

Three silver (I) supramolecular compounds constructed from pyridinium or methylimidazolium polycations: Synthesis, crystal structure and properties

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Abstract. Three metal halide cluster supramolecular polymers, $\{(TBP)[Ag_3Br_6]\}_n$ (**1**), $\{(TBI)[Ag_3Br_6]\}_n$ (**2**) and $\{(TBP)[Ag_3I_6]\}_n$ (**3**) (TBP=1, 3, 5-tris(N-pyridinium methyl)benzene, TBI=1, 3, 5-tris(methylimidazole methyl)benzene), have been synthesized and characterized by thermoanalysis and spectroscopic methods, as well as single-crystal X-ray diffraction. Complexes **1**, **2** and **3** all feature a one-dimensional chain structure, which is further extended by electrostatic attraction. The TGA, UV-Vis diffuse reflectance spectra in the solid state and optical band gap properties of the three complexes were also investigated.

Keywords. Supramolecule; one-dimension cluster; electrostatic attraction.

1. Introduction

In the last two decades, the chemistry of self-assembly in inorganic supramolecular network has attracted extensive attention, owing to the amazing accuracy and high efficiency in control and arrangement of specific building blocks.^{1–4} Supramolecular polymers are constructed generally via binding monomers or components together in macromolecules by highly directional noncovalent interactions such as hydrogen bonding, π - π interaction, metal-ligand interaction, electrostatic interaction, and so forth.^{5–7} The monomeric components, like guest units, host macromolecules, or even simple host-guest inclusion systems, can be modulated and integrated controllably to construct various supramolecular polymers with specific conformations or functions.^{8,9} Many researchers have been focused on the assembly of inorganic metallates with organic cations as the structure-directing and charge-compensating templates to form extended supramolecular materials. Because of the existence of multiple interaction sites, multication oriented hybrids may present new interesting topologies and novel functions endowed by host-guest interactions.^{10–14} Thus,

an intelligent choice of trivalent cations and transition metal complex anions may yield inorganic-organic hybrid materials with intriguing structure and desirable properties.^{15–19}

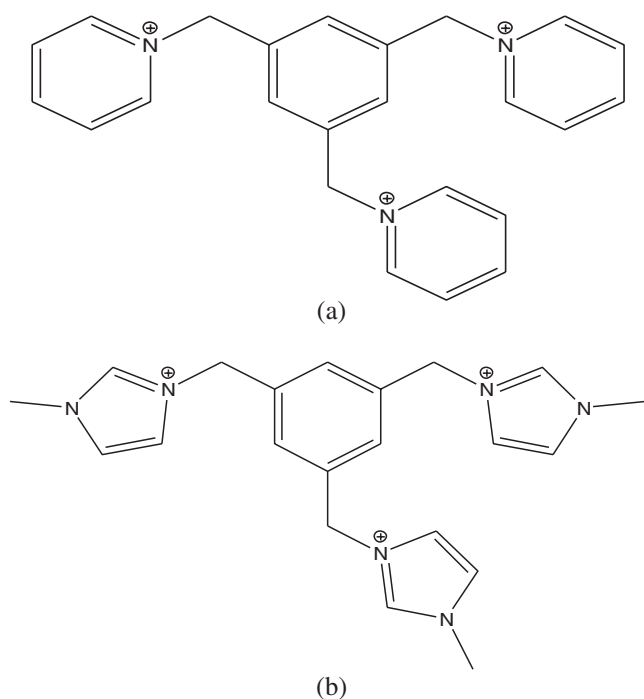
In the above context, herein we report the synthesis, structure and properties of $\{(TBP)[Ag_3Br_6]\}_n$ (**1**), $\{(TBI)[Ag_3Br_6]\}_n$ (**2**) and $\{(TBP)[Ag_3I_6]\}_n$ (**3**) (TBP=1,3,5-tri(N-pyridinium methyl)benzene, TBI=1,3,5-tri(methylimidazole methyl)benzene, scheme 1).

2. Experimental

2.1 Materials and measurements

Both the two cation templates TBP and TBI were prepared as bromine salt by direct alkylation of pyridinium or 1-methylimidazolium with 1, 3, 5-tris(bromomethyl)benzene, while acetonitrile served as solvent.^{20,21} Other chemicals and solvents were of reagent grade and used as purchased without further purification. Slow volatile approach at room temperature was used to generate the supramolecules, which was the only way that we got the single crystals (table 1). The IR spectrum was recorded on a Shimadzu IR-435 spectrometer from KBr pellets (4000–400 cm^{-1}). Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer.

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Scheme 1. The molecular structure of the title trications: (a)TBP; (b)TBI.

