Electronic Supporting Information (ESI)

$[Ag_4Br_6]$ cluster-based 3D bromoargentate hybrid: Crystal structure, optical/photoelectric performance and theoretical study

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1. More structural details of compound 1

Table S1 Selected bond lengths (Å) and bond angles (°) for compound **1**.

Ag(1)−N(1)	2.442(12)	Ag(1)−Ag(1)#1	3.149(2)
Ag(1)−Br(1)#1	2.7002(14)	Ag(1)−Ag(1)#3	3.149(2)
Ag(1)−Br(1)	2.7002(15)	Ag(1)−Ag(1)#4	3.149(2)
Ag(1)−Br(1)#2	2.7002(15)	Br(1)−K(1)	3.4639(18)
N(1)−Ag(1)−Br(1)#1	90.40(3)	N(1)−Ag(1)−Br(1)#2	90.40(3)
N(1)−Ag(1)−Br(1)	90.40(3)	Br(1)#1−Ag(1)−Br(1)#2	119.995(1)
Br(1)#1−Ag(1)−Br(1)	119.995(1)	Br(1)−Ag(1)−Br(1)#2	119.995(1)

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

Table S2 Hydrogen bonds (Å) and angles (º) for compound **1**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(1)−H(1B)···Br(1)#5	0.97	3.10	3.778(6)	127.9
C(1)−H(1B)···Br(1)#1	0.97	3.10	3.778(6)	127.9
C(1)−H(1A)···Br(1)	0.97	3.10	3.778(6)	127.9
C(1)−H(1A)···Br(1)#6	0.97	3.10	3.778(6)	127.9

Symmetry transformations used to generate equivalent atoms: #1 −*y*+1, *x*−1, −*z*; #6 *y*+1/2, −*x*+3/2, −*z*; #5 −*x*+3/2, −*y*+1/2, *z*.

Table S3 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for compound **1**.

	x	*y*	*z*	$U_{(eq)}$
Ag(1)	9178(1)	822(1)	822(1)	31(1)
Br(1)	10000	2442(1)	0	48(1)
K(1)	10000	5000	0	50(2)
N(1)	8137(5)	1863(5)	1863(5)	14(2)
C(1)	7500	2500	1237(9)	20(2)
N(2)	2500	2500	2500	23(6)

Table S4 Anisotropic displacement parameters (A^2 × 10^3) for compound **1**.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	31(1)	31(1)	31(1)	−5(1)	5(1)	5(1)
Br(1)	57(1)	30(1)	57(1)	0	34(1)	0
K(1)	50(2)	50(2)	50(2)	0	0	0
N(1)	14(2)	14(2)	14(2)	−2(3)	2(3)	2(3)
C(1)	19(3)	19(3)	21(6)	0	0	2(5)
N(1)	23(6)	23(6)	23(6)	0	0	0

Table S5 Hydrogen coordinates (× 10^4) and isotropic displacement parameters (A^2 × 10^3) for compound **1**.

	x	*y*	*z*	$U_{(eq)}$
H(1A)	7910	2910	817	23
H(1B)	7090	2090	817	23
H(1)	2330(100)	2051(19)	2051(19)	34

2. Crystal structure

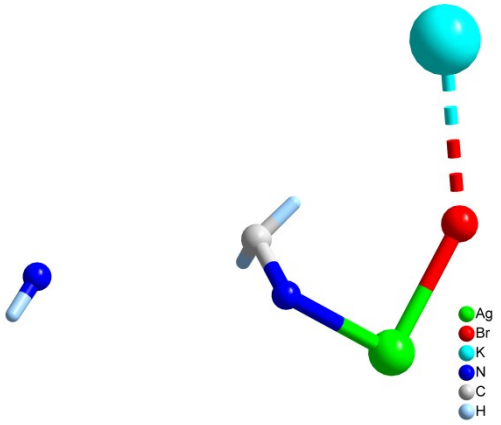

Fig. S1 The asymmetric unit of compound **1**.

