From Intermolecular Interactions to Functional Properties: Pressure-Tuned Behavior of π-Conjugated Molecular Crystals

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Abstract

Molecular crystals provide a unique platform for investigating the effects of compression on intermolecular interactions, as non-covalent contacts are generally far more responsive to pressure than covalent bonds. As a result, pressure offers an exceptional opportunity to continuously modify crystal packing and electronic structure, enabling direct observation of how structural changes translate into chemical and physical properties.

This talk addresses how high-pressure single-crystal X-ray diffraction, combined with optical spectroscopy, can be used to follow the evolution of intermolecular interactions in π-conjugated molecular crystals and correlate structural changes with their physical properties.

Particular attention is devoted to anthracene- and heptazine-based systems. In anthracene derivatives, compression progressively alters intermolecular π···π interactions and molecular packing, resulting in significant modifications of optical behavior. High-pressure crystallographic studies reveal the structural origins of these effects and provide insight into how subtle changes in intermolecular geometry influence the electronic structure of the crystal. In the most extreme cases, continued compression drives the system towards intermolecular bond formation, illustrating the intimate connection between non-covalent interactions and chemical reactivity in the solid state.

Complementary studies on heptazine-based materials demonstrate how pressure-induced modifications of crystal packing and supramolecular organization influence the response of π-conjugated chromophores. Particular emphasis is placed on the role of the crystal environment and co-crystallized species in governing structural adaptation under compression and shaping the resulting physical properties.

Together, these examples highlight how pressure can be employed to systematically manipulate intermolecular interactions in molecular crystals and establish direct links between crystal structure, electronic behavior, and functionality. The presented studies demonstrate the unique capabilities of high-pressure crystallography for understanding and ultimately controlling the properties of responsive organic materials.