A model NETZSCH TG 209 thermal analyzer was used to record simultaneous TG curves in the flowing atmospheric air at 20 mL/min at a heating rate of 5°C/min in the temperature range from room temperature to 800°C using aluminum crucibles. The UV-Vis diffuse reflectance spectra were measured at UV-Vis-NIR Cary 5000. The purity of the bulk microcrystalline materials obtained from the syntheses was checked by Powder X-ray diffraction analyses. PXRD patterns were recorded using Cu K α 1 radiation on a PAN analytical X'Pert PRO diffractometer.

2.2 Synthesis of complex 1

{(TBP)[Ag₃Br₆]}_n (**1**) was prepared as follows. A methanol solution of TBP (0.06 g, 0.1 mmol) was added to a stirring solution of AgBr (0.019 g, 0.1 mmol) dissolved in 4 mL DMF-H₂O in the presence of excess KBr (0.08 g, 0.4 mmol). The precipitate formed in the reaction was dissolved by adding more DMF (2 mL). The solution was then filtered and slowly

Table 1. Crystal data and structure refinement parameters for **1**, **2** and **3**.

Complex	1	2	3
Empirical formula	C ₂₄ H ₂₄ Ag ₃ Br ₆ N ₃	C ₂₁ H ₂₇ Ag ₃ Br ₆ N ₆	C ₂₄ H ₂₄ Ag ₃ I ₆ N ₃
Formula weight	1157.53	1166.56	1439.47
Crystal system	Monoclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /n
a/ Å	7.003(4)	6.94956(14)	7.2146(2)
b/ Å	17.255(10)	26.7873(6)	7.2146(2)
c/ Å	26.249(15)	17.3021(4)	26.8494(9)
α /°	90	90.00	17.7538(4)
β /°	90	101.204(2)	90.00
γ /°	100.272(7)	90.00	99.824(2)
V/ Å ³	3121(3)	3159.57(12)	90.00
Z	4	4	4
ρ /Mg cm ⁻³	2.464	2.452	2.822
μ /mm ⁻¹	9.565	23.844	56.837
F(000)	2160	2184.0	2592.0
Crystal size/mm	0.13 × 0.12 × 0.12	0.11 × 0.10 × 0.04	0.15 × 0.10 × 0.08
Reflections collected	17868	24303	12311
Independent reflections	10873	6167	6065
R _{int}	0.0816	0.0373	0.073
data/restraints/ parameters	10873 / 360 / 649	6167/0/329	6065/0/325
T/K	293(2)	291.15	291.15
Goodness of fit on F ²	0.958	1.023	1.031
Final R indices	R1 = 0.0686,	R1 = 0.0498,	R1 = 0.0688,
[I > 2 σ (I)]	wR2 = 0.1085	wR2 = 0.1351	wR2 = 0.1731
R indices (all data)	R1 = 0.2105,	R1 = 0.0646,	R1 = 0.0868,
	wR2 = 0.1507	wR2 = 0.1472	wR2 = 0.1917
Largest diff. peak	0.935	1.40	1.92
hole(e Å ⁻³)	-1.061	-1.21	-1.94

evaporated at room temperature. Rod-like crystals of $\{(TBP)[Ag_3Br_6]\}_n$ suitable for X-ray analysis were obtained after a week with satisfactory yield of 76%. The product was not soluble in common solvents. FTIR

