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Solvent-induced supramolecular isomerism in homochiral silver benzimidazolates

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ABSTRACT

Two pairs of enantiomers **R**-[Ag_4(hebim)$_4$] · 3DMAC (***R*-1**), **S**-[Ag_4(hebim)$_4$] · 3DMAC (***S*-1**), **R**-[Ag(hebim)] (***R*-2**) and **S**-[Ag(hebim)] (***S*-2**) [Hhebim = 2-(1-hydroxyethyl) benzimidazole] are reported. Complexes **1** and **2** are supramolecular isomers induced by solvent and are second harmonic generation (SHG) active. In addition, solid-state luminescent properties of **1** and **2** were investigated at room temperature.

Homochirality and helix are widespread phenomenon in nature and organism, such as DNA and polypeptides were found with helical structures related to their homochiral components (*e.g.* right-handed (Δ or P) and left-handed (Λ or M)) [1]. In coordination chemistry, great efforts have been made to introduce chirality into metal–organic complexes, thus proving enantiopure catalysis and separation [2,3]. There are two main synthetic approaches to prepare chiral metal–organic complexes. One is that chiral crystals were prepared by using achiral or racemic ligands through spontaneous resolution upon crystallization, which usually result in racemic mixtures [4]. The other, which is a more efficient synthetic strategy, is to use optically pure chiral multidentate ligands [5,6]. Up to present, although a number of metal benzimidazolates crystallize in chiral space group [4a-c], the enantiopure metal benzimidazolates have been reported extreme rarely [7].

It is well known that supramolecular isomerism is of great interest in the field of crystalline materials, because supramolecular isomers of the substance may have different physical properties [8,9]. The crystallization of supramolecular isomers could be affected by such factors as anion, solvent and pH value, and so forth [10]. Chen et al. reported a series of one-dimensional supramolecular isomers constructed from [Ag(ipim)] (ipim = isopropylimidazole) building blocks, with sinusoidal chain, quintuple helix and chicken-wire structures. The adjacent ipim^{-1} ligands show *cis*- or *trans*-conformations in three complexes, resulted from different reaction condition [10c]. Recently, we reported two pairs of polymorph isomers α-(*R*) or (*S*)-[Zn_2(pemp)(pempH)Cl] and β-(*R*) or (*S*)-[Zn_2(pemp)(pempH)Cl] ($pempH_2$ = (1-phenylethylamino)methylphosphonic acid), by using enantiopure optical ligand [11]. The isomerism was induced by additional organic molecules in experimental condition, which inspired our persistent interesting in homochiral crystallization of coordination complex. In this paper, we employ enantiopure 2-(1-hydroxyethyl)benzimidazole (Hhebim, Scheme 1), and two pairs of enantiomers ***R*-**[Ag_4(hebim)$_4$] · 3DMAC (***R*-1**, DMAC = Dimethylacetamide), ***S*-** [Ag_4(hebim)$_4$] · 3DMAC (***S*-1**), ***R*-**[Ag(hebim)] (***R*-2**) and ***S*-** [Ag(hebim)] (***S*-2**) are obtained successfully. More interestingly, complexes **1** and **2** are supramolecular isomers, attributed to different reaction solvent. The supramolecular isomerism in homochiral metal benzimidazolates has never been reported.

Pale-yellow crystals of ***R*-1** and ***S*-1** were synthesized by reaction *R*- or *S*-Hhebim with $AgNO_3$ in aqueous ammonia and DMAC mixed solvents. Complexes ***R*-2** and ***S*-2** were obtained by following a similar procedure except that methanol instead of DMAC was used as the starting solvent (Scheme 2, Fig. S2 and S3). The purpose of decorated 1-hydroxyethyl is to prepare enantiopure benzimidazole, and subsequently the chiral information is transferred into metal benzimidazolate motif.

