Polymorphism and structural characterization of a Silver(I) coordination polymer: an inorganic-polymer co-former in the preparation of curcumin containing co-crystals

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Within the relevant field of metal-containing polymers and their applications in the biomedical context [1], a Silver(I) coordination polymer of formula **[(bpy)Ag]OTf**$_\infty$ presenting polymorphism has been synthetized through reaction between the N^N ligand 2,2'-bipyridine (**bpy**) and Silver trifluoromethanesulfonate (**AgOTf**). By varying the stoichiometric ratios and the order of the addition of the reagents along the synthetic routine, two polymorphs have been synthesized and structurally characterized. The first polymorph of **[(bpy)Ag]OTf**$_\infty$, the α-form, crystallized in the $P3_121$ space group, is characterized by the alternance, along the polymeric chain, of Ag(I) ions with linear and tetrahedral geometry (Fig.1); this arrangement results in the generation of chiral helices [2]. In a second polymorph of **[(bpy)Ag]OTf**$_\infty$, indicated as the β-form ($P2_1/c$ space group), prepared by modifying the synthetic procedure adopted previously, all the Ag(I) ion adopts a slightly distorted linear geometry. The silver ions are coordinated to the nitrogen atoms of bridging **bpy** ligands, while the non-coordinated **OTf** anions are found weakly interacting with the metal centres (Fig.1). The β-polymorph presents a zig-zag conformation which, as already reported for 1D organic polymers [3], can generate pocket-like cavities able to accommodate organic molecules through non-covalent interactions, rising the role of inorganic-polymer co-former in the formation of biologically active co-crystals. Hence, the β-form of **[(bpy)Ag]OTf**$_\infty$ was used for the preparation of an inorganic-polymer co-crystal by using curcumin (**curc**) as the organic bioactive molecule. The **[(bpy)Ag]OTf**$_\infty$**-curc** co-crystal was obtained through a quick solution reaction and characterized through several techniques, including Powder X-Ray Diffraction (PXRD), Differential Scanning Calorimetry (DSC), ^{1}H-NMR, UV-visible and Infrared Spectroscopies. The instauration of weak intermolecular interactions between the keto-enolic function of **curc** and both the Ag(I) cationic chains and the triflate anions of the inorganic-polymer is the driving force for the formation of this multicomponent material. Considering the multiple biological functions of **curc** [4] and the well-known antimicrobial activity of silver compounds [5], the **[(bpy)Ag]OTf**$_\infty$**-curc** co-crystal could represent a multi-functional supramolecular system. Moreover, embedding the **[(bpy)Ag]OTf**$_\infty$**-curc** co-crystal into an ethylcellulose (EC) polymeric matrix, antimicrobial films with potential biomedical and food-packaging applications have been obtained and characterized.

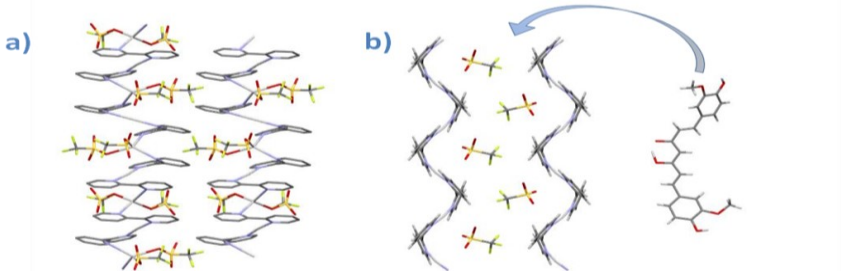

Figure 1. Packing view of the α-form (a) and the β-form (b) of **[(bpy)Ag]OTf**$_\infty$ along the a axis with its potential interactions with **curc**.

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