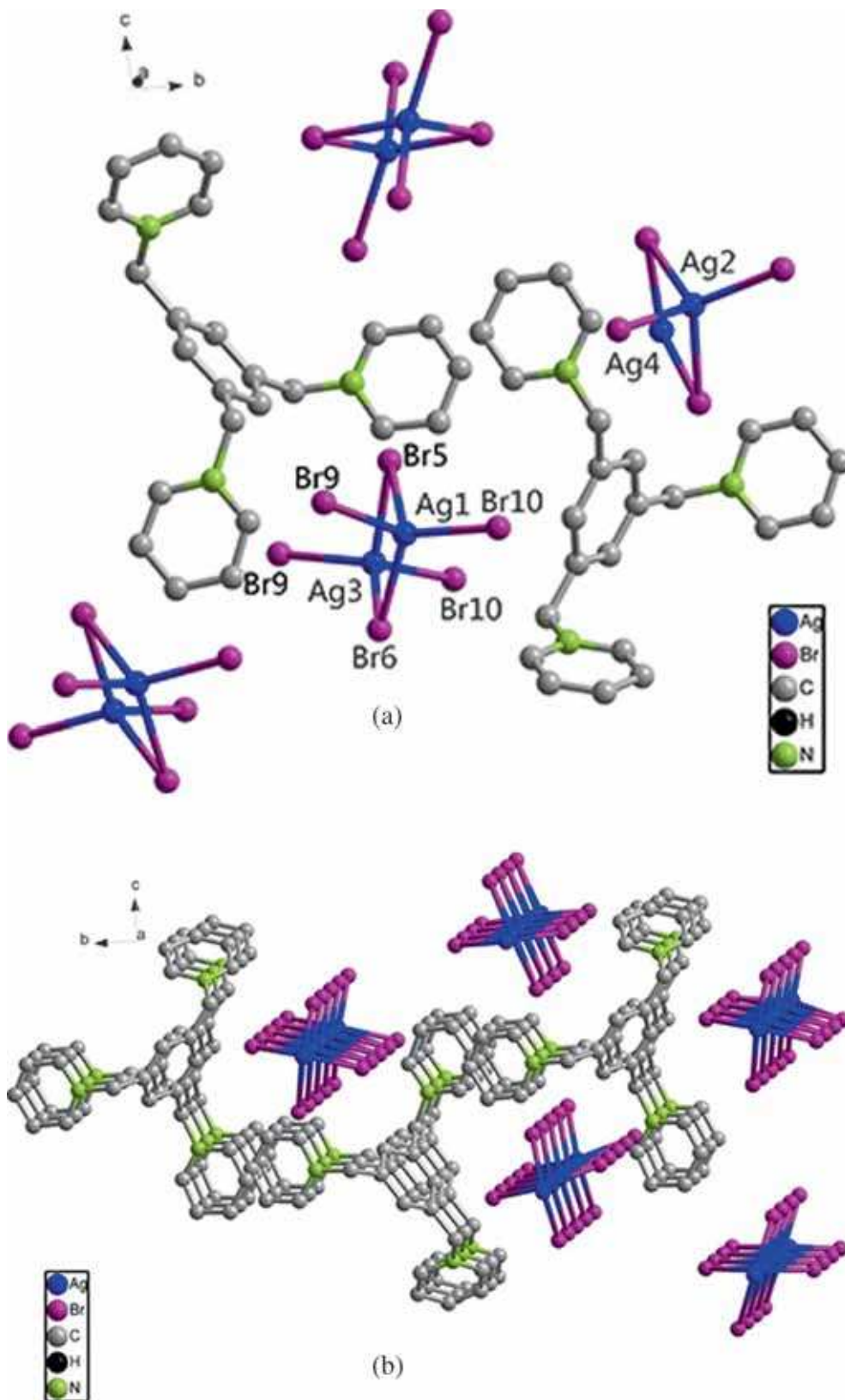


Figure 1. (a) The structural unit of compound 1; (b) the supramolecular architecture of 1.

(KBr, cm^{-1}): 3438(s), 3048(m), 1698(m), 1577(w), 1481(m), 1149(s), 690(w), 675(m), 618(s); Anal. Calcd. For $\text{C}_{24}\text{H}_{24}\text{Ag}_3\text{Br}_6\text{N}_3$: H 2.11, C 25.08, N 3.66%; Found: H 2.06, C 25.23, N 3.43%.