Single crystal structural analyses of ***R*-1** and ***S*-1** reveal that they are a pair of optical enantiomers and crystallize in the triclinic system, chiral space group *P*1, with Flack parameters of 0.06(3) and 0.04(3), respectively (Table S1). Hence, ***R*-1** conformation complex is taken as an example. The asymmetric unit of ***R*-1** consists of eight independent Ag atoms, eight hebim^{-1} ligands, and six DMAC solvent molecules (Fig. S1). Each Ag atom coordinates to two N atoms from different hebim^{-1} ligand, with the Ag–N bond lengths being 2.015(9)–2.116(8)

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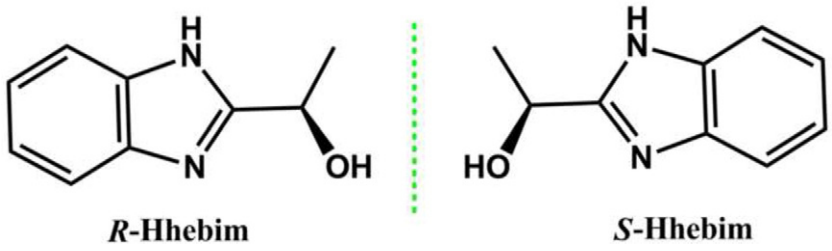


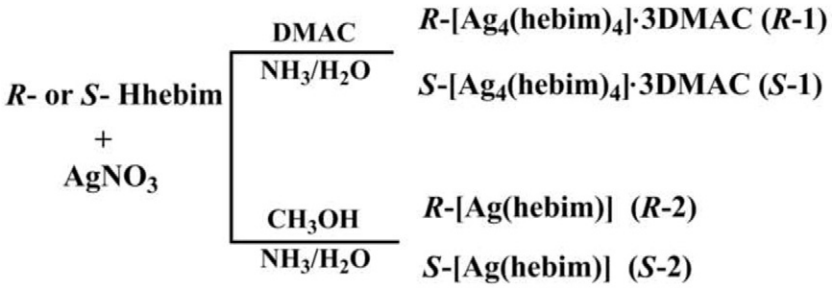
Scheme 1. The structure of Hhebim.

Å and the N–Ag–N bond angles ranging from 171.9(3) to 176.2(3)° (Table S2). The hebim^{-1} serves as bidentate ligand, which coordinates to two adjacent Ag atoms giving four Ag(1), Ag(3), Ag(5) and Ag(7) linear chains (Fig. 1a), and the adjacent hebim^{-1} ligands in each chain are oriented in a *trans*-conformation (the dihedral angles of adjacent hebim^{-1} planes are in the range of 10.1(1)–17.3(1)°). The interesting ladder-like hydrogen bonds were found between DMAC solvent and 1-hydroxyethyl (Fig. 1b and c). Among DMAC oxygen atoms, O13 and O14 atoms act as μ_2-bridge mode and the other oxygen as monodentate link mode. The hydrogen bonds O1···O9, O2···O14, O3···O10, O4···O14, O5···O11, O6···O13, O7···O12 and O8···O13 distances are in the range of 2.598(1)–3.234(1) Å. Parallel chains of Ag(1) and Ag(3), Ag(5) and Ag(7) stack in a vertical fashion (Fig. 3a).

