Pressure-induced Diels-Alder reactions in C₆H₆-C₆F₆ cocrystal towards graphane structure

Yajie Wang, Xiao Dong, Xingyu Tang, Haiyan Zheng,
Kuo Li, Xiaohuan Lin, Leiming Fang, Guang'ai Sun, Xiping Chen,
Lei Xie, Craig L. Bull, Nicholas P. Funnell, Takanori Hattori,
Asami Sano-Furukawa, Jihua Chen, Dale K. Hensley,
George Cody, Yang Ren, Hyun Hwi Lee and Ho-kwang Mao

Published version information

This is the peer reviewed version of the following article:

Citation: Y Wang et al. "Pressure-induced Diels-Alder reactions in C₆H₆-C₆F₆ cocrystal towards graphane structure." *Angewandte Chemie (International Edition)* vol. 58, no. 5 (2019): 1468-1473.

DOI: [10.1002/anie.201813120](https://doi.org/10.1002/anie.201813120)

Which has been published in final form at the DOI above. This article may be used for non-commercial purposes in accordance with Wiley-VCH terms and conditions for self-archiving.

Please cite only the published version using the reference above. This is the citation assigned by the publisher at the time of issuing the AAM. Please check the publisher's website for any updates.

Accepted Article

Title: Pressure-Induced Diels-Alder Reactions in C₆H₆-C₆F₆ Cocrystal towards Graphane Structure

Authors: Yajie Wang, Xiao Dong, Xingyu Tang, Haiyan Zheng, Kuo Li, Xiaohuan Lin, Leiming Fang, Guang'ai Sun, Xiping Chen, Lei Xie, Craig L. Bull, Nicholas P. Funnell, Takanori Hattori, Asami Sano-Furukawa, Jihua Chen, Dale K. Hensley, George Cody, Yang Ren, Hyun Hwi Lee, and Ho-kwang Mao

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201813120
Angew. Chem. 10.1002/ange.201813120

Link to VoR: <http://dx.doi.org/10.1002/anie.201813120>
<http://dx.doi.org/10.1002/ange.201813120>

Pressure-Induced Diels-Alder Reactions in C₆H₆-C₆F₆ Cocrystal towards Graphane Structure

Yajie Wang,^[b] Xiao Dong,^[b] Xingyu Tang,^[b] Haiyan Zheng,^{*,[a]} Kuo Li,^{*,[a]} Xiaohuan Lin,^[b] Leiming Fang,^[b] Guang'ai Sun,^[b] Xiping Chen,^[b] Lei Xie,^[b] Craig L. Bull,^[b] Nicholas P. Funnell,^[b] Takanori Hattori,^[b] Asami Sano-Furukawa,^[b] Jihua Chen,^[b] Dale K. Hensley,^[b] George Cody,^[b] Yang Ren,^[b] Hyun Hwi Lee,^[b] Hongkwang Mao^[b]

Abstract: Pressure-induced polymerization (PIP) of aromatics is a novel method to construct sp³-carbon frameworks, and nanothreads with diamond-like structures were synthesized by compressing benzene and its derivatives. Here by compressing benzene-hexafluorobenzene cocrystal (CHCF), we identified H-F-substituted graphane with a layered structure in the PIP product. Based on the crystal structure determined from the in situ neutron diffraction and the intermediate products identified by the gas chromatography-mass spectrum, we found that at 20 GPa CHCF forms tilted columns with benzene and hexafluorobenzene stacked alternatively, which leads to a [4+2] polymer, and then transfers to short-range ordered hydrogenated-fluorinated graphane. The reaction process contains [4+2] Diels-Alder, retro-Diels-Alder, and 1-1' coupling, and the former is the key reaction in the PIP. Our studies confirmed the elemental reactions of the CHCF for the first time, which provides a novel insight into the PIP of aromatics.