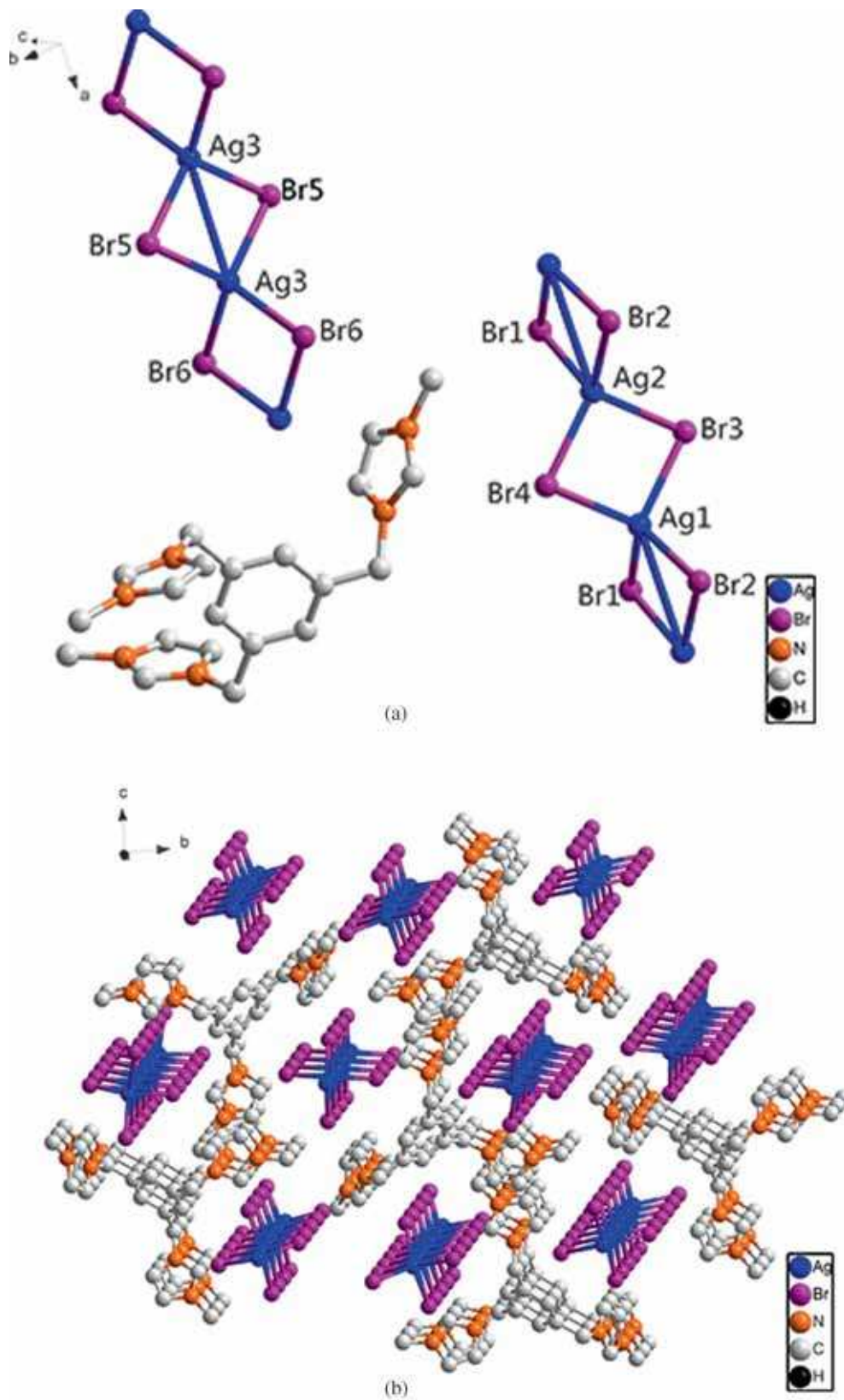


Figure 2. (a) The structural unit of compound 2; (b) the supramolecular architecture of 2.

