge-sharing Ag_2I_6 unit; (b) Structure of $DAST^+$; (c)

Packing diagram with inorganic locating in the cavities defined by head-to-tail arranged organic

chromophores in 1





Fig. 2 (a) 1-D $(Ag_2I_3)_n^{n-}$ chain built from edge-sharing Ag_4I_8 unit; (b) π - π stacking interactions between

head-to-tail arranged $\left(DMAQS \right)^{+}$ cations in 2





(b)







hydrogen bonds of 4





(b)



(c)

Fig. 4 (a) Structure of $(Ag_5I_7)_n^{2n-}$ zigzag-like chain built from cubane-like Ag_4I_4 nodes and AgI_4 tetrahedron; (b)Structure of un-symmetric (CEMAS)_{2n}²ⁿ⁺ chain based on C-H…N hydrogen bonds showing π - π stacking interactions; (c) Packing diagram of 5 showing the hydrogen bonds in 5





spectra for 1-5

ACS Paragon Plus Environment







Fig. 6 Solid-state emission spectra of compounds 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) and their corresponding

organic chromophores



Fig. 7 Phase-matchable curve for the experimental SHG intensities as a function of particle sizes. The



respective inset is comparative SHG signal for the powder samples of KDP and 5 with particle sizes of $300-350~\mu m$

Fig. 8 Total and partial density of states of 1(a) and 5(b)

For Table of Contents Use Only Combination of N-Arylstilbazolium Organic Nonlinear Optical Chromophores with Iodoargentates: Structural Diversities and Optical Properties

Yu-Kang Wang, Li-Ming Zhao, Yu-Qing Fu, Zhao Chen, Xiao-Yan Lin, Dao-Hua Wang, Yi Li, Hao-Hong Li, Zhi-Rong Chen



Combination of N-arylstilbazolium organic nonlinear optical chromophores with iodoargentates results in five new hybrids, among which cyano-bearing **5** is noncentrosymmetrical exhibiting second harmonic generation (SHG) active. UV/Vis/near-IR adsorptions and near-IR photoluminescences have been observed. This work provides a hint that the NCS structure can be achieved with the presence strong hydrogen bond acceptor, although the organic chromophores are also stacked as head-to-tail arrangements.