Sp³-hybridized carbon-based materials have gained constant attention due to their outstanding mechanical and optical properties.^[1] However, their types are very limited compared to the diversity of the carbon-based molecules. Applying extreme pressure to unsaturated molecules like aromatics is proved to be

effective to construct sp³-hybridized carbon materials.^[2] It is well known that benzene polymerizes into amorphous hydrogenated carbon under high pressure,^[3] and with anisotropic stress, a well-ordered single-crystal carbon nanothread was reported, which is recognized as an ultra-thin sp³ carbon nanowire.^[2a,2b] Similarly, single-crystal carbon nitride was synthesized by compressing pyridine slowly.^[2c] Recently, it was reported that aniline forms diamond-like polyaniline under external pressure and the H-bond between the NH₂ groups is believed to be responsible for better crystallinity.^[2d] Besides the one dimensional structure, the graphane structure can also be obtained by compressing the aromatics under high pressure and high temperature conditions.^[4]

The reaction mechanism of these pressure-induced polymerization (PIP) was explored from various perspectives. Various possible connections between benzene molecules were theoretically proposed, and the energies of the formed dimers were examined to evaluate the corresponding reactions.^[5,6] Experimentally, a possible reaction route including a [4+2] cycloaddition reaction followed by an intramolecular 'zipper' cascade reaction was proposed according to the π-π stacking of the benzene molecules and the structural model of the product.^[2a] All of these reports suggest the reaction starts from the bonding between the π-π stacked aromatics. However, more experimental work is needed to understand the elemental reactions in the PIP process and its relation to the π-π stacking.

C₆H₆-C₆F₆ 1:1 cocrystal (abbreviated as CHCF hereafter) provides an appropriate π-π stacking model due to the strong electrostatic attraction between C₆H₆ and C₆F₆. The alternate stacking of C₆H₆ and C₆F₆ can be recognized as half of benzene molecules being substituted by hexafluorobenzene, which provides a tracer during the reaction. Here, we report the PIP of CHCF and its reaction mechanism under applied pressure. The product of PIP contains a hydrogenated-fluorinated graphane-like structure. Diels-Alder, retro-Diels Alder and 1-1' coupling reactions were identified during this process and the former is the key elemental reaction directing to the polymerized material. We described the PIP route of the aromatic molecules systematically, which also provides an alternative method for constructing substituted graphane with atomic-level uniformity.

CHCF forms rhombohedral crystals (phase I, *R-3m*) around room temperature and experiences three phase transitions to form phase II (*I2/m*), III (*P-1*), and IV (*P2₁/a*) at low temperature and ambient pressure.^[7] In all the phases, C₆H₆ and C₆F₆ are alternately stacked.^[7] Under high pressure, phase V (*P2₁/c*), VI, VII, and VIII were identified and PIP was observed at ~ 20 GPa after phase VIII.^[8] Combining in situ synchrotron X-ray diffraction (XRD, Fig.S1), constant wavelength and time of flight (TOF) neutron diffraction under high pressure (Fig.S2), we determined the structures of phase VI, VII, and VIII ab initio (Fig.S3),

- [a] Drs. H. Zheng, K. Li
Center for High Pressure Science and Technology Advanced Research, Beijing, 100094, P. R. China
E-mail: zhenghy@hpstar.ac.cn; likuo@hpstar.ac.cn
- [b] Drs. Y. Wang, X. Dong, X. Tang, X. Lin, H. Mao
Center for High Pressure Science and Technology Advanced Research, Beijing, 100094, P. R. China
Drs. L. Fang, G. Sun, X. Chen, L. Xie
Key Laboratory of Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621999, P. R. China
Drs. C. L. Bull, N. P. Funnell
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom
Drs. T. Hattori, A. Sano-Furukawa
J-PARC Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
Drs. J. Chen, D. K. Hensley
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, United States
Drs. G. Cody, H. Mao
Geophysical Lab, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC, 20015, United States
Dr. Y. Ren
Advanced Photon Source, Argonne National Laboratory, Lemont, IL, 60439, United States
Dr. H. H. Lee
Pohang Accelerator Laboratory, POSTECH, Pohang 790-784, Republic of Korea

Supporting information for this article is given via a link at the end of the document.

including the atomic positions using Rietveld refinement (Table S1). The C_6H_6 and C_6F_6 molecules are still alternately stacked to form columns in these phases; however, the columns are tilted significantly, which are quite different from those under low temperature. In order to understand the crystal structure at reaction pressure threshold more precisely, we further optimize the structure of phase VIII by using the Density Functional Theory (DFT) calculation based on the experimental result at 20 GPa, which was shown in Figure 1. The stacked aromatic rings are progressively tilted away from the previous column axis (c-axis), and actually form closed packed layers on the (102) plane. Every aromatic ring is curved and stacked on the interstitial site among three rings of the neighbored layer, with two of the three rings of the same type. Along the [001] direction, the nearest C...C distance between the C_6F_6 and C_6H_6 molecules in the column is ca. 2.8 Å, close to the critical reaction distance between the benzene molecules (2.8–3.0 Å) at 298 K (Fig. 1b).^[9] This indicates a high possibility of the addition reaction between the C_6F_6 and C_6H_6 in the CHCF columns.