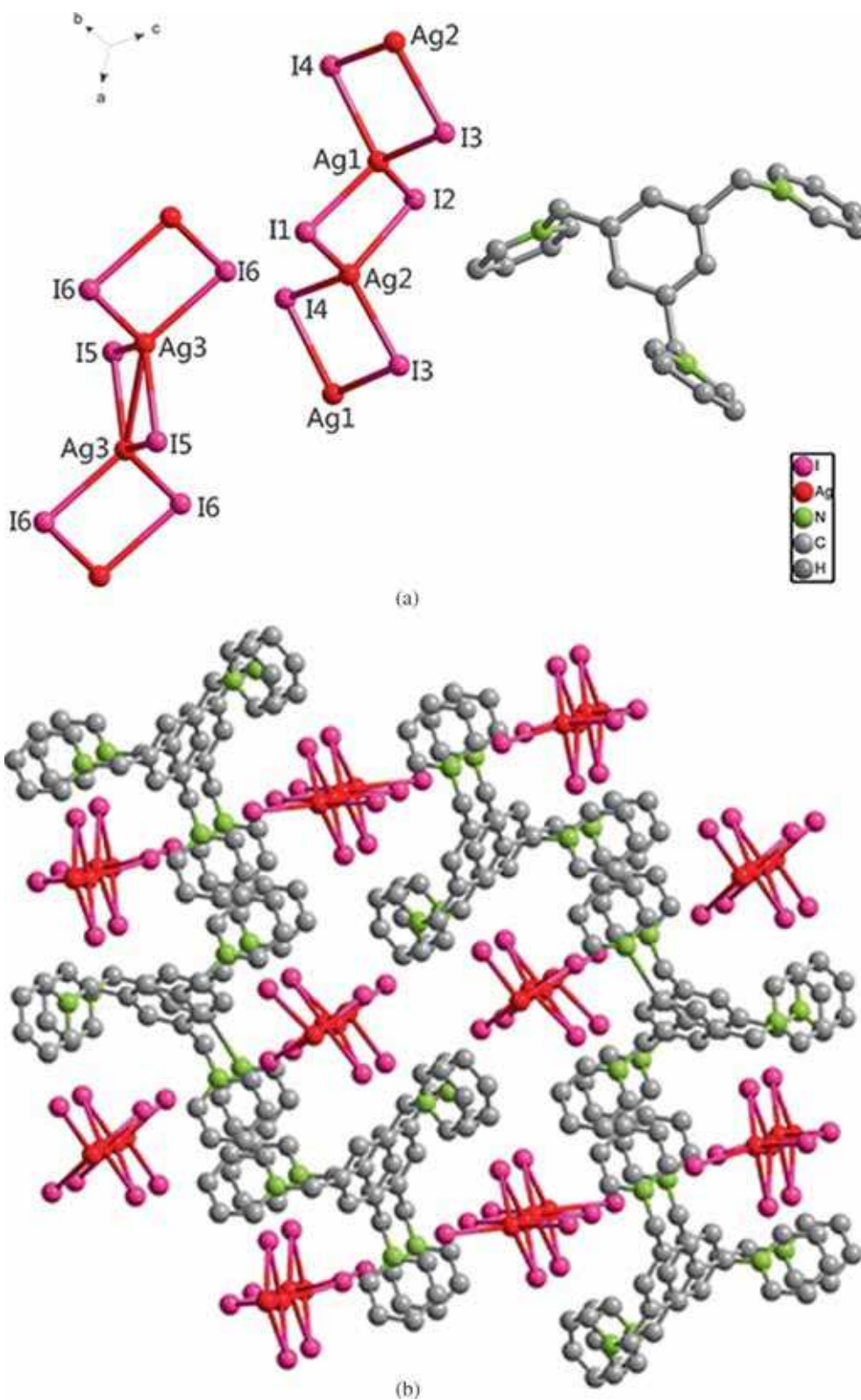


Figure 3. (a) The structural unit of compound 3; (b) the supramolecular architecture of 3.

2.3 Synthesis of complex 2

$\{(TBI)[Ag_3Br_6]\}_n$ (2) was synthesized by a similar procedure to complex 1, except use of trication TBI

(0.06 g, 0.1 mmol) instead of TBP. Yellow rod-like crystals were obtained with yield of 59%. FTIR (KBr, cm^{-1}): 3439(m), 3131(s), 3078(s), 1656(w), 1571(s),

1556(s), 1440(m), 1359(m), 1155(s), 828(s), 618(s). Anal. Calcd. For $C_{21}H_{27}Ag_3Br_6N_6$: H 2.33, C 21.62, N 7.20%; Found: H 2.45, C 21.87, N 6.99%.

2.4 Synthesis of complex 3

$\{(\text{TBP})[\text{Ag}_3\text{I}_6]\}_n$ (**3**) was synthesized by a similar procedure to complex **1**, by using AgI (0.024 g, 0.1 mmol) instead of AgBr. Yellow needle-like crystals were obtained with yield of 63%. FTIR (KBr, cm^{-1}): 3442(s), 1701(w), 1629(s), 1577(m), 1477(s), 1158(s), 1116(m), 674(s); Anal. Calcd. For $C_{24}H_{24}Ag_3I_6N_3$: H 1.68, C 20.03, N 2.92%; Found: H 1.52, C 20.13, N 2.81%.

3. Results and Discussion

3.1 Crystal structures of the complexes

Compounds **1**, **2** and **3** all exhibited an unusual one-dimensional anion structure, and were composed of two independent TBP^{3+} and TBI^{3+} trications as the structural template and one inorganic framework anion, $[\text{Ag}_3\text{Br}_6]^{3-}$ or $[\text{Ag}_3\text{I}_6]^{3-}$.

Complex **1** crystallizes in monoclinic space group P-1. In the polyanionic chain, due to the same coordinated environment, Ag(1) and Ag(3) are four-coordinated in a distorted tetrahedral geometry by four μ_2 -Br ions (μ_2 -Br5, μ_2 -Br6, μ_2 -Br9 and μ_2 -Br10), the same to Ag(2), which is also four-coordinated in a distorted tetrahedral geometry as shown in figure 1a. The bond lengths of Ag(1) centers with four μ_2 -Br ions (μ_2 -Br5, μ_2 -Br6, μ_2 -Br9 and μ_2 -Br10) are 2.748(3), 2.680(3), 2.750(3) and 2.671(3) Å respectively, and the bond angles of Br(6)-Ag(1)-Br(5) and Br(10)-Ag(1)-Br(9) are 98.33(8) and 102.30(9)°, respectively. In addition, each of the Ag(1) and Ag(3) center is bridged together by four μ_2 -Br ions which are μ_2 -Br5, μ_2 -Br6, μ_2 -Br9 and μ_2 -Br10 to form AgBr_2Ag unit respectively, as shown in figure 1b.

Complex **2** crystallizes in monoclinic space group $P2_1/c$. In the crystal of compound **2**, the central Ag(1) ion was four coordinated, completed via four μ_2 -Br ions in a typical distorted tetrahedral geometry similar to complex **1**. The coordination environment of Ag(1) is as shown in figure 2a. The Ag-Br distances ranged from 2.664 to 2.761 Å and the bond angles of Br(2)-Ag(1)-Br(1) and Br(3)-Ag(1)-Br(4) are 103.39(3) and 97.64(3)° respectively. Two adjacent Ag ions were bridged by two μ_2 -Br ions (μ_2 -Br1 and μ_2 -Br2) to form an AgBr_2Ag rhombohedral unit. Interestingly, compared with compound **1**, there existed a weak $\text{Ag}\cdots\text{Ag}$ contact with an $\text{Ag}\cdots\text{Ag}$ distance of 3.372 Å in the AgBr_2Ag units bridged by μ_2 -Br(1) and μ_2 -Br(2) ions,

and the $\text{Ag}\cdots\text{Ag}$ bonds also appear in the AgBr_2Ag units bridged by two μ_2 -Br5 ions with an $\text{Ag}\cdots\text{Ag}$ distance of 3.270 Å. As shown in figure 2b, the two types of AgBr_2Ag units were alternately linked by sharing Ag centers to form an infinite chain.

