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Hierarchically responsive and photochromic imidazopyridazinium iodoargentate hybrid materials

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ABSTRACT

Three iodoargentate hybrids, $[MIPDz]_2[Ag_2I_4]$ (**1**), $[AIPDz][Ag_2I_3]$ (**2**), and $[MIPDz]_2[Ag_5I_7]$ (**3**) ($MIPDz^+$ = methylimidazopyridazinium, $AIPDz^+$ = acetonylimidazopyridazinium), have been successfully synthesized, which exhibit improved photochromic properties and hierarchically responsive mechanism from optically inert response to photolysis of iodoargentates, until photoinduced intermolecular electron transfer with Ag particles as secondary electron donor.

1. Introduction

Photochromic materials, especially for organic-inorganic hybrids composed of electron donor-acceptor units have received considerable attention, due to their potential application in various technological areas, such as protection, decoration, optical switching, memory, filtering, display, modulators, and so on [1–5]. Photoactive silver halides have been extensively investigated in the basic and practical fields such as traditional photography [6,7], photochromic glasses [8,9] and photocatalysts [10–12]. Compared with silver iodide, semiconductive iodoargentates possess structural diversity and tunable electron behaviors [13–16]. Besides of thermochromic properties on the basis of intermolecular charge transfer (CT) [17,18], we have recently reported a few of photochromic iodoargentates matched with moderately electron-deficient monocyclic pyridine derivatives such as *N*-methyl-4-carbomethoxypyridinium ($MCMP^+$), monoprotonated pyrazinium ($Hpyz^+$) and methylnicotinohydrazide (MNH^{2+}), which exhibit unique photoinduced intermolecular electron transfer (ET) as well as the generation of colored organic radicals [19–21]. The novel donating-accepting matching relationship is a new strategy constructing photochromic materials with improved photosensitivity. In contrast to the extensively investigated ET photochromic hybrids of chlorometallates, carboxylates, zoelites, and phosphates matched with strong electron acceptors of viologens, naphthenediimides (NDIs) and tris(4-pyridiniumyl)-1,3,5-triazine (TPT) [22–27], electron-deficient variation for organic moieties can effectively modulate the electron behavior of iodoargentates from CT thermochromism to ET photochromism .

Structurally different from pyridine derivatives, imidazopyridazine and its derivatives possess relatively weak electron accepting capabilities due to the π-conjugation effect, which have been widely researched in biology, medical chemistry, and organic synthesis [28–31]. The introduction of electron-deficient alkylated imidazopyridazinium into iodoargentates should lead to some excellent performance for photochromic properties.

Based on the above consideration, using alkylated imidazopyridazinium as structural directing agents, three organic-inorganic iodoargentate hybrids, $[MIPDz]_2[Ag_2I_4]$ (**1**), $[AIPDz][Ag_2I_3]$ (**2**), and $[MIPDz]_2[Ag_5I_7]$ (**3**) ($MIPDz^+$ = methylimidazopyridazinium, $AIPDz^+$ = acetonylimidazopyridazinium), have been successfully synthesized and characterized. All three compounds exhibit hierarchically photochromic behavior with fast response and wide color range, which is ascribed to two completely different coloration mechanism of photolysis of iodoargentates and photoinduced secondary ET.

2. Experimental section

2.1. Materials and methods

All reagents and solvents were commercially available and used as received without further purification. A 300 W mercury lamp (~365 nm) system with temperature control equipped with an IR filter was used to prepare colored samples for electron paramagnetic resonance (EPR), and UV–vis spectrophotometer studies, and the distances between these samples and the Hg lamp are around 20 cm. The

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FT-IR spectra were measured with a Nicolet 5DX spectrometer as KBr disks (4000-500 cm^{-1}) (Fig. S1). Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku UItima IV-185 diffractometer at room temperature. UV–vis absorption spectra were measured at room temperature with a METASH UV-9000S UV–vis spectrophotometer. EPR spectra were carried out on a Bruker A300-10/12 electron paramagnetic resonance spectrometer at room temperature.

2.2. Synthetic procedures and characterization

*2.2.1. Synthesis of [MIPDz]$_2$[Ag$_2$I$_4$] (**1**)*

Compound **1** was synthesized by the solvothermal reaction of AgI (0.282 g, 1.2 mmol), imidazopyridazine (0.077 g, 0.65 mmol), NaI·2H_2O (0.279 g, 1.5 mmol), HI (45%, 0.2 mL) and methanol (5.0 mL) in a 15 mL Teflon-lined autoclave at 110 °C for 3 days. Yellow rod crystals of **1** were obtained by filtration and washed with acetonitrile. The yield based on Ag is 39.8%. Anal. Calcd. (%) for $C_{14}H_{16}N_6Ag_2I_4$: C 16.96, H 1.63, N 8.47; found: C 17.02, H 1.56, N 8.52. IR data (KBr, cm^{-1}): 3139 m, 3098 m, 3064 m, 2934w, 1740w, 1632 m, 1401s, 1317 m, 1234s, 1156 m, 1080 m, 944w, 784s, 748s, 562 m.

