

Designing molecular terahertz generation crystals: optimal packing could be just one carbon away

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Organic nonlinear optical materials are used for a wide range of applications, including terahertz (THz) and second harmonic generation. Optimal molecular arrangements in the crystal structure are judged by θ_p , which refers to the angle between the main transfer axis and the crystallographic axis. θ_p ranges from 0° for perfectly aligned noncentrosymmetric packing to 90° for centrosymmetric arrangement. Because noncentrosymmetric packing is essential to obtain a second-order material response, several strategies have been designed to overcome the anti-parallel arrangements often favored by dipole-dipole interactions. One of the most common approaches involves inducing hydrogen-bonding networks between chromophores. However, hydroxyl groups decrease the molecular hyperpolarizability compared to N-alkyl and O-alkyl groups, such as -OMe or -N(Me₂). A different method takes advantage of the ability of organic salts to pair the same THz-generating cation with different anions introducing different interactions and thereby changing the molecular packing from centrosymmetric to noncentrosymmetric. Here, we introduce an additional means of controlling crystal structure: cation modification. By switching a methyl (1-carbon) for an ethyl (2-carbon) group in the quaternary nitrogen moiety of the cation, we observe dramatic changes in θ_p from 90° to 0° without significantly impacting hyperpolarizability. We attribute this packing behavior to the increased steric effect of the ethyl group that results in larger intermolecular distances and so enables a parallel, noncentrosymmetric arrangement of chromophores in the crystalline state. This engineering strategy will deeply impact the way crystals for nonlinear optical applications are designed.

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