Figure 1. The crystal structure of C_6D_6 - C_6F_6 before reaction (20 GPa). a) viewed perpendicular to (102) and b) approximately along [010]. The black, pink, and green atoms are carbon, hydrogen (deuterium) and fluorine, respectively. This crystal structure is optimized by the DFT calculation based on the structure obtained from the Rietveld refinement result of the neutron data collected at PLANET, J-PARC Center^[10] at 20 GPa.

Upon further compression of phase VIII using a Paris Edinburg (PE) press, we obtained white solid samples, and their morphology varied with the applied pressure. The product recovered from 18 GPa (PE18) has an irregular morphology (Fig. S4), while that obtained from 20 GPa (PE20) shows an obviously layered structure under scanning electron microscope (SEM, Fig. 2a). When recovered from 17 GPa, the solid sample (PE17) is too limited to be analyzed, which means most of the aromatic molecules did not react and evaporated upon decompression. The Energy Dispersive Spectroscopy (EDS) obtained from SEM shows PE20 maintains most of the fluorine atoms (Table S2). Using solid-state nuclear magnetic resonance (ssNMR, Fig. 2b), we found three types of carbon species, $C(sp^2)$ (131 ppm), $C(sp^3)$ connecting to fluorine ($F-CR_3$) (94 ppm) and non-fluorine atoms ($H-CR_3$) (38 ppm), respectively. The ratio of the peak area of the $C(sp^2)$ and $C(sp^3)$ is 1:4, which indicates the $C(sp^3)$ is the dominant species. This is consistent with the 1H -ssNMR result (Fig. S5), which is well fitted using three peaks at 1.3, 2.5, and 6.3 ppm, and recognized as H on $C(sp^3)$ ($H-CR_3$), $C(sp^3)$ connected to a fluorine atom ($H-CFR_2$) and $C(sp^2)$ ($H-CR=CR_2$), respectively. Hence, the ssNMR data proves that the sample is mainly a H-F bonded sp^3 -C material.

When we measured EDS by using the transmission electron microscope (TEM) of 200 kV, PE20 lost most of fluorine (Table

S2), and the corresponding image shows a curved layered structure with the interlayer d-spacing of 3.7 Å (Fig. 2c and 2d), consistent with that in graphite.^[11] This suggests that PE20 has a layered graphitic skeleton constructed by $C(sp^3)$, F and H atoms, and lost F and H when irradiated by the 200 kV electron beam. The graphitic skeletal of PE20 is confirmed by the pair distribution function (PDF) and TEM with lower voltage. The $S(Q)$ of neutron and X-ray PDF show bands at $d = 2.2$ Å and 1.1 Å, which are ascribed to the 100 and 200 scattering of the 2D graphitic lattice, respectively (Fig. 2e). X-ray PDF ($G(r)$, Fig. 2f) also shows clear feature of hexagonal rings at $r = 1.4$, 2.5 and 2.9 Å, corresponding to the distance between 1-2, 1-3 and 1-4 positions of a hexagonal carbon ring. When using a 120 kV TEM, a diffraction ring at $d = 4.1$ Å was observed in the selected area electron diffraction (SAED) pattern (Fig. 2g). This d-spacing is much smaller than the interlayer spacing of graphane (4.7 Å),^[12] but close to twice of the $d(100)$ of the graphitic lattice, and hence implies a superlattice of graphene, like a 2×2 lattice (hexagonal lattice with $a = 4.7$ Å and $d(100) = 4.0$ Å, grey dashed line in Fig. 2h) or its distorted relatives (the orthorhombic lattice in blue in Fig. 2h). This probably results from the ordered bonding of H and F to the graphitic skeletal, but the details are complex and beyond the scope of this paper (Fig. S6).