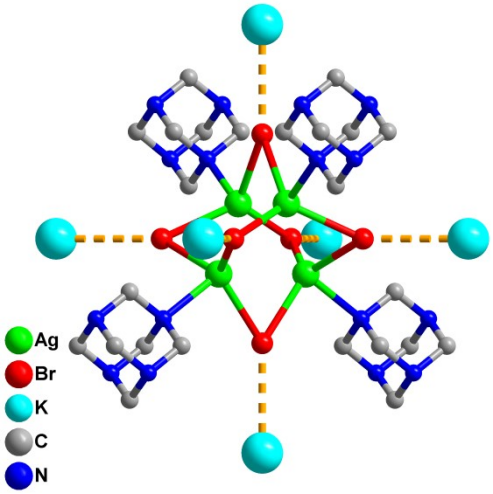

Fig. S2 A comprehensive view of the coordination environment among the [Ag_4Br_6] cluster, Hmta ligands and the K^+ ions.

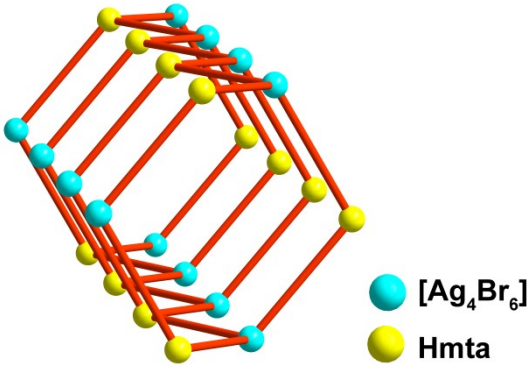

Fig. S3 The simplified topology for showing the 1D channel.

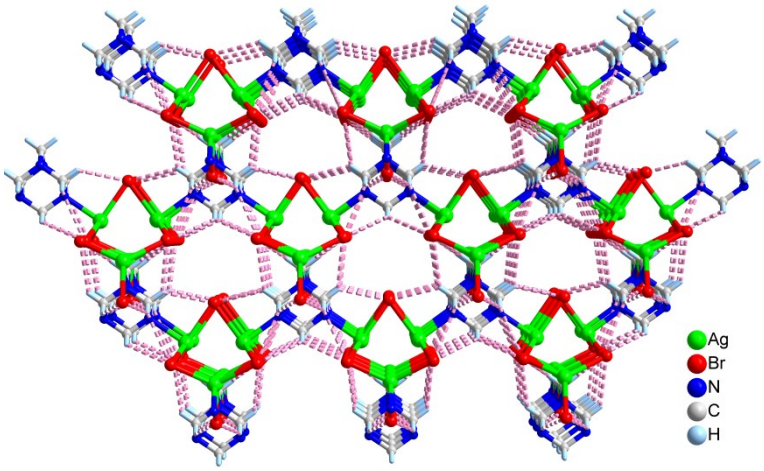

Fig. S4 Stacking diagram of compound **1** viewed along the [1 1 0] direction; dashed lines show the interactions of C−H···Br.

