Four imidazolium iodocuprates based on anion−π and π−π interactions: Structural and spectral modulation

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Four imidazolium iodocuprates, $[(1,3\text{-dimethylimidazole})(Cu_2I_3)]_n$ (**1**), $[(1,2,3\text{-trimethylimidazole})(Cu_2I_3)]_n$ (**2**), $[(1,3\text{-dimethylimidazole})(Cu_3I_5)]_n$ (**3**) and $[(1,3\text{-dimethylbenzimidazole})(CuI_2)]_n$ (**4**) have been solvothermally synthesized and optically characterized. Results exhibit that cationic spatial orientation, anion−π and π−π interactions are beneficial to structural diversity and band gap modulation of iodocuprate hybrids. The UV−vis diffuse reflectance spectra show that compounds **1−4** are potential semiconductor materials.

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1. Introduction

Halometallate hybrids based on the crystal and energy-gap engineering have attracted considerable interest [1−10] in the last few years. As an important branch of the semiconducting materials, iodocuprate hybrids are especially interesting due to their structural diversity [11−13] and bandgap-related properties, such as photocatalytic [14] and second harmonic generation (SHG) [15]. It is well known that bandgaps can usually reflect the charge carrier mobility ability of semiconductor materials and consequently determine their application ranges [16−18]. Generally, two strategies are used to modulate the bandgaps of hybrids: one is changing the bonding features or dimension of inorganic frameworks [19,20]; another is introducing organic functional cations [21−23]. The latter is viewed as an more effective and active strategy, and various aromatic cations have been extensively used, especially for pyridine-based organic cations, which not only reveal versatile directing effects based on their multiple noncovalent interactions such as π−π stacking interactions, anion−π interactions and hydrogen bonding [24−27], but also endow the resulted hybrids with intriguing thermo- or photochromism on the basis of the versatile intermolecular charge transfer or electronic transfer

[28−31]. In contrast, among the five-membered heterocyclic compounds, imidazolium are especially intriguing because of it largely used for anion recognition and room temperature ionic liquid (RTIL) through hydrogen bonds [32−35]. As an unusual noncovalent interaction, anion−π interaction is propitious to form the charge transfer complexes, consequently used in the design of anion-sensing receptors [36−44]. Meanwhile, weak stacked π−π interaction among the imidazolium π systems can be parallel, rotated or antiparallel, which was used to stabilize structure of imidazolium ionic liquids and salts, and explore in molecular recognition [42,45−47]. In a word, the imidazolium based on the weak interactions (anion-π、 π−π) in halometallate hybrids have been paid few attentions [48−51]. Structurally, reasonable control alkylation of imidazole can endow these imidazolium derivatives with more flexible spatial orientation and further potential anion−π or π−π stacking interactions improve their charge carrier mobility, which may be beneficial to the structural diversity and energy gap modulation [52] of iodocuprate hybrids.

On the basis of the above consideration, four imidazolium iodocuprates hybrids $[(1,3\text{-dimethylimidazole})(Cu_2I_3)]_n$ (**1**), $[(1,2,3\text{-trimethylimidazole})(Cu_2I_3)]_n$ (**2**), $[(1,3\text{-dimethylimidazole})(Cu_3I_5)]_n$ (**3**) and $[(1,3\text{-dimethylbenzimidazole})(CuI_2)]_n$ (**4**) *via in situ* route were synthesized by selecting the flexible imidazole derivatives as structure directing agents, and their effect of cationic spatial orientation and functional modulation were also investigated.

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2. Experimental

2.1. Materials and methods

All reagents and solvents were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet 5DX spectrometer. XRPD data were recorded in a Rigaku Ultima IV−185 diffractometer. Elemental analyses were carried on Perkin−Elmer 240 elemental analyzer. UV−Vis diffuse reflectance spectra were measured at room temperature with a Varian Cary 5000 UV−Vis spectrophotometer (the values of Eg were obtained with the use of a straightforward extrapolation method [53,54]). Thermogravimetric (TG) behavior was investigated on a HTG-3 thermogravimetric analyzer at 10 °C·min^{-1} in air from room temperature to 800 °C.