Figure 2. a) SEM images, b) ^{13}C CPMAS ssNMR, c) TEM image (200 kV), d) the corresponding statistical results of d-spacing in c), and e) the total structure factor $S(Q)$ derived from synchrotron X-ray and neutron diffraction of PE20. f) Experimental (X-ray) and calculated $G(r)$. g) SAED pattern (120 kV TEM) of the sample PE20. The modelled PDF in Fig. 2f is derived from the h) proposed H-F graphane model viewed along [001].

All the above results indicate that PE20 has a short-range ordered hydrogenated-fluorinated graphitic structure (or hydrogenated-fluorinated graphane). The synchrotron X-ray and neutron PDF of PE20 show clear band at $d = \sim 6.5$ Å (Fig. 2e), which is the typical interlayer distance of fluorinated graphite.^[13] Based on these experimental results and the reaction route

mentioned later, we proposed a hydrogenated-fluorinated (H-F) graphane model for PE20 (Fig.2h) and simulated the G(r) pattern, which fits the experimental data very well (Fig.2f).

Figure 3. IR absorption spectra of PE17 (orange), PE18 (pink), PE20 (red), and CHCF starting material (black), and the calculated IR spectrum of H-F graphane model. The assignments of the peaks in PE20 are presented in Fig.S7 based on the calculated results. The assignments of the peaks in CHCF cocrystal are listed in Table S3 in supporting information.^[8]

The H-F graphane model for PE20 is also confirmed by the IR spectra. We optimized the proposed H-F graphane model by DFT and calculated its IR spectrum. As shown in Figure 3, among the recovered samples, PE20 featured several strong new peaks at 934, 1260, 1329, and 2924 cm^{-1} as well as a peak at 1179 cm^{-1} with medium intensity, agrees well to the calculated IR spectrum of the H-F graphane. The peaks at 3060 cm^{-1} ($\text{C}(\text{sp}^2)\text{-H}$ stretching), 1526 cm^{-1} ($\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)$ stretching), 1018 cm^{-1} and 987 cm^{-1} ($\text{C}(\text{sp}^2)\text{-F}$ stretching) are similar to the peaks of benzene or hexafluorobenzene, and are attributed to their fragments (Fig. 3, marked by stars). The peak at 2924 cm^{-1} is from the $\text{C}(\text{sp}^3)\text{-H}$ stretching which is much stronger than the peaks above 3000 cm^{-1} . This means PE20 mainly contains sp^3 -carbon. The contribution from F atoms are mainly located in the intermediate frequency range (933-1150 cm^{-1}), while the modes between 1160 and 1400 cm^{-1} are dominated by the carbon and hydrogen atoms. The peak at 934 cm^{-1} contains the C-F stretching, which is lower than that in F-graphane ($\text{C:F}=1:1$).^[13a, 14] This is because the C-F stretching red-shifts when fluorine atoms of F-graphane were partly substituted by hydrogen atoms.^[15] The peaks at 1179 cm^{-1} , 1260 cm^{-1} and 1329 cm^{-1} are contributed by the C-H deformation and C-C stretching. The details of assignment are summarized in Figure S7 in the supporting information.

More importantly, in the IR spectra of PE17 and PE18, the new bands at around 699, 740, 1406 and 1753 cm^{-1} are more intense than those in PE20 (red dashed arrows), and therefore, most likely result from intermediate products. Specifically, the peak at 699 cm^{-1} is likely from the olefinic CH wag bands of *cis*-1,2-substitution.^[16] The peak at 740 cm^{-1} is assigned to the olefinic CH out-of-plane vibration and is a feature of the 1,3-cyclohexadiene with a conjugated double bond, other than 1,4-cyclohexadiene.^[17] Correspondingly, the peak at 1406 cm^{-1} is assigned to the C-H in-plane deformation related to non-

fluorinated C=C bonds.^[16a,18] These features clearly evidenced the 1,2-addition of benzene. On the other side, the intense band at around 1750-1756 cm^{-1} is attributed to the C=C vibration of the non-conjugated *cis*-1,2-difluorosubstituted olefin, thus, suggesting the occurrence of 1,4-addition for C_6F_6 .^[19] All these results indicate that the [4+2] reaction happens between the C_6F_6 and C_6H_6 . The decreasing intensities of these featured peaks under higher pressure indicated that the [4+2] products are related to the intermediate product, which continues to react at higher pressure.

Figure 4. a) A histogram of the comparison between the relative abundance of major components in different high-pressure samples; b) the high-resolution mass spectra of the $\text{C}_6\text{H}_6\text{-C}_6\text{F}_6$ tetramer at the retention time of 35.96 min in sample PE20.

