# Transformation of dense AgI into a silver-rich framework iodide using thiophenol as mineralizer

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ABSTRACT

A new three-dimensional framework iodide, $(DabcoH)_2[(Dabco)_2Ag_{14}I_{16}]$ (**1**), was solvothermal synthesized by transformation of dense AgI using *p*-methylthiophenol as mineralizer, and characterized by elemental analysis, single-crystal and powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry analysis, UV–vis diffuse reflectance spectroscopy and fluorescence spectroscopy. Compound **1** crystallizes in the trigonal space group *R-3c*, $a = 13.4452(2)$ Å, $c = 63.725(2)$ Å, $V = 9976.5(4)$ Å$^3$, $Z = 6$. It features a 3D silver-rich $[(Dabco)_2Ag_{14}I_{16}]^{2-}$ anionic framework built up from corner-sharing of hybrid $[(Dabco)_2Ag_{14}I_{19}]^{5-}$ clusters, with protonated DabcoH$^+$ as counterions residing in the channels. UV–vis reflectance spectroscopy reveals the band gap of **1** is 3.3 eV. Compound **1** exhibits a strong photoluminescent emission band at 567 nm upon excitation at 489 nm.

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## 1. Introduction

Microporous materials with regular pore architectures are of great interest due to their chemical diversity and immense practical importance for commercial applications such as gas storage, ion exchange, and catalysis [1]. During the past decades, the design synthesis of novel microporous crystalline materials with new compositions and framework topologies has been significantly advanced, leading to the generation of an even greater variety of novel porous materials ranging from microporous oxides (phosphates, germinates) to oxide/fluoride, nitrides, and sulfides [1–5]. In 1997, Martin and Zubieta introduced a new type of microporous compounds, which utilized halide ions as replacements for the O$^{2-}$ anions, and tetrahedral transition metal cations Zn$^{2+}$ or Cu$^+$ substitution for high valent main-group cations such as Si$^{4+}$, Al$^{3+}$ or Ge$^{4+}$ in microporous oxides, respectively [6,7]. In contrast to remarkable stability of traditional microporous materials, the reactivity and polarizablity of metal–halide building blocks make microporous halides have potential catalytic, optical and ion transport applications [8]. However, only a few 3-D open framework halides have been reported so far [6–23].

Among the metal halides family, Ag–I compounds represent a unique system, in which monovalent Ag$^+$ can adopt diverse

coordination modes(2, 3, 4) and AgI$_x$ polyhedra exhibit flexible linkages ranging from corner to edge and face-sharing [24–28]. In combination with covalent characteristic of Ag–I bond and possible Ag–Ag argentophilic interactions, Ag–I based system has great potential to form diverse and stable open framework. Though extensive research efforts were devoted to synthesis of Ag–I compounds in past decades, limited progress have been achieved in Ag–I-based 3D frameworks [9,11], and most of the compounds reported are low-condensed degree clusters or chains [23–36]. This is in part due to the low solubility of AgI. In most synthesis systems, excess I$^-$ as mineralizer was unavoidably introduced to increase the solubility of AgI, while may decrease the condensation degree of AgI$_x$ building units and lead to the formation of low dimensional structures. Therefore, it is of great challenge to design and synthesize high dimensional framework Ag–I compounds. One possible strategy to access high dimensional framework Ag–I compounds is introducing new mineralizers into the syntheses systems, which can overcome the low solubility of AgI, and improve condensation degree of AgI$_x$ building units under specific condition.

Inspired by the F$^-$ anion method in synthesis of high-silica zeolites [37–39], and based on our previous work in design synthesis of Cu$^+$ or Ag$^+$-containing framework chalcogenides [40–42], we developed a new method to synthesize Ag–I compounds by using *p*-methylthiophenol (HSPhMe-4) as mineralizer. In this paper, we report the solvothermal synthesis of a new 3-D framework iodide, $(DabcoH)_2[(Dabco)_2Ag_{14}I_{16}]$, by the transformation of dense AgI. It features a high Ag/I ratio framework built up

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from $[(Dabco)_2Ag_{14}I_{19}]^{5-}$ clusters, with monoprotonated Dabco molecules located in the channels.

## 2. Materials and methods

### 2.1. Materials and physical measurements

All reagents were purchased from commercial sources and were used without further purification. Energy dispersive spectroscopy (EDS) was made on a JEOL JSM-5600LV scanning electronic microscope. Elemental analysis(C, H, N) was carried out on a Vario EL III elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out using Mettler Toledo Star under a flow of nitrogen (40 mL/min) from 35 to 750 °C at heating rate of 5 °C/min. Powder X-ray diffraction (XRD) data were obtained using a Ultima III diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). The data were collected at room temperature with a step size of 0.02° and the operating power was 40 kV/40 mA. The UV–vis spectrum was measured at room temperature using SHIMADAZU UV-2550 double-beam, double monochromator spectrophotometer, equipped with an integrating sphere at 293 K, and a BaSO4 plate was used as reference. The reflectance data collected was converted to the adsorption data using the Kubelka–Munk functions. The photoluminescence spectra of compound 1 were recorded on an Edinburgh FLS-980 fluorescence spectrometer using single photon counting measurement.

