

## Search of new Nitrogen-doped carbon materials by compressing molecular crystals

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### Abstract

Synthesis under high pressure is a powerful technique to obtain novel materials. We here report ultra-high pressure experiments to search new nitrogen-doped carbon materials. Single crystal of organic molecules with nitrogen atoms are used as precursor. After high pressure treatment at room temperature, precursor molecules underwent oligomerization accompanied by transformation from  $sp^2$ -hybridization carbon atoms to  $sp^3$  ones.

### 1. Introduction

Nitrogen (N)-doped carbon materials exhibit various useful properties, such as catalytic activity, magnetism, semiconductor functions, and so on. These properties depend on hybridization of atoms, structure of carbon skeleton, and doping nitrogen species. In other words, new materials can be obtained by controlling these factors. We focus on synthesis under high pressure to search novel N-doped carbon materials with useful functions.

High pressure synthesis is a versatile tool for creating new materials. Under high pressure, interatomic distances are reduced and electronic structure is modified. Metastable materials can be created due to those effects.

When aromatic molecular solids are placed under high pressure, Diels-Alder-like reaction occurs and they polymerize or oligomerize[1]. This type of reactions on simple aromatic molecules has been reported. However, that of heteroatom-containing polycyclic aromatic molecules has rarely been reported.

In order to investigate the reactions of heterocyclic aromatic compounds compressed under high pressure and explore the possibility to synthesize new N-doped carbon materials, we carried out experiments compressing N-containing aromatic molecules under ultrahigh pressure ( $\geq 2$  GPa).

### 2. Methods

#### Experimental

We used cubic anvil press to achieve ultrahigh pressure. The precursor was quinoxalino[2',3':9,10]phenanthro [4,5-abc]phenazine (TQPP) or dibenzo[a,c]dibenzo[5,6:7,8]quinoxalino[2,3-i]phenazine (DDQP). The molecular structures of TQPP and DDQP are shown in Fig. 1.

The cell assembly for high pressure experiments is shown in Fig. 2. The cell assembly was compressed to 5 GPa at room temperature using cubic anvil apparatus. The pressure was ramped up to 5 GPa in 60 minutes, and then was retained for 24 hours.

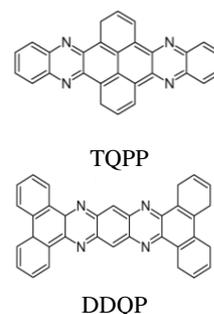


Fig. 1. Molecular structures of TQPP and DDQP

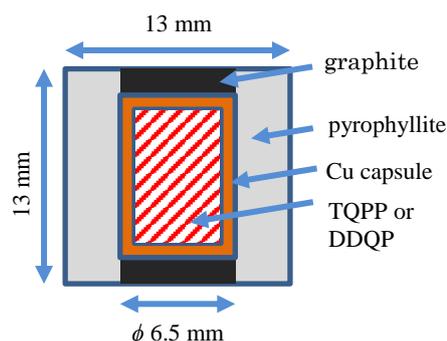


Fig. 2. Sample cell assembly for high pressure experiment using cubic anvil press apparatus. Pyrophyllite plays a role of pressure transmission medium.

The pressure was decreased to ambient pressure in 90 minutes. After that the samples were recovered from press, the recovered samples were characterized by MALDI-TOF-MS, IR, Raman spectroscopy, and powder X-ray diffraction.

#### Ab-initio calculation

We used DFT package VASP [2] to understand the process in computer. We used PBE functional [3] and plane wave. Hydrostatic pressure was simulated by adjusting cell parameters and calculating the total energy change.

### 3. Results and Discussion

#### MALDI-TOF-MS

By MALDI-TOF-MS, the mass numbers corresponding to TQPP dimer, DDQP dimer and trimer were found in the recovered samples. However, the yield of oligomerization was not very high, and unreacted precursor was observed in the product.