The complex **3** consists of $[\text{TBP}]^{3+}$ cations and $[\text{Ag}_3\text{I}_6]^{3-}$ anions and it also exhibits one-dimensional structure. The structure unit and the crystal packing diagram of complex **3** are shown in figure 3a. The bond lengths of Ag(1) centers with four μ_2 -I ions (μ_2 -I1, μ_2 -I2, μ_2 -I3 and μ_2 -I4) are 2.849, 2.884, 2.836 and 2.924 Å, respectively, and the bond angles of I(1)-Ag(1)-I(2), I(3)-Ag(1)-I(4) are 103.54 and 98.15° respectively. The distances of Ag(2)-I range from 2.812 to 2.895 Å, and the bond angles of I(1)-Ag(2)-I(2), I(3)-Ag(2)-I(4) are 104.50 and 99.40° respectively. Being like with compound **2**, there also existed a weak

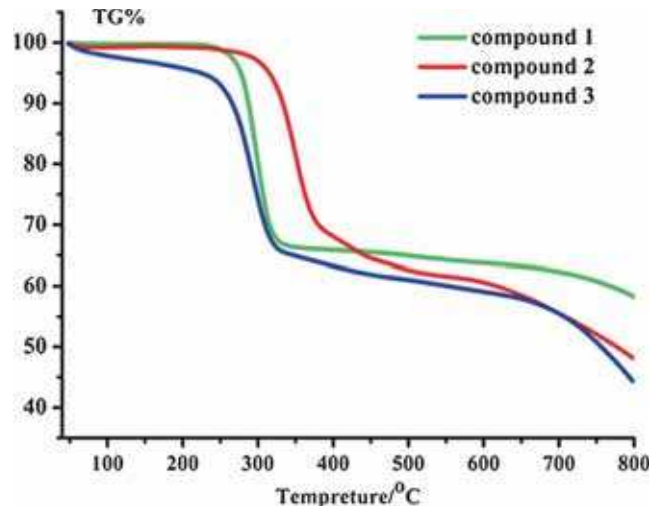


Figure 4. The TG curves of compounds **1-3** in a flowing air of 20 mL/min at a heating rate of 5°C/min.

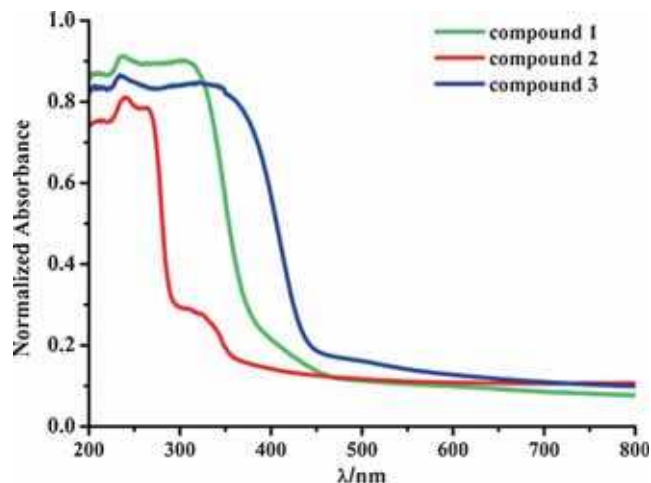


Figure 5. The UV-Vis spectra of compound **1-3**.

