

Evolution of the crystal structures and spectroscopic in polymorphs of 1,8-diacetylpirene

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Pyrene and its derivatives constitute one of the better studied groups of organic fluorophores characterized by relatively long-lived fluorescence, high quantum yields and high environment sensitivity. That includes sensitivity to specific crystalline environment and pressure.

Multi-substituted pyrene derivatives have already found applications in pressure sensors^[1] but even some relatively simple pyrene derivatives show enhanced solid-state fluorescence, related to formation of excimers. Specific molecular ordering, related to $\pi\cdots\pi$ -stacking in the crystal lattice, seems to augment this process. The phenomenon is interesting, as clustering of molecules is sometimes raised as the reason for fluorescence quenching in other materials.

Pyrene ketones are known to be among the Polycyclic Aromatic Hydrocarbons (PAH-s) which are highly luminescent in the solids state. While there is literature describing how the number and exact positions of acyl substituents to pyrene moiety influence luminescent properties of resulting pyrene ketones^[2], there have been no studies on how the different crystal packing in polymorphs of pyrene ketones affects their luminescent properties in the solid state.

Here we present the results of structural and spectroscopic investigation of 1,8-diacetylpirene (2''AP), a known pyrene-based fluorophore, claimed to have its crystal structure uniquely determined by the positions of its acyl substituents^[2]. We characterize a phase transition occurring in the structure of a reported polymorph under hydrostatic pressure. A slight reorientation of one of the acyl substituents results in a change in the network of intermolecular interactions and flattening of the π -

stacked layers of 2''AP in the crystal structure. The structural change is accompanied by the significant change in the luminescence spectra. In addition, a structure of the new orthorhombic polymorph of 2''AP, showing distinct luminescence from the known polymorph and no indications of pressure-induced phase transitions, is being presented.

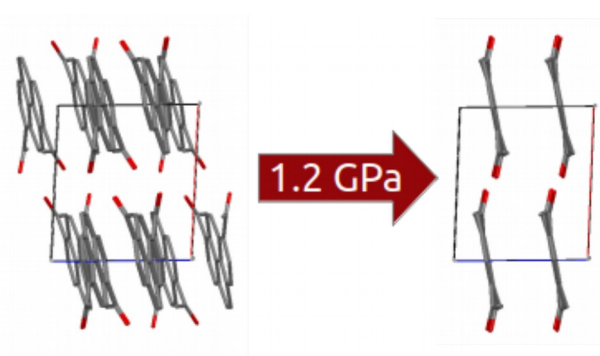


Figure 1. Pressure induced phase transition in 2''AP, view along [010] direction.

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