2.2. Preparation of compounds 1-4

Four compounds were prepared through the similar procedure except for the variation of imidazole derivatives (N, N-carbonyldiimidazole (0.016 g, 0.10 mmol) in **1**, 2-methylimidazole (0.008 g, 0.10 mmol) in **2**, imidazole (0.006 g, 0.10 mmol) in **3**, benzimidazole (0.016 g, 0.10 mmol) in **4**).

A mixture of CuI (0.085 g, 0.50 mmol), imidazole derivatives (0.10 mmol), acetone (4 ml), methanol (4 ml) and concentrated HI (0.1 ml, 45%) were stirred for 30 min at room temperature, then sealed in a 15 ml Teflon-lined stainless steel vessel, heated at 160 °C for 5 days.

For compound **1**, black-red block crystals were obtained in 41.2% yield (based on Cu). Anal. Calcd (%) for $C_5H_9Cu_2I_3N_2$: C 9.92, H 1.49, N 4.63%. Found: C 9.94, H 1.47, N 4.68%. IR (KBr, cm^{-1}): 3443 s, 3146w, 3110w, 3096w, 2944w, 2920w, 2853w, 1611 m, 1572 m, 1511 s, 1462w, 1168 m, 827 m, 743w, 616 m. For compound **2**, pale yellow block crystals were obtained in 40.0% yield (based on Cu). Anal. Calcd (%) for $C_6H_{11}Cu_2I_3N_2$: C 11.63, H 1.78, N 4.52%. Found: C 11.61, H 1.79, N 4.50%. IR (KBr, cm^{-1}): 3436 s, 2919 m, 2850w, 1635 m, 1458w, 1396w, 1241w, 1127w, 1085w, 734w, 651w. For compound **3**, brown plate crystals were obtained in 48.5% yield (based on Cu). Anal. Calcd (%) for $C_{10}H_{18}Cu_3I_5N_4$: C 11.77, H 1.76, N 5.49%. Found: C 11.79, H 1.75, N 5.50%. IR (KBr, cm^{-1}): 3429 s, 3134w, 3111w, 3079w, 2923w, 2854w, 1623 m, 1559 m, 1164 s, 826w, 750 m, 616 m. For compound **4**, pale yellow rod crystals were obtained in 38.9% yield (based on Cu). Anal. Calcd (%) for $C_9H_5CuI_2N_2$: C 23.56, H 1.10, N 6.11%. Found: C 23.55, H 1.09, N 6.10%. IR (KBr, cm^{-1}): 3436 s, 3142w, 3117w, 3065w, 3044 s, 2934w, 2853w, 1616 m, 1565 s, 1462 m, 1349w, 1265 m, 1214 m, 1120 m, 1100 m, 1011w, 860w, 757 s, 592w, 559w.

2.3. X-ray crystallography

Single-crystal X-ray diffraction data of **1**−**4** were collected at 293 K on an Oxford Gemini diffractometer (Mo Kα, λ = 0.71073 Å). An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [55,56]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXS-97 program [57,58]. The Cu1/Cu1′ in compound **2** are disordered, with fixed occupancy of 0.95 and 0.05, respectively. The crystallographic data of **1**−**4** are listed in Table 1, the most relevant lengths and angles of **1**−**4** are listed in Table 2, the C−H···I hydrogen bonds are listed in Table S1 and selected bond lengths and bond angles are listed in Table S2 of the supporting information.