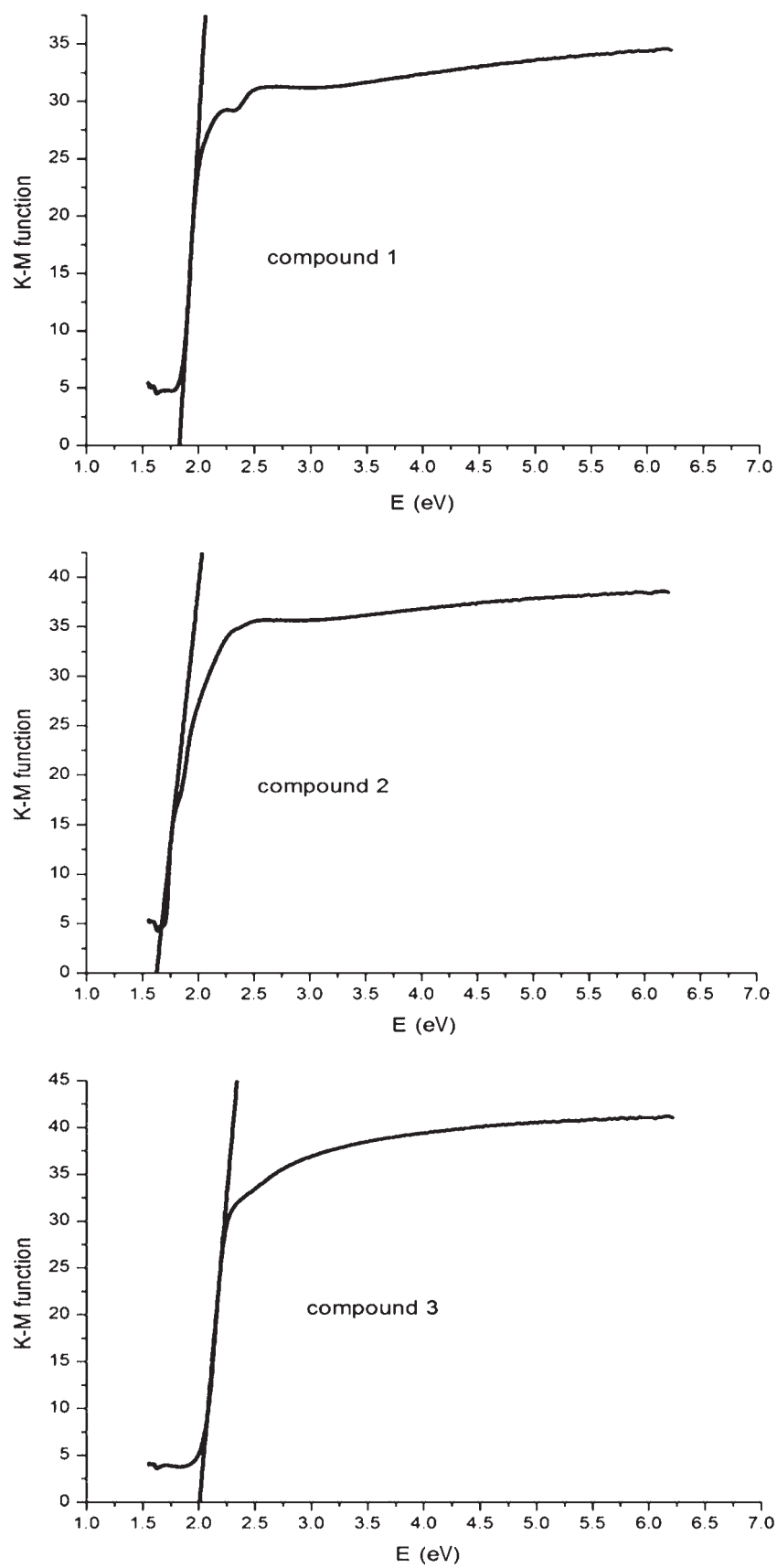


Figure 6. K-M function versus energy (eV) curve compounds 1, 2 and 3.

Ag···Ag contact with an Ag···Ag distance of 3.308 Å in the AgI₂Ag units bridged by two μ_2 -I5 ions, while the Ag···Ag bond did not appear in the AgI₂Ag units bridged by μ_2 -I1 and μ_2 -I2 ions. As shown in figure 3b, the two types of AgI₂Ag units were alternately linked by sharing Ag centers to form an infinite chain.

3.2 Thermogravimetric analysis

The thermogravimetric analysis experiments of complexes **1**, **2** and **3** were investigated under air atmosphere, using a temperature gradient from room temperature to 800°C at a rate of 5°C/min as shown in figure 4. Complex **1** is similar to complex **2**, which remains stable up to 260°C. Then weight loss occurs in the range of 260–320°C (complex **2** is 260–450°C), which corresponds to the release of cation TBP (TBI in complex **2**). We think that the further weight loss is due to the collapse of the anionic skeleton and decomposition to Ag₂O. In complex **3**, the moisture of the sample caused the slight loss in weight under 250°C. Then weight loss occurs in the range of 250–300°C, which corresponds to the release of cation TBP. The weight loss from 573 to 727°C, the same as in compounds **1** and **2**, which can be attributed to anionic skeleton collapsing and Ag₂O decomposing.

3.3 UV-Vis property

The UV-Vis absorption spectra of **1–3** in the solid state are shown in figure 5. The electronic spectra of **1** and **3** show similar absorbance with the bands centered around 230 nm suggesting the domination of $\pi \rightarrow \pi^*$ transition from benzene ring in templates. The absorption band of compound **2** observed at ~240 nm shows a strong resemblance to those of **1** and **3** on account of $\pi \rightarrow \pi^*$ transition with the benzene ring due to conjugation effect.

