

Cocrystals of 1,8-diacetylpyrene with TCNB: their relative stability, mechanical and photoluminescent properties

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Cocrystallization, as a means to obtain cost-effective functional materials with predictable properties from neutral molecular building blocks has found applications in production of luminescent materials [1]. Comparative study of cocrystals with various substrate ratios should provide an opportunity to investigate materials containing different packing motifs. We present a study of three distinct cocrystals of 1,8-diacetyl-pyrene (bAP) with 1,2,4,5-tetra-cyano-benzene (TCNB) obtained by crystallization from various solvents and their structures determined by single-crystal X-ray diffraction combined with Hirshfeld Atom Refinement (HAR) [2]. The new crystalline materials vary in the bAP:TCNB ratios, molecular packing and symmetry. A common structural motif, accounting for noticeable anisotropy of thermal expansion coefficients and uniform orange photoluminescence in these cocrystals is an infinite ROD consisting of alternating bAP and TCNB moieties π -stacked in 1:1 or 2:1 ratios. Face-to-face π -stacking is one of the dominant interactions.

The unique propensity for crystal jumping in the cocrystals with 1:1 bAP:TCNB ratio has been tentatively ascribed to the presence of corrugated tapes of bAP and TCNB molecules linked with C—H ... O and C—H ... N interactions and the flattening of these tapes as a result of increased tape's thermal vibrations. Anisotropic Displacement Parameters obtained for this cocrystals from HAR and periodic calculations utilizing CASTEP[3] and CRYSTAL[4] programme are compared.

Periodic DFT calculations allowed us to predict relative stability of these cocrystals and their interconversion at 0K and room temperatures, respectively. NoMoRe [5] programme refining frequencies obtained from periodic DFT calculations against experimental data empower deriving the thermodynamic properties and establishing relative stability of the cocrystals .

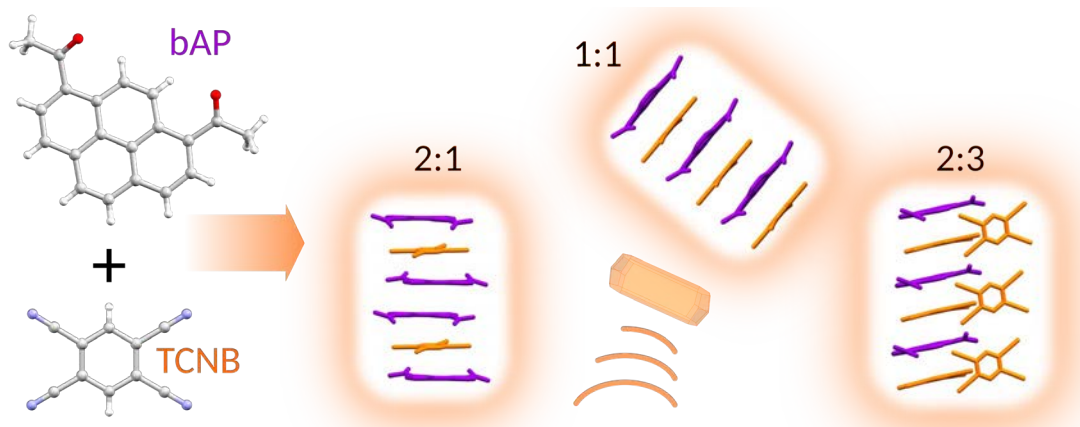


Figure 1. New cocrystals of 1,8-diacetyl-pyrene (bAP) with 1,2,4,5-tetra-cyano-benzene (TCNB)

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