### 2.2. Synthesis

Compound 1 was prepared as follows: AgI (11.8 mg, 0.05 mmol), 1,4-diazabicyclo[2.2.2]octane (Dabco)(11.2 mg, 0.1 mmol) and HSPhMe-4 (15.0 mg, 0.12 mmol) were placed into a Pyrex-glass tube, then about 0.5 mL acetonitrile were added as solvent. After the mixture being stirred thoroughly, the glass tube was flame sealed (reagents filled about 10% volume of the tube) under air atmosphere, placed in a stainless-steel autoclave, into which distilled water as a media for heat transferring was added to 80% filling, and heated at 105 °C for 3 days, and then cooled to room temperature naturally. The products were washed with acetonitrile and ethanol several times, respectively. Colorless block shining crystals were obtained in 89% yield (11.2 mg) based on AgI. EDS analysis on several crystals gave an average Ag/I ratio of 7:8. Elemental analysis (%) calc. for 1 ($C_{24}H_{50}N_8Ag_{14}I_{16}$): C, 7.22; H, 1.25; N, 2.81. Found: C, 7.35; H, 1.20; N, 2.98.

### 2.3. Crystallographic studies

A suitable single crystal of 1 was carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. The intensities of the crystal data were collected on Bruker Smart APEX II diffractometer equipped with graphite monochromitized Mo Ka radiation ($\lambda = 0.71073$ Å) at room temperature. The structure were solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELX-97 [43]. All non-hydrogen atomic positions were located in Fourier maps and refined anisotropically, while all of the hydrogen atoms were refined with isotropic displacement parameter [44]. The Ag(3) atom in the structural model shows disorder over two positions, each of which has a occupancy of 0.5. The hydrogen atoms of Dabco molecules were located at geometrically calculated positions except the protonated hydrogen atom from the DabcoH$^+$, which was located from the difference Fourier maps. Crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. Crystallographic data for the structure reported in

this paper have been deposited with the Cambridge Crystallographic Data Centre with CCDC no. 1006756. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

## 3. Results and disccussion

### 3.1. Synthesis

Our research showed that HSPhMe-4 is essential for the syntheses; otherwise 1 cannot be synthesized. In the syntheses of compound 1, HSPhMe-4 serves as a mineralizer, which can effectively increase the solubility of AgI. According to the "Soft and Hard Acids and Bases" principle (SHAB) [45], S atom in thiophenol is a typical soft base, which is readily to coordinate with soft acid metal cations with $d^{10}$ electron configuration, such as Ag$^+$ and Cu$^+$, to form stable and soluble complex [46–48]. Our experimental results reveal that HSPhMe-4 can dissolve AgI in acetonitrile. Worth noting is that the synthesis of compound 1 was carried out in I$^-$-deficient system, which is different from routine synthesis system in presence of excess I$^-$. For comparison, NH$_4$I was selected as mineralizer in the solvothermal syntheses, however, compound 1 can not be isolated, but a new iodide (DabcoH) [(DabcoH)Ag$_2$I$_4$] formed, which contains a 1-D hybrid [(DabcoH) Ag$_2$I$_4$]$^-$ anionic chain with low Ag/I ratio(0.5) [49]. Therefore, HSPhMe-4 not only serves as an effective mineralizer capable of increasing the solubility of AgI, but also allows the assembly of Ag–I units with high condensation degree, further to access high dimensional framework iodides.

### 3.2. Structural description

Single crystal X-ray diffraction reveals that Compound 1 crystallized in trigonal space group $R$-3c, and contains a 3D anionic $[(Dabco)_2Ag_{14}I_{16}]^{2-}$ framework with protonated DabcoH$^+$ residing in the channels. As shown in Fig. 1, the asymmetric unit of 1 consists of three crystallographically independent Ag$^+$ ions, four I$^-$ ions, one

**Table 1**
Crystallographic data of 1.

| Empirical formula | $C_{24}H_{50}N_8Ag_{14}I_{16}$ |
|---|---|
| Formula weight | 3991.30 |
| Crystal system | Trigonal |
| Space group | $R$ -3c |
| $T$(K) | 293(2) |
| Wavelength(Å) | 0.71073 |
| Unit cell dimensions | $a = 13.4452(7)$ Å |
|  | $b = 13.4452(7)$ Å |
|  | $c = 63.725(2)$ Å |
|  | $\alpha = 90.0°$ |
|  | $\gamma = 120.0°$ |
| Volume (Å$^3$) | 9976.5(4) |
| Z | 6 |
| $D_c$(g cm$^{-3}$) | 3.986 |
| $\mu$ (mm$^{-1}$) | 11.517 |
| $F(000)$ | 10,536 |
| $\theta$ range (°) | 1.86–26.40 |
| Limiting indices | $16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-78 \leq l \leq 79$ |
| Reflections numbers | 26,642 |
| Unique data | 2276 |
| Observed data(I > 3σ(I)) | 2000 |
| $R_{int}$ | 0.0284 |
| Goodness-of-fit on $F^2$ | 1.086 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0541$, $wR_2 = 0.1738$ |
| R indices (all data) | $R_1 = 0.0592$, $wR_2 = 0.1801$ |
| Largest diff-peak and hole | 2.803/ − 3.989 Å$^{-3}$ |