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Structurally dependent thermochromism of two iodoargentate hybrids based on the intermolecular charge transfer

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ABSTRACT

Two iodoargentates directed by N-alkylated 3-cyanopyridiniums, $[(EC)(Ag_2I_3)]_n$ (1) and $[(PC)(Ag_5I_6)]_n$ (2) (EC = N-ethyl-3-cyanopyridinium, PC = N-propyl-3-cyanopyridinium) have been solvothermally synthesized. Structural analysis reveals that the variation of N-substituents on 3-cyanopyridinium is responsible for change of the inorganic moieties (belt-like chain for 1 and columnar chain for 2) and consequent packing modes, which further results in the shift of absorption edges and different thermochromic behavior (from yellow at room temperature to almost colorless for 1 and pale yellow for 2 at liquid nitrogen temperature), as proved by UV–vis spectra.

1. Introduction

Design and synthesis of organically directed halometallates are of continuous interest for their structural diversity and electron-rich feature, which endow them with intriguing semiconducting, luminescent, nonlinear optical properties [1–6]. Recently reported thermochromic iodoplumbates [7–10] and iodobismuthates [11,12] as well as photochromic chlorobismuthates [13–16] and iodoplumbates [17] exhibit interesting component-structure-property relationship. Comparatively, chromism based on organic-inorganic iodoargentate hybrids is rarely reported [18,19].

As one of the decisive components, organic cations not only act as structural directing agents (SDAs) to impact the bonding features and electronic structures of inorganic moieties, but also can respond to the external stimuli and even realize electronic interactions with inorganic moieties, which make it possible to functionally hybridize at the molecular level [20–23]. Pyridiniums possess excellent electron–accepting ability, which can form colored charge transfer (CT) complexes with electron-rich halide ions and present reversible thermochromism in liquid crystals which origin from the association and dissociation of CT complexes [24,25]. However, the chromic behavior loses response once the CT complexes are entrapped in solid state, especially in the crystalline states. Obviously, limitation in types of halide anions, charge donating ability and consequently close packing modes largely prevent these electronically active species from responding to the external stimuli. Comparatively, halometallates, especially iodometallates can aggregate into different inorganic moieties [26–29], which can effectively modulate their charge donating ability and packing patterns with charge acceptors, further giving rise to multiform responses [30–34]. Obviously, rational design of functional halometallates based on their electron-rich feature means opportunity as well as challenge.

Recently, we focused our attention on the synthesis and thermochromic characterization of pyridinium-directed iodoargentate hybrids and found that the thermochromism depends on the charge accepting ability of pyridinium cations (4-cyanopyridnium and 3-cyanopyridinium) [18,19]. As an extension of previous work, two as-synthesized iodoargentate hybrids, $[(EC)(Ag_2I_3)]_n$ (**1**) and $[(PC)(Ag_5I_6)]_n$ (**2**) directed by N-alkylated 3-cyanopyridiniums are prepared, and their optical and thermochromic properties are characterized. Interestingly, their absorption edges and thermochromic behavior are structurally dependent.

2. Experimental

2.1. Materials and methods

All chemicals were commercially purchased and used without further purification. FT-IR spectra (4000–400 cm^{-1}) were

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Table 1
Crystallographic data and refinement parameters of compounds **1** and **2** at 293 (2) K and 100.00 (10) K.

Compound	**1**	**2**	**2a**
CCDC code	1011598	1011599	1028849
Temperature (K)	293 (2)	293 (2)	100.00 (10)
Empirical formula	$C_8H_9N_2$ Ag_2I_3	$C_9H_{11}N_2Ag_5I_6$	$C_9H_{11}N_2Ag_5I_6$
Formula weight	729.61	1447.95	1447.95
Crystal size (mm)	0.07 × 0.03 × 0.01	0.07 × 0.05 × 0.03	0.07 × 0.05 × 0.03
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*2 (1)/*m*	*Pbca*	*Pbca*
a (Å)	10.1740 (8)	23.3666 (9)	23.1540 (6)
b (Å)	6.5937 (4)	8.0003 (3)	8.0316 (2)
c (Å)	12.0743 (11)	25.3805 (12)	24.8635 (7)
α (°)	90	90	90
β (°)	109.303 (9)	90	90
γ (°)	90	90	90
V (Å^3)	764.46 (10)	4744.6 (4)	4623.7 (2)
Z	2	8	8
D_c (g cm^{-3})	3.170	4.054	4.160
F (000)	648	5056	5056
μ (mm^{-1})	8.593	11.858	12.169
Reflections collected	3115	15513	11724
Unique reflections	1633	4645	4074
R_{int}	0.0245	0.0399	0.0234
Goodness-of-fit on F^2	1.025	1.032	1.208
R_1/wR_2, $[I \geq 2\sigma(I)]$[a,b]	0.0408/0.0874	0.0496/0.1011	0.0337/0.0661
R_1/wR_2, (all data)	0.0612/0.1023	0.0716/0.1118	0.0394/0.0679
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.769/−1.034	4.238/−2.358	1.667/−1.224