3. Results and discussion

3.1. Infrared spectral aspects

The IR spectra of compounds **1**−**4** (Fig. S6) present similar features due to the presence of imidazolium. The C−H stretching vibrations of imidazolize ring are observed as the medium or weak bands in the range of 3146–3111 cm^{-1}, while the phenyl is observed as strong band at ca. 3044 cm^{-1}. Medium or weak bands in the range of 2944–2854 cm^{-1} indicate the C−H stretching vibrations of methyl groups. Medium bands in the range of 1635–1611 cm^{-1} indicate the C=C stretching vibration and 1462–1164 cm^{-1} can be assigned to the C−N stretching vibration of imidazolize ring [59].

In order to investigate the effect of the cationic substituted groups on the overall hybrids, N,N-carbonyldiimidazole, 2-methylimidazole, imidazole and benzimidazole are chosen as precursors and transformed *via in situ* methylation. And **3** may indicate the hydrolysis of N,N-carbonyldiimidazole in **1** and structural difference of the final resultants implies a special influence of imidazole precursors. Interestingly, formation of the same organic cation, 1,3-dimethylimidazolium for **1**.

3.2. Structural description

Four compounds are all featured as chain-like inorganic motif with different architectures.

{[1,3-dimethylimidazole][Cu2I3]}n (1) Compound **1** crystallizes in the orthorhombic space group *Pbcn* and the asymmetric unit contains one copper (I) atom, two iodine atoms and half of a 1,3-dimethylimidazolium (Fig. S1). As shown in Fig. 1(a), I (1) and I (2) adopt μ_3-and μ-bridging modes respectively. Each monovalent Cu atom is tetrahedrally coordinated and bridged by one μ-I (2) atom and three μ_3-I (1) atoms, resulting in a distorted tetrahedral environment. The Cu−I bond distances range from 2.5468 (14) to 2.8125 (18) Å, while the I−Cu−I bond angles vary between 97.46 (5) and 120.53 (6)°. And the Cu···Cu distances (Cu(1)−Cu(1A) = 2.489 (3) Å) are shorter than the sum of van der Waals radius of the Cu(I) ion (1.4 Å) [48,60], indicating a strong Cu−Cu d^{10}-d^{10} interaction. Adjacent CuI$_4$ tetrahedral are connected together *via* alternative edge- and face-sharing modes, giving rise to a Cu$_2$I$_3$ polymeric chain along the c-axis, which is chargely balanced by 1,3-dimethylimidazolium. Such a chain is similar to the reported compound of {[^{i}Pr$_2$EtNH]$_n$ [Cu$_2$I$_3$]}$_n$ [61].

Noteworthy, imidazole ring is almost parallel to the inorganic chain and two methyl groups point toward the inter-chain space. Especially, each imidazole ring is sandwiched between two μ-I (2) atoms (Fig. 1(b)) from adjacent inorganic chains with distance (4.144 Å) between μ-I atom and centroid of the imidazole ring, which is fall in the range of anion−π interaction (3.82–4.26) [41–43] and the angle of the I···centroid axis to the plane of the imidazolium ring is 66.2° (Fig. 1(c)), indicating weak anion−π interaction (Table 2) [62,63].

{[1,2,3-trimethylimidazole][Cu2I3]}n (2) Compound **2** crystallizes in the monoclinic *I2/a* space group and the asymmetric unit contains two copper atoms, three iodine atoms and a 1,2,3-trimethylimidazolium (Fig. S2). As shown in Fig. 2(a), Cu(1) is disordered, I (1)/I (2) and I (3) adopt μ_3-and μ-bridging modes respectively and two distinct Cu atoms are four-coordinated in a distorted tetrahedral geometry by one μ_3-I (1) atom, two μ_3-I (2) atoms and one μ-I (3) atom for Cu(1), two μ_3-I (1) atoms, one μ_3-I (2) atom and one μ-I (3) atom for Cu(2). The Cu−I distances, I−Cu−I angles and Cu−Cu distances are in the range of 2.5525(8) −2.9347(11) Å, 98.58(3)−125.77(4)° and 2.4585(11)−2.7698(18) Å, respectively. The shortest Cu···Cu distance is 2.4585 (11) Å, shorter