3.4 Study of optical band gap

To explore conductivity of the compounds **1**, **2** and **3**, the UV-Vis diffuse reflectance spectra were measured to obtain their band gaps (E_g). The band gap (E_g) was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function F against energy E .^{22,23} Kubelka-Munk function, $F = (1 - R)^2 / 2R$, was converted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at a given wavelength. The

F versus E plots, are shown in figure 6, and the E_g values assessed from the respective steep absorption edge are 1.83 eV for **1**, 1.63 eV for **2** and 2.02 eV for **3**, which indicate that these complexes are potential semi-conductive materials.²³

3.5 XRPD analysis

The experimental powder X-ray diffraction patterns in comparison with simulated XRD patterns from single-crystal X-ray data of the three coordination polymers are shown in figure S1. Their peak positions are in good consistency with each other, indicating the phase purity of the samples.

4. Conclusion

In summary, three metal halide cluster supramolecular polymers were obtained via slow evaporation approach at room temperature from methanol and DMF system through trication-templated self-assembly strategy. The inorganic moiety in compounds **1**, **2** and **3** take single chain framework with TBP and TBI trications surrounding them. These novel supramolecular networks provide new insights into the construction of solid-state materials, in particular modular open framework or porous materials, which is a subject of current intense investigation. Exploiting the methodology described here in more complex systems is under way.²⁴

Supplementary Information

The supporting information, available at www.ias.ac.in/chemsci, contains important bond distances and angles for **1–3**, experimental and simulated powder XRD patterns. CCDC1034460, 1034461 and 1034462 contain the supplementary crystallographic data for compounds **1–3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

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References

1. Li L, Yue J M., Qiao Y Z, Niu N N and Hou H W 2013 *Cryst. Eng. Comm.* **13** 3835

2. Wang Z M, Hu K L, Gao S and Kobayashi H 2010 *Adv. Mater.* **22** 1526
3. Zhu L L, Ma X, Ji F Y, Wang Q C and Tian H 2007 *Chem.–Eur. J.* **13** 9216
4. Sun S, Zhang R, Anderson S, Pan J, Akermark B and Sun L 2006 *Chem. Commun.* **40** 4195
5. Brunsveld L, Folmer J B, Meijer E W and Sijbesma R P 2001 *Chem. Rev.* **101** 4071
6. De Greef T F A, Smulders M M J, Wolffs M, Schenning A P H J, Sijbesma R P and Meijer E W 2009 *Chem. Rev.* **109** 5687
7. Aida T, Meijer E W and Stupp S I 2012 *Science* **335** 813
8. Ma X and Tian H 2014 *Acc. Chem. Res.* **47** 1971
9. Sakamoto K, Takashima Y, Yamaguchi H and Harada A 2007 *J. Org. Chem.* **72** 459
10. Gomez-Casado A, Dam H H, Yilmaz M D, Florea D, Jonkheijm P and Huskens J 2011 *J. Am. Chem. Soc.* **133** 10849
11. Badjica J D, Nelson A, Cantrill S J, Turnbull W B and Stoddart J F 2005 *Acc. Chem. Res.* **38** 723
12. Lee M, Niu Z, Slebodnick C and Gibson H W 2010 *J. Phys. Chem. B* **114** 7312
13. Jiang X M, Zhang M J, Zeng H Y, Guo G C and Huang J S 1999 *J. Am. Chem. Soc.* **121** 452
14. Hu J S, Q L Zhang M D, Yao X Q, Li Y Z, Guo Z J, Zheng H G and Xue Z L 2012 *Chem. Commun.* **48** 681
15. Lee J W, Samal S, Selvapalam N, Kim H J and Kim K 2003 *Acc. Chem. Res.* **36** 621
16. Liu D, Li H X, Liu L L, Wang H M, Li N Y, Ren Z G and Lang J P 2010 *Cryst. Eng. Comm.* **12** 3708
17. Yan X Z, Xu D H, Chi X D, Chen J Z, Dong S Y, Ding X, Yu Y H and Huang F H 2012 *Adv. Mater.* **24** 362
18. Yue J M, Niu Y Y, Zhang B, Ng S W and Hou H W 2011 *Cryst. Eng. Comm.* **13** 2571
19. Niu Y Y, Wu B L, Guo X L, Song Y L, Liu X C, Zhang H Y, Hou H W, Niu C Y and Ng S W 2008 *Cryst. Growth Des.* **8** 2393
20. Baron M, Tubaro C, Basato M, Natile M M and Graiff C 2013 *J. Organomet. Chem.* **723** 108
21. Ibrahim H, Koorbanally N A, Ramjugernath D, Bala M D, Nyamori V O and Anorg Z 2012 *Allg. Chem.* **638** 2304
22. Xia Y, Wu P F, Wei Y G, Wang Y and Guo H Y 2006 *Cryst. Growth Des.* **6** 253
23. Liu H Y, Bo L, Yang J, Liu Y Y, Ma J F and Wu H 2011 *Dalton Trans.* **40** 9782
24. Li L, Yue Z C, Zhang W L, Zhang B, Niu Y Y and Hou H W 2013 *Cryst. Eng. Comm.* **15** 8395