Optical enantiomers (***R*-2**) and (***S*-2**) adopt left-handed (*M*) and right-handed (*P*) helical chains along *c* axis and crystallize in a pair enantiomorphic space groups $P6_522$ and $P6_122$ [12], with Flack parameters of 0.09(13) and 0.04(10), respectively (Table S1). Complex ***R*-2** contains one independent Ag(hebim) building units with two independent Ag atoms (half occupy for Ag1 and Ag2; Fig. 2a). Each Ag atom coordinates to two N atoms from different hebim^{-1} ligands with the Ag–N bond lengths being 2.075(6) and 2.061(8) Å and the N–Ag–N bond angles being 177.7(4) and 168.7(4)°, slightly different from those of ***R*-1** (Table S3). The adjacent two hebim^{-1} ligands in ***R*-2** are oriented in *cis*-conformation to give an arc fragment decorated with 1-hydroxyethyl groups (the dihedral angles of adjacent hebim^{-1} planes are in the range of 7.3–28.1°). These arc fragments interconnect into a single-stranded left-handed (*M*) helix with 6_5 screw axis (Fig. 2b), with all 1-hydroxyethyl groups of hebim^{-1} ligands pointing toward the channel of the helix. The *M*- or *P*-helix can be rationalized into a 12_1 one (Fig. 2c), which does not exist as a crystallographic symmetry, but can exist as a molecular symmetry [13]. The pitch of the helix is 21.679(2) Å and the Ag · · · Ag distances are 6.191(1) Å. The adjacent chains of ***R*-2** stack in a parallel offset fashion filling in the occupied space (Fig. 3b). The shortest interchain Ag · · · Ag distance is 3.670 Å, longer than the sum of the van der Waals radii for Ag (3.44 A°), which means that there is no argentophilic interaction between the helical chains. Complex ***S*-2**, as enantiomeric isomer of ***R*-2**, adjusts its overall structure with *P* helicity. As is well known, conformation of adjacent imidazole plays an important role in structural formation of binary metal imidazolates, *e.g.*, *all-trans*-conformation imidazole anion in binary metal imidazolates predominately forms zigzag chain, while, helical chain or polygon is generated [8d,9a]. Taking silver 2-methylimidazolate (mim) isomers as an example, 2_1 helical chain, octagon, S shape chain, and zigzag chain were corresponding to *all-cis*-conformation, *all-cis*-conformation, *cis*- and *trans*-conformation, and *all-trans*-conformation of adjacent mim^{-1} ligand, respectively [13]. Herein, the hebim^{-1} ligands are oriented in an *all-trans*-conformation in ***R*-1** and an *all-cis*-conformation in ***R*-2**, which match the relationship between conformation of adjacent imidazole and crystal structure. Therefore, the structure of single-stranded helical chain in compound ***R*-2** is a significant structure different from linear structure in compound **R-1**.

The similar composition of [Ag(hebim)] building units and different structure of compounds ***R*-1** and ***R*-2** suggest that the two compounds are supramolecular isomers. Considering that each 1D chain motif was constructed independent of the reaction stoichiometry, the concentrations of reactants and reaction temperature, the supramolecular isomerism could be induced by different reaction solvent. Remarkably, strong hydrogen bond interactions (between solvent and ligand) adjust *all-trans*-conformation of adjacent hebim^{-1} ligand in ***R*-1**, and in such case, one-dimensional linear chains are formed. In other words, only in complex ***R*-2**, the formation of helical silver benzimidazolate motif is efficiently induced by chiral information of hebim^{-1} ligand [14]. The case between compounds ***S*-1** and ***S*-2** is similar to that of compounds ***R*-1** and ***R*-2**.

So far, a few examples of homochiral supramolecular isomers have been prepared and crystallographically characterized [15]. These include 1D and 3D supramolecular isomers $[Mn^{II}(L\text{-mal})(H_2O)(CH_3OH)]_2$ and $[Mn^{II}(L\text{-mal})(H_2O)_2] \cdot H_2O$ (L-mal = L(-)-malic acid) [15a], several Ag(I) supramolecular isomers induced by $CF_3CO_2^{-1}$, $CF_3SO_3^{-1}$ and NO_3^{-1} anions, based on 1,1′-$C_{20}H_{12}${NHC(O)-4-C_5H_4N}$_2$ and 1,1′-$C_{20}H_{12}${NHC(O)-3-C_5H_4N}$_2$ ligands [15b], interpenetrated and non-interpenetrated complexes *meso*-$[LCu_2(H_2O)_2] \cdot (DMF)_8 \cdot (H_2O)_4$, *R*-$[LCu_2(H_2O)_2] \cdot (DMF)_{16} \cdot (H_2O)_{19}$ and *R*-$[LCu_2(H_2O)_2] \cdot (DEF)_{12} \cdot (H_2O)_{16}$ (L = 2,2′-diethyoxy-1,1′-binaphthyl-4,4′,6,6′-tetrakis (4-benzoic acid)) [15c], two-, three- and four-fold helices Ag(I) supramolecular isomers $[AgL(NO_3)]$, $[AgL(PF_6)_{1/6}(OH)_{5/6}]$ and $[AgL(ClO_4)]$, built from axial chiral 3,3′-bipyridine-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl ligands [16]. In fact, although a few above homochiral supramolecular isomers were investigated, supramolecular isomerism in homochiral metal–organic complexes has been studied deficiently. Compared to the reported homochiral supramolecular isomers, in



Scheme 2. Synthesis of the supramolecular isomers.