



Self-assembly of five new organic–inorganic hybrids based on two new flexible tricationic templates

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ARTICLE INFO

Article history:

Received 31 July 2014

Received in revised form 5 November 2014

Accepted 12 November 2014

Available online 9 December 2014

Keywords:

Haloclusters

Self-assembly

Flexible tricationic template

ABSTRACT

Five new haloclusters, namely, $\{[\text{Tbmpm}](\text{MeOH})[\text{Cu}_3\text{Br}_6]\}$ (**1**), $\{[\text{Tbmpm}][\text{Cu}_2(\text{SCN})_5]\}_n$ (**2**), $\{[\text{Tbmpm}][\text{Ag}_4\text{Br}_7]\}_n$ (**3**), $\{[\text{Tbmpm}]_{0.5}[\text{Ag}_2\text{Br}_{2.2}(\text{SCN})_{0.7}]\}_n$ (**4**) and $\{[\text{Tbpm}][\text{Cu}_2(\text{SCN})_5]\}_n$ (**5**) [Tbmpm-3Br = 1,3,5-tri(4-methylpyridiniummethyl)-2,4,6-trimethylbenzene tribromide and Tbpm-3Br = 1,3,5-tri(4-methylpyridiniummethyl) benzene tribromide] were synthesized by the cation-templated self-assembly with Cu/AgX (X = Br, I, SCN) in N, N-dimethyl formamide (DMF) and MeOH system. The X-ray crystallography analysis showed that these compounds were all composed of discrete organic cations and halocluster anions. Compound **1** has a trinuclear structure, compound **2** exhibits an anion complex composed of 1D chain and mononuclear structure, compounds **3** and **4** present similar 1D silver cluster. More interesting, compound **5** possesses a rare 2D polypseudorotaxane structure. The H-bonds and electrostatic interactions between the organic counterions and inorganic moieties also do the contribution to the crystal packing. These compounds were further characterized by IR spectra, UV–Vis, PXRD, and thermal gravimetric analysis (TGA). Their luminescent properties were also investigated in the solid state.

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1. Introduction

The rational design and synthesis of inorganic–organic hybrid materials have attracted considerable interest over the past decades not only for the structural diversity, but also due to their multifunctional applications in different areas, such as adsorption, magnetism, photochemical areas, ion exchange, catalysis and so on [1–7]. In these hybrids, the inorganic component may confer thermal stabilities and useful functional properties, while the organic component provides designability and multiconfiguration. The combination of these two kinds of components may result in diverse structures and new physical properties. Among the various families of inorganic–organic hybrid polymers, Cu(I) or Ag(I) halides and pseudohalides which features d^{10} shell layer are an important branch for their large structural variation and rich properties. To date, they have been reported to exhibit rich anion structures, ranging from 0-D oligomers, 1-D chains, 2-D layers to 3-D frameworks [8,9]. Based on the reported examples, we found that the utilization of heterocyclic nitrogen-containing organic cations

(frequently called as structure-directing agents, SDAs) to construct haloclusters supramolecular compounds with interesting structural and properties has become a very active and important synthetic strategy [10–14]. The selection of SDAs is crucial because their nature such as size, symmetry and valence may have a profound impact on the final structures of anion hosts.

Our group has been long devoted to the construction of halocluster supramolecular compounds based on monocations and dications. Recently inspired by the lack of supramolecular hybrids induced by multivalent cations, two semi-rigid cations Tbmpm and Tbpm (Scheme 1) which possess three $-\text{CH}_2-$ groups between the pyridine and benzene ring, and could rotate freely around the C–N bonds to give different conformations were encountered in our investigation. Multication-oriented hybrids may present new interesting topologies because of the existence of multiple interaction sites, and new functions endowed by host–guest interactions [15]. As part of our ongoing interest in understanding the effect of SDAs on the organic–inorganic halocluster supramolecular systems, in this work, we reported the syntheses, crystal structures and properties of five new halocluster supramolecular compounds: $\{[\text{Tbmpm}](\text{MeOH})[\text{Cu}_3\text{Br}_6]\}$ (**1**), $\{[\text{Tbmpm}][\text{Cu}_2(\text{SCN})_5]\}_n$ (**2**), $\{[\text{Tbmpm}][\text{Ag}_4\text{Br}_7]\}_n$ (**3**), $\{[\text{Tbmpm}]_{0.5}[\text{Ag}_2\text{Br}_{2.2}(\text{SCN})_{0.7}]\}_n$ (**4**) and $\{[\text{Tbpm}][\text{Cu}_2(\text{SCN})_5]\}_n$ (**5**). The X-ray crystallography analysis

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showed that compound **1** has a trinuclear structure, compound **2** exhibits a anion complex composed of 1D chain and mononuclear structure, compounds **3** and **4** present similar 1D silver cluster, whereas, compound **5** possesses a rare 2D polypseudorotaxane structure.