To identify the intermediates, we extracted the soluble molecules from the samples and made Gas Chromatography-Mass Spectrometry (GC-MS) investigation. Over 170 compounds were detected in PE20 (Table S4), but not in the starting material. Twelve primary compounds with an abundance of >1% are $\text{C}_{12}\text{H}_5\text{F}_5$ (24.54%), $\text{C}_{24}\text{H}_{12}\text{F}_{12}$ (22.01%), $\text{C}_{11}\text{H}_5\text{F}_5$ (10.72%), $\text{C}_{12}\text{H}_{10}$ (9.04%), $\text{C}_{11}\text{H}_5\text{F}_5$ (2.40%), $\text{C}_{18}\text{H}_{10}\text{F}_6$ (2.11%), $\text{C}_{18}\text{F}_{18}$ (1.84%), $\text{C}_{18}\text{H}_6\text{F}_{12}$ (1.66%), C_{10}H_8 (1.42%), $\text{C}_{18}\text{H}_{12}\text{F}_6$ (1.28%), $\text{C}_{12}\text{H}_3\text{F}_5$ (1.18%), and $\text{C}_{17}\text{H}_6\text{F}_{12}$ (1.12%). By comparing the retention time to commercial samples and examining the National Institute of Standards and Technology /Wiley standard library, $\text{C}_{12}\text{H}_5\text{F}_5$, $\text{C}_{12}\text{H}_{10}$ and C_{10}H_8 are identified as 2,3,4,5,6-pentafluorobiphenyl, biphenyl and naphthalene, respectively (Fig.S8).

Similar results are also observed in PE17 and PE18 (Table S5 and Table S6). Figure 4a displays the relative abundance of those representative products. $C_{12}H_5F_5$ is the predominant product, indicating that the 1-1' coupling reaction between C_6H_6 and C_6F_6 is a typical reaction of CHCF under applied pressure (Scheme 1a). Considering H migrates to N in acetonitrile at a distance of 2.0 Å,^[20] the elimination of H, F species is not surprising, because the shortest intermolecular distance between H and F is 2.2 Å in phase VIII (Fig.1b). However, this does not mean that the 1-1' coupling reaction constructs the polymerized material. This is first because terphenyl ($C_{18}H_{14}$) and their fluorinated derivatives $C_{18}(H,F)_{14}$ like $C_{18}H_{10}F_4$, $C_{18}H_9F_5$, $C_{18}H_5F_9$, and $C_{18}H_4F_{10}$ were detected in a very small amount in all samples; in total 1.38% for PE17, 1.17% for PE18, and 1.06% for PE20. This indicates no successive reaction is promoted via this pathway. Secondly, the IR spectra of the recovered samples significantly differ from that of the poly-aryl molecules (Fig.S9).

In contrast, a series of dimers ($C_{12}H_6F_6$), trimers ($C_{18}H_6F_{12}$ and $C_{18}H_{12}F_6$) and tetramers ($C_{24}H_{12}F_{12}$) were identified, which highlights the addition between benzene and hexafluorobenzene. As shown in Figure 4a, it is notable that the $C_{24}H_{12}F_{12}$ tetramer has a much higher content when synthesized under higher pressure (PE20), which has the second highest percentage in total. Therefore, it is reasonable to infer that the addition reaction is the pathway to synthesize the CHCF polymer. In the MS of the tetramer $C_{24}H_{12}F_{12}$, the fragment $C_6H_6^+$ ($m/z = 78.0465$) and $C_6F_6^+$ ($m/z = 185.9900$) are detected, and $C_{18}H_{12}F_6^+$ and $C_{12}H_6F_6^+$ are also remarkably detected. However, no $C_{12}H_{12}^+$ and $C_{12}F_{12}^+$ ions are identified (Fig.4b). This indicates the tetramers have an alternate connection like $C_6H_6-C_6F_6-C_6H_6-C_6F_6$. Considering the [4+2] Diels-Alder reaction concluded from the IR result, the PIP of C_6H_6 and C_6F_6 is most likely a process of serial [4+2] Diels-Alder reactions. We also identified a significant amount of 1,2,3,4-tetrafluonaphthalene in the GC-MS result, which probably comes from the following reaction process. The product of the Diels-Alder reaction undergoes a retro-Diels Alder reaction to eliminate a $C_2(H,F)_2$ molecule and then followed by an elimination of two F/H species (Scheme 1a). This serial [4+2] Diels-Alder reaction of aromatics is also proposed in the literature,^[2a,5] and is consistent with the crystal structure of phase VIII in the view of topo-chemistry.

