

## A pressure-induced centrosymmetric to non-centrosymmetric phase transition in a fluorescent organic rotor

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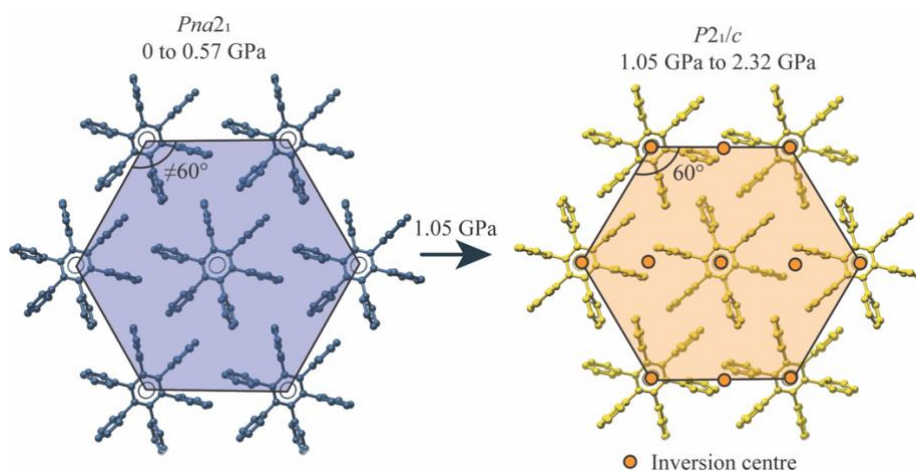
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Fluorescent solids are essential components of photovoltaic devices.[1-4] Organic molecules with aromatic components and rotor-like geometries exhibit solid-state fluorescence due to the formation of an ‘immobile’ network of intermolecular aromatic interactions ( $\text{CH}\cdots\pi$  and  $\pi\cdots\pi$ ) in the crystal.[5] The loose crystal packing of organic rotors is also conducive to mechanofluorochromic and piezochromic behaviour, as the  $\text{CH}\cdots\pi$  and  $\pi\cdots\pi$  interactions are perturbed under a mechanical stimulus.[6] Structure-property relationships in these systems are recognised but underdeveloped. Hexaphenylbenzene is a common fluorophore in organic crystals and is therefore a good case study to examine structure-property relationships.[7]

Here, the effect of pressure on hexaphenylbenzene has been examined by *in situ* high-pressure single crystal X-ray diffraction to 2.32 GPa, allowing structure-pressure relationships to be drawn and structure-fluorescence relationships to be inferred. Hydrostatic compression causes the intermolecular  $\pi\cdots\pi$  interactions to gradually shorten, indicating the likelihood for mechanofluorochromism. However, the  $\text{CH}\cdots\pi$  are the most important to the stability and compressibility of the crystal, which is an important consideration for crystal engineering of organic rotors.

Compression of the intermolecular interactions in hexaphenylbenzene under pressure prompts an uncommon non-centrosymmetric to centrosymmetric phase transition from orthorhombic  $Pna2_1$  to monoclinic  $P2_1/c$  at 1.05 GPa. The phase transition is caused by anisotropic compression of hexagonally packed layers of molecules so that they adopt a perfect hexagonal arrangement, generating inversion symmetry (Fig. 1). Such transitions in organic crystals are scarce, and there are presently no reports of an organic crystal undergoing such a phase transition under applied pressure.



**Figure 1.** Pressure-induced non-centrosymmetric (blue) to centrosymmetric (yellow) phase transition in hexaphenylbenzene, showing the arrangement of molecules changing from distorted hexagonal to perfect hexagonal, generating inversion symmetry.

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