Pressure-induced Diels-Alder reactions in C_6H_6—C_6F_6 Co-crystal towards graphane structure

With support from the National Natural Science Foundation of China and the Top 1000-Talents Awards, the research team led by Dr. Zheng HaiYan (郑海燕) and Dr. Li Kuo (李阔) from the Center for High Pressure Science and Technology Advanced Research in Beijing recently synthesized H-F-substituted graphane (H, F-graphane) with a layered structure by compressing 1 : 1 C_6H_6—C_6F_6 co-crystal (abbreviated as CHCF), in contrast to previously reported nanothreads. The neutron diffraction and gas chromatography-mass spectrum (GC-MS) proved that the Diels-Alder reaction was the key reaction in the polymerization process. This work provides a novel method for constructing substituted graphane with atomic-level uniformity, which was published in *Angewandte Chemie International Edition* (2019, 58, 5:1468—1473).

Synthesis of bulk graphane with controllable and uniform modification at the atomic-level is still a considerable challenge. Applying extreme pressure to unsaturated molecules is effective for constructing novel carbon structures. In their previous study (*J Phys Chem C*, 2016, 120(51): 29510—29519), the team identified four new phases of CHCF (V, VI, VII, and VIII), and an irreversible pressure-induced polymerization (PIP) was observed following phase VIII. In the present work, the team synthesized H,F-graphane successfully by introducing the CHCF, the typical building block in supramolecular chemistry, to extreme conditions.

Despite the extreme difficulty of the limited data quantity available, the authors determined all the high-pressure structures, including the crystal structure at the reaction threshold at 20 GPa, by using multiple neutron sources in China, Japan, and the UK. C_6H_6 and C_6F_6 remain stacked alternatively in a column before the reaction, suggesting a high possibility of additional reaction between them. The authors used IR, X-ray pair distribution function (PDF), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and solid-state nuclear magnetic resonance (ssNMR) to investigate the product, and concluded a short-range-ordered H,F-graphane with H and F in order. Furthermore, based on the intermediates detected by GC-MS, the elemental reactions were deduced, confirming that the Diels-Alder is the key PIP reaction. To summarize the whole reaction process, CHCF undergoes Diels-Alder reactions to form the [4 + 2] polymer, and then the polymer connects to its neighbors to form H-F graphane with a layered structure by eliminating some C, H, and F species.

For the first time, the PIP process, and especially the experimental evidence of the elemental reactions of CHCF are reported, which provides valuable insight for other aromatics. The formation of H,F-graphane highlights that the PIP of substituted aromatics is an alternative method to construct sp^3-hybridized carbon materials with diverse structure.

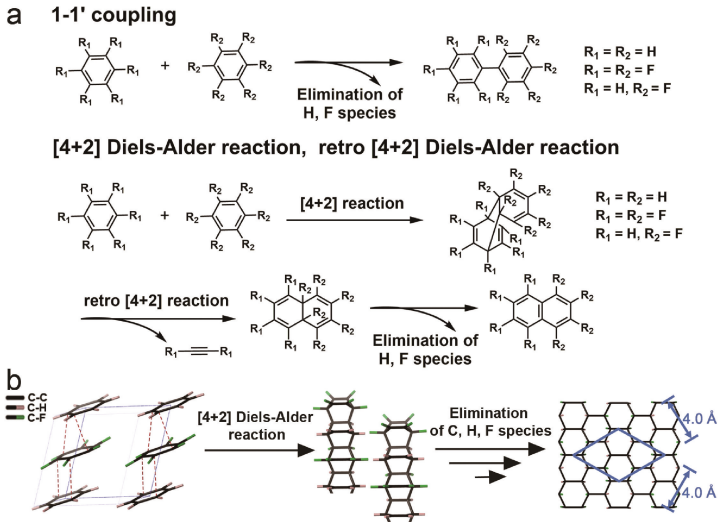

Figure (a) The selected elemental reactions, and (b) the proposed reaction route of C_6H_6—C_6F_6 co-crystal.