3. EDX

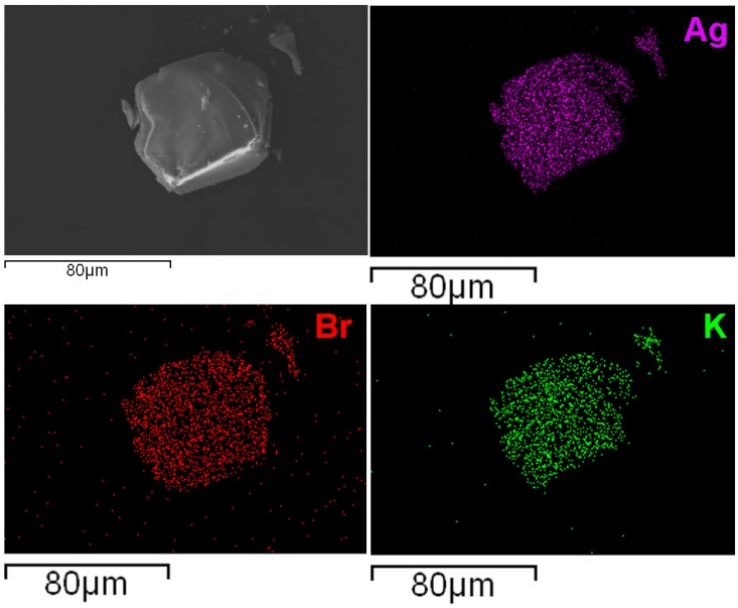

Fig. S5 The SEM and element mapping of Ag, Br and K for compound **1**.

4. DSC

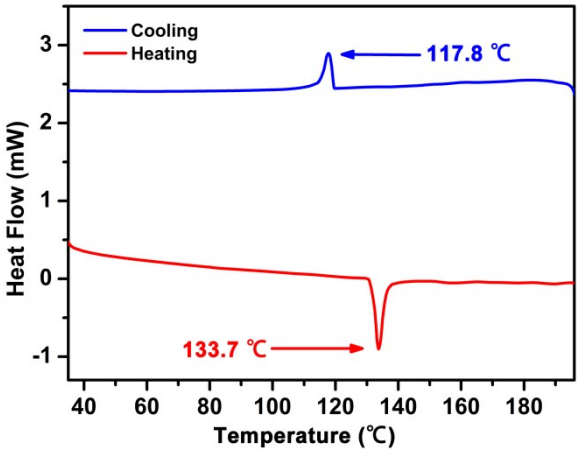

Fig. S6 The DSC curves of compound **1**.

5. Tauc plot

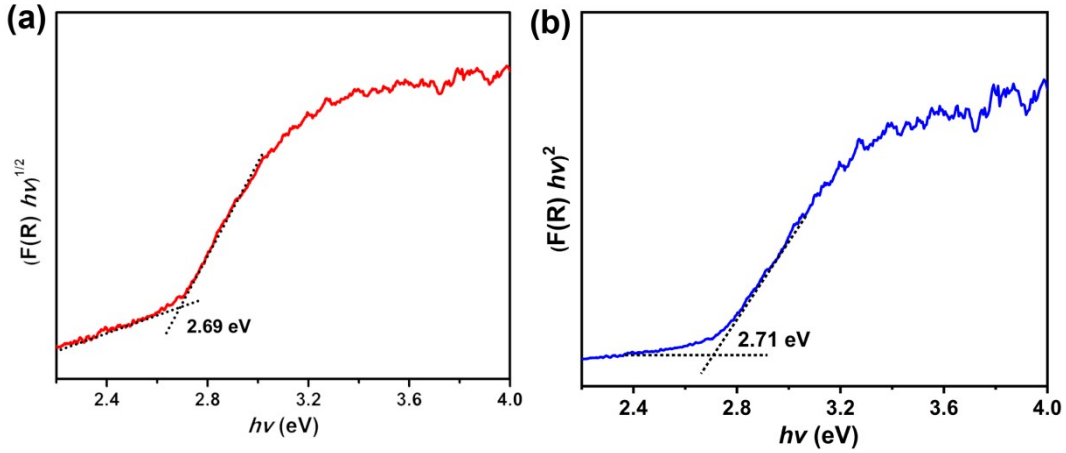

Fig. S7 Tauc plots of compound **1** corresponding to an indirect (a) and a direct (b) optical bandgap.

