

**Experiment title:**

Crystal structure compression of polycyclic arene-perfluoroarene co-crystals and pressure-induced polymer formation

**Experiment number:**

CH-6143

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In recent years, pressure-induced polymerization of aromatic compounds has become a well-established route for the generation of novel carbon nanomaterials containing  $sp^3$  carbon-bonded networks (e.g., [1-4]). In our recent study, we have shown that the application of supramolecular synthons, such as the arene-perfluoroarene  $\pi$ -stacking system, is a valuable tool in order to induce polymerization along the stacking direction and, hence, obtain highly ordered polymers of columnar hydrofluorocarbons at high pressures [1]. The attractive interaction between arenes and perfluorinated arenes is due to their inverse C-H vs. C-F bond polarities [5] and results in an alternating face-to-face stacking of the non- and perfluorinated molecules (Fig. 1). From our results on 1:1 co-crystals of naphthalene and anthracene with (bicyclic) perfluoronaphthalene obtained at ESRF (report CH-5078, [1]), we postulated that variation of the starting polycyclic aromatic molecules will provide a useful means by which to control the width and lateral extension of the columns formed in the polymer [1].

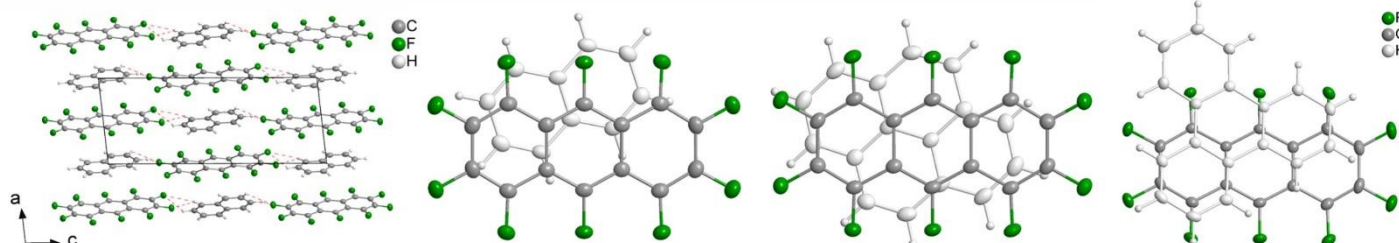


Fig. 1. From left to right: Molecular  $\pi$ -stacking of NDFA and molecular overlap of decafluoroanthracene with naphthalene (NDFA), pyrene (PDFA), and triphenylene (TriDFA).

In order to verify this, we have grown novel 1:1 co-crystals of naphthalene, pyrene, and triphenylene with tricyclic perfluoroanthracene (NDFA, PDFA and TriDFA, respectively, Fig. 1) and collected single-crystal synchrotron X-ray diffraction data up to 30 GPa. Diffraction data were collected on two crystals (each for NDFA and PDFA) or three crystals (TriDFA) with different orientations, which were combined in the crystal structure refinements. This improved the completeness of the high-pressure data, which usually suffer from the restriction of access to the reciprocal space induced by the high-pressure cell. And this is especially important for low-

symmetry compounds. For TriDFA, an additional twin component was included in the data reduction, which further improved the excellent data quality and, hence, quality of the structural model. Helium was used as the pressure-transmitting medium and was incorporated in the crystal structures of all compounds at high pressure.

## Main results

Our experiments confirmed the earlier proposed high-pressure structural stability of the  $\pi$ -stacked polycyclic arene–perfluoroarene co-crystals as none of the compounds showed a phase transition prior to the onset of polymerization. The pressure-induced polymerization reaction along the  $\pi$ -stacks, and hence the collapse of the  $\pi$ -stacking interaction, was followed by single-crystal X-ray diffraction, which showed a strong reduction along the  $\pi$ -stacking direction, which is the  $a$  axis in all three compounds (Fig. 2). The reduction of the  $a$  axis was irreversible upon decompression, which supports the interpretation as a polymerization reaction. Although diffraction data quality significantly decreased in the polymer phases by loss of long-range order, short-range order still allowed the indexation of several reflections and, hence, determination of the polymers' unit cell metrics. These results proved to be similar to the results obtained in our earlier experiment on the 1:1 co-crystals of naphthalene and anthracene with perfluoronaphthalene [1]. Full data analysis will give important information on the evolution of the co-crystals' structures prior to polymerization, and information on the polymer structures will be complemented by high-pressure spectroscopy and theoretical computations. The results of this experiment promise to contribute to the understanding of the tailor-made design of novel hydrofluorocarbon materials via application of supramolecular synthons such as the arene–perfluoroarene interaction.

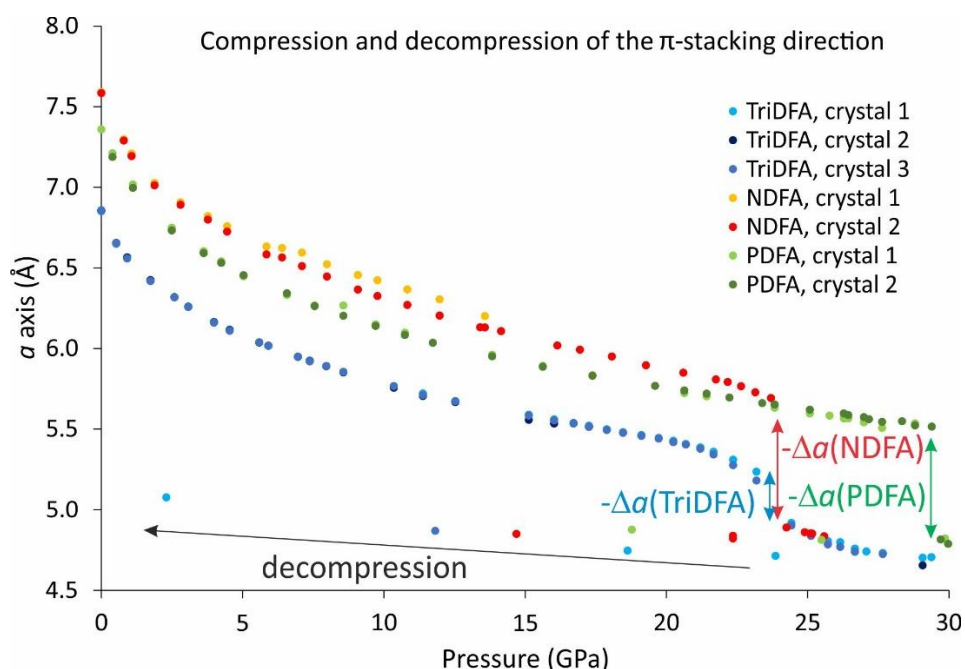


Fig. 2. Pressure evolution of the  $a$  cell parameters of the individual crystals of NDFA, PDFA and TriDFA. At ca. 23–24 GPa for NDFA and TriDFA, and ca. 29 GPa for PDFA, respectively, considerable shortening of the  $\pi$ -stacking direction is observed, attributed to pressure-induced polymerization and concomitant breakdown of  $\pi$ -stacking. Decompression data (indicated by the arrow) confirm the irreversibility of the reactions.

## References

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