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$.

measured with a Nicolet 5DX spectrometer using KBr pellets. X-ray powder diffraction (XRPD) patterns were obtained with a Rigaku Ultima IV-185 diffractometer. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 240 elemental analyzer. UV–vis absorption spectra were recorded on a Varian Cary 5000 UV–vis spectrophotometer at room temperature and 77 K. The values of E_g were evaluated with the straightforward extrapolation method [35,36].

2.2. Compound preparation

2.2.1. Preparation of {[N-ethyl-3-cyanopyridinium][Ag_2I_3]}$_n$ (**1**)

3-Cyanopyridinium (0.068 g, 0.65 mmol), concentrated HI (0.35 mL, 45%), AgI (0.705 g, 3 mmol), acetonitrile (5 mL) and ethanol (2 mL) were mixed and stirred for 30 min at room temperature, then sealed in a 15 mL Teflon-lined stainless steel vessel, heated at 110 °C for 3 days, and then cooled to room temperature. Yellow rod crystals were achieved in 41.2% yield (based on Ag). Anal. Calcd for $C_8H_9N_2Ag_2I_3$: C, 13.17; H, 1.24; N, 3.84%. Found: C, 13.15; H, 1.26; N, 3.82%. IR (KBr, cm^{-1}): 2923 m, 2850w, 2252w, 1631s, 1135s, 679w, 620w.

2.2.2. Preparation of {[N-propyl-3-cyanopyridinium][Ag_5I_6]}$_n$ (**2**)

Compound **2** was synthesized similar to **1** except that n-propanol (2 mL) was used to displace ethanol (2 mL). Yellow rod crystals were gained in 32.3% yield (based on Ag). Anal. Calcd for

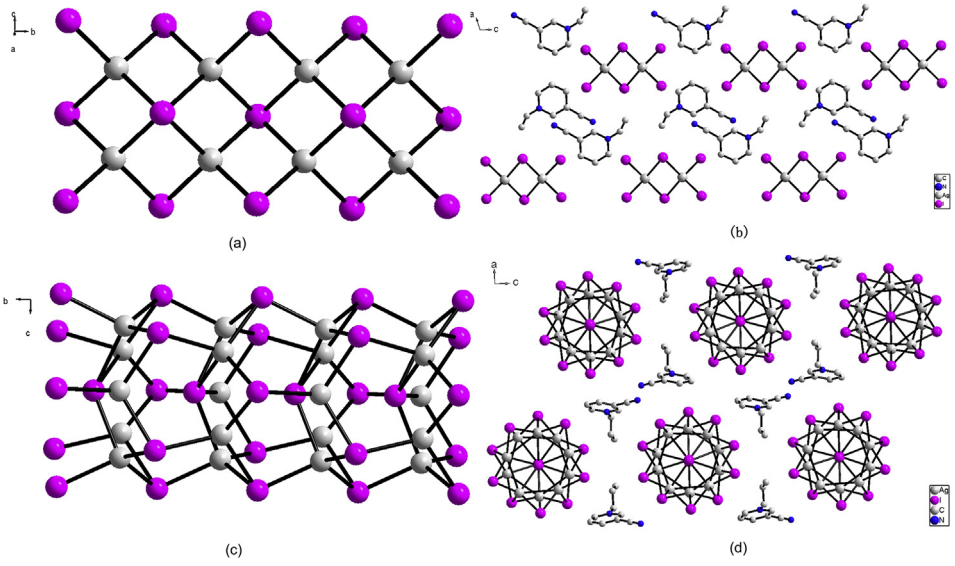

Fig. 1. The inorganic chains of compounds **1** (a) and **2** (c) along the *a*-axis; packing structures of compounds **1** (b) and **2** (d) along the *ac*-plane (H atoms are omitted for clarity).