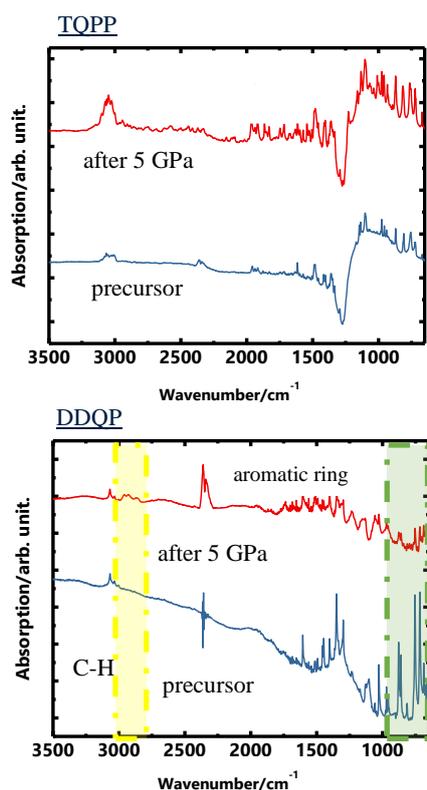


Fig. 3. IR spectra of precursors (blue line) and the samples after 5 GPa application (red line; measured at ambient pressure). Green and yellow areas in the spectra of DDQP are assigned to absorption of CH out-of-plane deformation of aromatic ring and CH stretching of alkane, respectively.

#### IR spectra

IR spectra of precursors and the samples after applying 5 GPa are shown in Fig. 3. In the spectrum of the DDQP after 5 GPa, adsorption around 900-675  $\text{cm}^{-1}$  was significantly decreased compared with that of DDQP precursor. Additionally, new absorption band was observed in 3000-2840  $\text{cm}^{-1}$  in the DDQP after 5GPa. Absorptions around 900-675  $\text{cm}^{-1}$  and 3000-2840  $\text{cm}^{-1}$  correspond to CH out-of-plane deformation of aromatic ring and CH stretching of alkane, respectively. It indicates that carbon atoms of DDQP transformed from  $\text{sp}^2$ -hybridization to  $\text{sp}^3$ .

On the other hand, the features mentioned above were not observed in the spectra of TQPP precursor and after 5 GPa application. It is assumed that the yield is low in the pressure-induced oligomerization of TQPP.

#### Ab-initio DFT calculations

To analyze oligomerization and structure of product, structural optimization calculation was performed starting from structure of TQPP crystal obtained by single crystal X-ray diffraction. When the structure was compressed with quasi-hydrostatic condition in simulation, TQPP molecules in the crystal polymerized and column-like one dimensional polymer was obtained (Fig.4). Simulation of DDQP is under way.

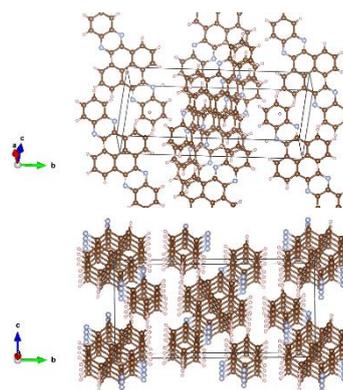


Fig. 4. Crystal structure of TQPP determined experimentally (above) and Structure of column-like polymerized TQPP obtained by structural optimization under compression (below)

#### Discussion

According to DFT calculation, TQPP polymerize under compression. However, TQPP dimer was only obtained as a minor product in the experiment and unreacted precursor remained. It is considered that the polymerization is reversible and polymer decomposes into monomer and dimer while releasing the pressure. Similar phenomenon was reported in benzene under high pressure process [4]. It is assumed that high pressure and high temperature synthesis is appropriate to achieve irreversible polymerization.

#### 4. Conclusion

Crystals of N-doped polyacene TQPP and DDQP was compressed to 5 GPa at room temperature for 24 hours using cubic anvil press. After releasing the samples at room temperature, the both molecules underwent pressure-induced oligomerization. In oligomerization of DDQP, FTIR showed that carbon atoms of DDQP transformed from  $\text{sp}^2$ - to  $\text{sp}^3$ -hybridization.

The present results demonstrate that molecules with complex structures can oligomerize by just applying pressure. It will be promising approach to create new materials with useful functions because the high pressure treatment is versatile.

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