

## Nonlinear optical organic–inorganic crystals: synthesis, structural analysis and verification of harmonic generation in tri-(o-chloroanilinium nitrate)

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### Abstract

The structural and nonlinear optical properties of a new anilinium hybrid crystal of chemical formula  $(C_6H_7NCl^+NO_3^-)_3$  have been investigated. The crystal structure was determined from single-crystal X-ray diffraction measurements performed at a temperature of 100 K which show that the compound crystallizes in a noncentrosymmetric space group (Pna2<sub>1</sub>). The structural analysis was coupled with Hirshfeld surface analysis to evaluate the contribution of the different intermolecular interactions to the formation of supramolecular assemblies in the solid state that exhibit nonlinear optical features. This analysis reveals that the studied compound is characterized by a three-dimensional network of hydrogen bonds and the main contributions are provided by the O...H, C...H, H...H and Cl...H interactions, which alone represent 85% of the total contributions to the Hirshfeld surfaces. It is noteworthy that the halogen...H contributions are quite comparable with those of the H...H contacts. The nonlinear optical properties were investigated by nonlinear diffuse femtosecond-pulse reflectometry and the obtained results were compared with those of the reference material LiNbO<sub>3</sub>. The hybrid crystals exhibit notable second (SHG) and third (THG) harmonic generation which confirms its polarity is generated by the different intermolecular interactions. These measurements also highlight that the THG signal of the new anilinium compound normalized to its SHG counterpart is more pronounced than for LiNbO<sub>3</sub>.