2. Experimental

2.1. Materials and methods

The trication 1,3,5-tri(4-methylpyridiniummethyl)-2,4,6-trimethylbenzene tribromide (Tbmpm-3Br) and 1,3,5-tri(4-methylpyridiniummethyl) benzene tribromide (Tbpm-3Br) were prepared from refluxing reactions of 1,3,5-tri(bromomethyl)-2,4,6-trimethylbenzene and 1,3,5-tri(bromomethyl) benzene with excess 4-methylpyridine in ethanol solvent [16–18]. Other chemicals were obtained from commercial sources and used as received without further purification. The IR spectra were recorded on a Shimadzu IR-435 spectrometer from KBr pellets (4000–400 cm^{−1}). A model NETZSCHTG209 thermal analyzer was used to record TG curves in flowing air atmosphere of 20 mL·min^{−1} at a heating rate of 5 °C·min^{−1} in the temperature range 45–700 °C using platinum crucibles. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. The UV–Vis diffuse reflectance spectra were measured at UV–Vis-NIR Cary 5000. Photoluminescent measurement of **1–4** in solid state is conducted on a HITACHI F-7000 spectrophotometer and the data is collected at room temperature. 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 Kα1 radiation on a PAN analytical X'Pert PRO diffractometer.

2.2. Complex synthesis

2.2.1. Synthesis of {[Tbmpm](MeOH)[Cu₃Br₆]} (1)

A methanol solution of Tbmpm-3Br (0.067 g, 0.1 mmol) was added dropwise to a stirring solution of CuBr (0.014 g, 0.1 mmol)

dissolved in 5 mL of DMF/H₂O (volume ratio of 4:1) in the presence of excess KBr (0.024 g, 0.2 mmol). Pale yellow precipitates appeared and DMF was added continuously until the precipitates disappeared completely. The solution was then filtered and slowly evaporated in a vial at room temperature. Lilac crystals of **1** suitable for X-ray analysis were obtained after 2 days in about 49% yield. The product is not soluble in common solvents. *Anal. Calc.* for C_{41.33}H_{53.33}Br₈Cu₄N₄O_{1.33}: C, 32.57; H, 3.50; N, 3.68. Found: C, 32.62; H, 3.48; N, 3.70%. IR(KBr): 3473.04(w), 3106.90(w), 3042.21(w), 1975.66(w), 1637.05(vs), 1567.57(w), 1509.36(w), 1464.97(s), 1373.14(w), 1317.61(w), 1269.36(w), 1154.10(s), 1140.07(s), 1033.22(w), 1020.08(s), 948.30(w), 861.92(w), 820.72(s), 775.62(w), 765.18(w), 698.47(w), 678.84(w), 527.12(w), 491.16(w), 474.47(w) cm^{−1}.

2.2.2. Synthesis of {[Tbmpm][Cu₂(SCN)₅]}_n (2)

Light yellow crystals **2** were obtained under conditions similar to that described for **1** only with CuSCN (0.012 g, 0.1 mmol) instead of CuBr. Yield: 70%. *Anal. Calc.* for C₃₅H₃₆Cu₂N₈S₅: C, 49.10; H, 4.24; N, 13.09. Found: C, 49.16; H, 4.20; N, 13.15%. IR(KBr): 3500.11(w), 3046.14(w), 2089.29(vs), 2076.27(vs), 1637.41(m), 1569.11(w), 1510.70(w), 1464.46(m), 1374.84(w), 1321.75(w), 1258.37(w), 1235.30(w), 1206.29(w), 1155.15(m), 1137.27(w), 1052.17(w), 1031.71(w), 820.43(m), 801.62(w), 761.90(w), 710.43(w), 698.31(w), 524.17(w), 477.26(w) cm^{−1}.

