

# Evolution of polarity in molecular crystals

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Application of a general principle of polarity formation in molecular crystals<sup>1,2</sup> has become a basis for elaborate theoretical and synthetic concepts to grow polar materials. Solid solution formation is a save way to induce polarity formation in organic crystals. Molecular recognition at surfaces produces in orientational disorder, which can lead to grow-in polarity.

Organic solid solutions  $H_{1-x}G_x$  of donor/acceptor (D, A) disubstituted p-systems co-crystallized by use of a host (H: D- $\pi$ -D, A- $\pi$ -A) and a guest compound (G: D- $\pi$ -A) offer a broad range for tuning polar properties.<sup>3</sup> Scanning pyroelectric microscopy and phase-sensitive second-harmonic microscopy were developed to investigate the spatial inhomogeneity in polar crystals.<sup>4</sup>

Two  $H_{1-x}G_x$  mixtures in the range of  $0 < x \leq 1$  were investigated by second-harmonic microscopy and thermal analysis. 4,4'-dinitrostilbene (H: DNS) and 4-chloro-4'-nitrostilbene (G: CNS) both crystallize in  $P2_1/c$  featuring only small differences in cell parameters: They form solid solutions over the complete range of  $x$ . The polarity increases as a function of the ratio  $x$  of CNS. Also 4,4'-dicyanostilbene (H: DCyS) and 4-cyano-4'-ethinylstilbene (G: CNS) both crystallize in  $P2_1/c$ , but in very different crystal structures. Only partial solid solution formation is possible. In this case, polarity increases towards the miscibility gap of both compounds.

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