6. XPS

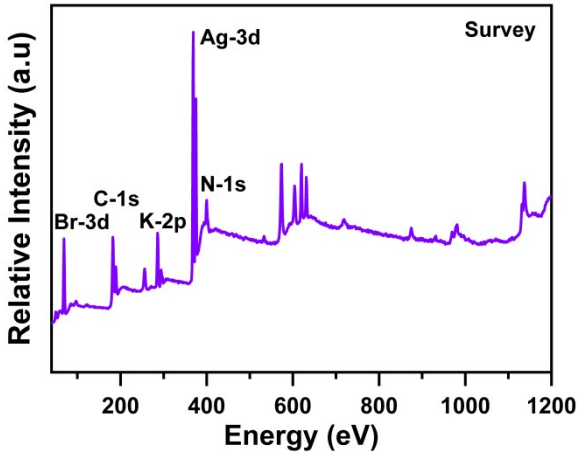

Fig. S8 The XPS survey spectrum of compound **1**.

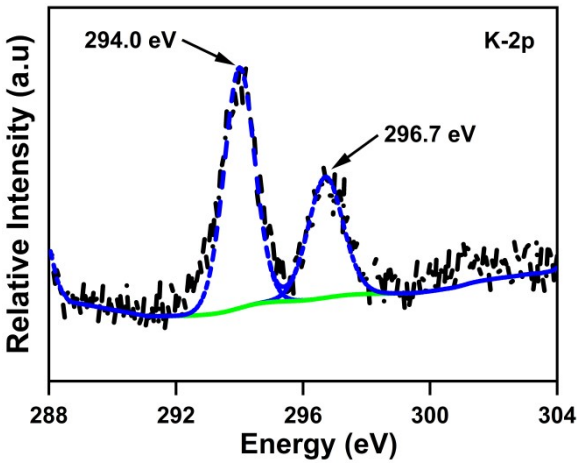

Fig. S9 The high-resolution K-2p peaks in compound **1**.

7. DFT calculations

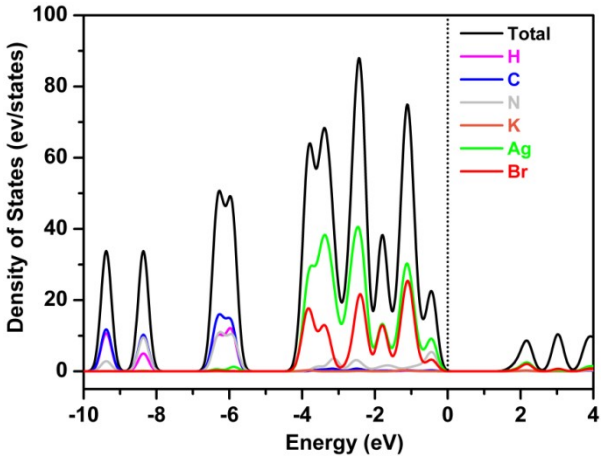

Fig. S10 The total density of states and partial density of states of compound **1**. Fermi level is set at 0 eV (dashed line).

Table S6 Summary of some representative haloargentate and halocuprate clusters coordinated by Hmta ligand and the derivative.

Compound	Dimension	Cluster unit	Ligand	Ref.
$K[NH_4][Ag_4Br_6(Hmta)]$	3D	$[Ag_4Br_6]$	Hmta	This work
$[NH_4][Me\text{-}Hmta][Ag_4Br_6(Hmta)]$	3D	$[Ag_4Br_6]$	Hmta	[1]
$[Hmta][Ag_4I_4(Hmta)]$	3D	$[Ag_4I_4]$	Hmta	[2]
$[NH_4][Ag_5I_6(Hmta)]$	2D	$[Ag_5I_6]$	Hmta	[3]
$[Ag_8I_6(Hmta)_2]I_2$	3D	$[Ag_8I_6]$	Hmta	[2]
$[Cu_4Cl_6(Hmta)][Cu_3(OH)(Hmta)]\cdot 3H_2O$	3D	$[Cu_5Cl_6]$; $[Cu_6Cl_6]$	Hmta	[4]
$[Cu_4(\mu\text{-}Cl)_6(\mu_4\text{-}O)Cu(OH)_2(\mu\text{-}PTA{=}O)_4]\cdot 2Cl\cdot EtOH\cdot 2.5H_2O$	3D	$[Cu_4Cl_6O]$	PTA=O	[5]
$[Et\text{-}Hmta][Cu_4I_6(Et\text{-}hmta)]\cdot CH_3CN$	2D	$[Cu_4I_6]$	Et-Hmta	[6]

Table S7 Summary of the band gaps of representative organic-inorganic hybrid haloargentates in the literature.