*2.2.2. Synthesis of [AIPDz][Ag$_2$I$_3$] (**2**)*

Compound **2** was prepared similar to that of **1** except for the addition of acetone (3.0 mL). Yellowish rod crystals of **2** were obtained by filtration and washed with acetone. The yield based on Ag is 33.2%. Anal. Calcd. (%) for $C_9H_{10}N_3OAg_2I_3$: C 13.99, H 1.30, N 5.44; found: C 14.05, H 1.25, N 5.48. IR data (KBr, cm^{-1}): 3430s, 3125 m, 3063w, 2918 m, 1734s, 1632 m, 1422 m, 1388s, 1347 m, 1254w, 1167s, 1060 m, 786s, 738s, 717 m, 546w.

*2.2.3. Synthesis of [MIPDz]$_2$[Ag$_5$I$_7$] (**3**)*

The yellowish block crystals of **3** were obtained similar to that of **1** except for amount of AgI (0.470 g, 2 mmol). The yield based on Ag is 50.8%. Anal. Calcd. (%) for $C_{14}H_{16}N_6Ag_5I_7$: C 9.91, H 0.95, N 4.96; found: C 9.86, H 0.90, N 4.92. IR data (KBr, cm^{-1}): 3161w, 3119w, 3057w, 2366w, 1634 m, 1559 m, 1415s, 1374s, 1313 m, 1224 m, 1151w, 1087w, 914w, 793s, 758s, 723s, 663w, 574 m.

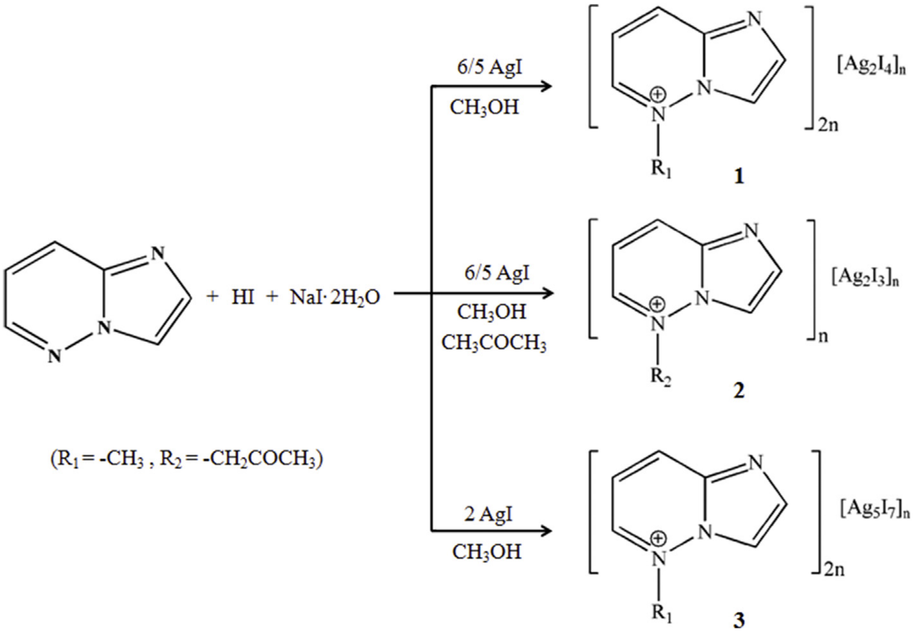
2.3. Single crystal X-ray structure determination and refinement

Single crystals of **1**, **2** and **3** were mounted with glue on glass fiber and crystal data were collected at 273 K on the Bruker D8 Venture diffractometer using graphite monochromated Mo-Kα (λ = 0.71073 Å). Data reduction was accomplished by the CrysAlisPro (Oxford Diffraction Ltd., version 1.171.33.55) program. An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [32]. All three structures were solved by direct methods and refined on F^2 by full-matrix leastsquares techniques with the SHELXL-97 crystallographic soft-ware package [33,34]. For the structure of **3**, some Ag centers are disordered over three positions with occupancy 0.8/0.1/0.1 for Ag3/Ag3A/Ag3B. All non-hydrogen atoms were refined anisotropically. The crystallographic data are shown in Table S1 and the selected bond lengths and angles are listed in Table S2 of the Supporting Information.

3. Result and discussion

3.1. Preparation

Compounds **1**–**3** were *in situ* generated under solvothermal conditions from the mixture of imidazopyridazine, AgI, NaI·2H_2O, HI, methanol and acetone, in which the $MIPDz^+$ and $AIPDz^+$ cations were originated from cleavage of the C-O bond of methanol or C-H of acetone followed by alkylation of imidazopyridazine. Variation of imidazopyridazine/AgI ratios (see Scheme 1), leads to the formation of three chain-like iodoargentates from [Ag$_2$I$_4$] (**1**), [Ag$_2$I$_3$] (**2**) to [Ag$_5$I$_7$] (**3**), exhibiting a concentration-dependent aggregating tendency and chain-like crystallizing preference (Table 1). Especially, coexistence of **2** and **3** (entry 3 in Table 1) obviously indicates a transient crystallizing state of iodoargentates.



Scheme 1. Preparation of compounds **1**–**3**.