2.2.3. Synthesis of {[Tbmpm][Ag₄Br₇]}_n (3)

Colorless crystals **3** were obtained under conditions similar to that described for **1** only with AgBr (0.018 g, 0.1 mmol) instead of CuBr. Yield: 63%. *Anal. Calc.* (%) for C₁₅H₁₈Ag₂Br_{3.50}N_{1.50}: C, 25.21; H, 2.54; N, 2.94. Found: C, 25.26; H, 2.50; N, 2.98%. IR(KBr): 3444.33(w), 3109.03(w), 3044.67(w), 1635.87(s), 1567.66(w), 1508.83(w), 1466.24(s), 1433.20(w), 1371.91(w), 1314.66(w), 1245.77(w), 1143.42(s), 1034.77(w), 843.87(w), 833.40(w), 819.31(s), 758.31(w), 699.28(w), 685.40(w), 527.61(w), 505.44(w), 480.13 cm^{−1}.

Table 1

Crystal data and structure refinement for **1–5**.

Complexes	1	2	3	4	5
Empirical formula	C _{41.33} H _{53.33} Br ₈ Cu ₄ N ₄ O _{1.33}	C ₃₅ H ₃₆ Cu ₂ N ₈ S ₅	C ₁₅ H ₁₈ Ag ₂ Br _{3.50} N _{1.50}	C _{15.71} H ₁₈ Ag ₂ Br _{2.79} N _{2.21} S _{0.71}	C ₃₂ H ₃₀ Cu ₂ N ₈ S ₅
Formula weight	1520.99	856.10	714.73	699.21	814.02
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	P2 ₁ /n	P2 ₁ (1)/n	pnma	pnma	Pbca
a (Å)	13.4904(9)	10.4155(5)	18.488(2)	19.0513(8)	11.1963(2)
b (Å)	20.5228(13)	9.5475(6)	20.099(2)	19.9105(8)	18.6975(4)
c (Å)	13.4954(9)	38.386(3)	10.415(1)	10.5667(4)	33.9086(8)
α (°)	90	90	90.000	90	90.00
β (°)	92.341(4)	94.046	90.000	90	90.00
γ (°)	90	90	90.000	90	90.00
V (Å ³)	3733.2(4)	3807.7(4)	3870(2)	4008.2(3)	7098.5(3)
Z	3	4	8	8	8
ρ (Mg cm ^{−3})	2.030	1.493	2.453	2.317	1.523
μ (mm ^{−1})	8.144	1.429	9.247	7.589	4.516
F(000)	2208	1760	2680	2646	3328.0
Crystal size (mm)	0.21 × 0.20 × 0.20	0.19 × 0.17 × 0.14	0.30 × 0.30 × 0.20	0.20 × 0.20 × 0.20	0.16 × 0.16 × 0.14
T (K)	296(2)	293(2)	293(2)	296(2)	291.15
Reflections collected	37709	33285	32449	34683	14529
Independent reflections	6559 [R _{int} = 0.0866]	7754 [R _{int} = 0.0422]	4547 [R _{int} = 0.0757]	5106 [R _{int} = 0.0494]	6302 [R _{int} = 0.0688]
Data/restraints/parameters	6559/0/406	7754/0/457	4547/0/221	5106/19/249	6302/0/431
Goodness-of-fit (GOF) on F ²	0.985	1.002	1.107	1.035	1.056
Final R indices [I > 2σ (I)]	R ₁ = 0.0454, wR ₂ = 0.1007	R ₁ = 0.0448, wR ₂ = 0.0870	R ₁ = 0.0377, wR ₂ = 0.1010	R ₁ = 0.0649, wR ₂ = 0.1619	R ₁ = 0.0631, wR ₂ = 0.1619
R indices (all data)	R ₁ = 0.0709, wR ₂ = 0.1122	R ₁ = 0.0778, wR ₂ = 0.1018	R ₁ = 0.0543, wR ₂ = 0.1103	R ₁ = 0.1323, wR ₂ = 0.1923	R ₁ = 0.0873, wR ₂ = 0.1839
Largest difference in peak	0.741	0.389	0.757	1.936	0.57
Hole (e Å ^{−3})	−0.853	−0.324	−1.187	−1.738	−1.32

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