Compound	Space group	Band gap (eV)	Ref.
$K[NH_4][Ag_4Br_6(Hmta)]$	$F\bar{4}3m$	2.68	This work
$[Co(phen)_3]_2Ag_{11}I_{15}\cdot H_2O$	$P63/m$	2.84	[7]
$[(Ni(bipy)_3][H\text{-}2,2\text{-}bipy]Ag_3I_6$	$C2$	2.75	[8]
$[Zn(bipy)_3]Ag_3I_5$	$P2_12_12_1$	2.61	[9]
$K[Zn(bipy)_3]_2Ag_6Br_{11}$	$R\bar{3}$	2.61	[10]
$[Zn(bipy)_3]_2Ag_{13}Br_{17}$	$Pcca$	2.71	[10]
$[MV(Ag_2Br_4)]_n$	$P2_1/n$	2.79	[11]
$[NH_4]_2AgBr_3$	$Pnma$	2.50	[12]
$[(EC)(Ag_2I_3)]_n$	$P2_1/m$	2.80	[13]
$[(PC)(Ag_5I_6)]_n$	$Pbca$	2.72	[13]
$[Ni(DMSO)_6][Ag_5I_7]$	$Pbcm$	2.73	[14]
$[V(DMSO)_5(H_2O)][Ag_6I_8]$	$P2_1/c$	2.61	[14]
$[Ni(phen)_3]_2Ag_{13}Br_{17}\cdot 2DMSO\cdot 3H_2O$	$I2_13$	2.24	[15]
$[C_4H_{10}N]_4AgBiBr_8$	$C2/m$	2.85	[16]
$[Co(bipy)_3]Ag_3I_6$	$R\bar{3}$	2.03	[17]
$[Co(phen)_3]Ag_2I_4\cdot 3DMF$	$P\bar{1}$	2.59	[18]

Table S8 Summary of the photocurrent densities of similar haloargentates in this work and references.

Compound	Light source	Photocurrent density (μA cm^{-2})	Ref.
$K[NH_4][Ag_4Br_6(Hmta)]$	$\lambda > 420$ nm	0.38	This work
$[Co(bipy)_3]_2Ag_4Bi_2Br_{16}$	$\lambda > 420$ nm	1.10	[19]
$[Ni(bipy)_3]AgBiBr_6$	$\lambda > 420$ nm	0.28	[20]
$[Fe(bipy)_3]AgBiBr_6$	$\lambda > 420$ nm	2.2	[20]
$[Fe(phen)_3]Ag_2PbBr_6$	$\lambda > 420$ nm	0.4	[21]
$[Ni(phen)_3]Ag_2PbBr_6$	$\lambda > 420$ nm	0.07	[21]
$[NH_4][Fe(bipy)_3]_2[Ag_6Br_{11}]$	$\lambda > 420$ nm	3.0	[22]
$[Co(phen)_3]Ag_2PbI_6$	$\lambda > 420$ nm	0.16	[23]
$[Ni(5,5\text{-}dmpy)_3]Ag_7I_9 \cdot CH_3CN$	$\lambda > 420$ nm	0.14	[23]
$[Co(5,5\text{-}dmpy)_3]Ag_5I_8$	$\lambda > 420$ nm	0.14	[23]
$[Ni(5,5\text{-}dmbpy)_3]_2Ag_{4.9}I_{8.9} \cdot 4H_2O$	$\lambda > 420$ nm	0.5	[24]
$[Ag_2I_2(phen)]_n$	$\lambda > 420$ nm	0.32	[25]
$[AgI(bpt)]_n$	$\lambda > 420$ nm	0.66	[25]

8. Reference

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