So far there is still a gap between the serial [4+2] product and H-F graphane, which is still under investigation. By comparing their structures, we arguably propose a reaction model as shown in Scheme 1b. The [4+2] polymer ribbons connect to their neighbours to form H-F graphane with a layered structure by eliminating some C, H and F species. This model well explains all of our experimental results.

To conclude, in this paper we determined the crystal structures of all the $C_6H_6-C_6F_6$ cocrystal phases under high pressure and found it finally polymerized into H-F graphane with layered structure. Several elemental reactions including the Diels-Alder, retro-Diels Alder, and 1-1' coupling reactions are discerned and the serial [4+2] Diels-Alder reaction is evidenced to be the key step of the PIP. Our investigation described the PIP process, especially the elemental reactions of CHCF for the

first time, which will provide an insight into the other aromatics. The formation of fluorinated graphane highlights that the PIP of the substituted aromatics is an alternative method to construct sp^3 -hybridized carbon materials with diverse structures.

Scheme 1 a) The selected elemental reactions of CHCF cocrystal under high pressure; b) The proposed reaction route from CHCF cocrystal to H,F-graphane. A 2x2 superlattice is shown in blue line on the product.

Experimental Section

Benzene (99.9%) and hexafluorobenzene (99.9%) were purchased from Sigma Aldrich and used without further purification. The $C_6H_6-C_6F_6$ cocrystal (CHCF) was prepared by mixing equimolar amounts of C_6H_6 and C_6F_6 at 298 K, and storing it in a sealed bottle at low temperature. In situ high-resolution X-ray diffraction of CHCF was conducted at Beamline 5A XRS-MS of PLS-II at Pohang Accelerator Laboratory (PAL). The neutron diffractions with a constant wavelength were collected on the Fenghuang diffractometer of China Mianyang Research Reactor (CMRR), Institute of Nuclear Physics and Chemistry, China Academy of Engineer Physics. Neutron measurements with TOF were measured at PEARL, ISIS^[21] and BL11 PLANET of J-PARC Center.^[10] The samples PE17, PE18, and PE20 were synthesized by a VX3 PE press equipped with double-toroid sintered diamond anvils. SEM images were recorded on a Carl Zeiss Merlin Compact Field-emission scanning electron microscope operated at 1.0 kV and the EDS result was obtained in a Carl Zeiss Merlin SEM operating at 10 kV with a system from Bruker Nano GmbH using a XFlash detector 5030. Solid 1H and ^{13}C NMR experiments were performed with a Varian-Chemagnetic Infinity 300 Nuclear Magnetic Resonance spectrometer. The TEM and SAED patterns were recorded under a bias voltage of 120 kV (ZEISS, Libra 120), and field-emission high resolution TEM were operated under a higher bias voltage of 200 kV (JEOL, JEM-2100F). High-energy PDF measurement was performed at the beamline 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The neutron PDF measurement was carried out in NOMAD, Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). Mid infrared spectra were measured on a Bruker VERTEX 70v FTIR spectrometer with an IR microscope. High-resolution GC-MS measurements were performed on a Thermo Scientific™ Q Exactive™ GC hybrid quadrupole-Orbitrap mass spectrometer. Details of the in situ high-pressure XRD, neutron diffraction, the synthetic method of the samples PE17, PE18, and PE20, ssNMR, X-ray and neutron PDF measurement, GC-MS measurement, and computational simulation methods are given in the Supporting Information.

Acknowledgements

The authors acknowledge the support of the National Natural Science Foundation of China (NSFC) (Grant Nos.: 21601007, 21771011 and 21875006). The authors also acknowledge the support from the Top 1000-Talents Award. Experiments at the ISIS Neutron and Muon Source were supported by a beamtime allocation from the Science and Technology Facilities Council.^[22] Neutron diffraction experiments at J-PARC were performed through the J-PARC user programs (No.2016A0191). The research at Oak Ridge National Lab's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). Electron microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. The research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The calculations were performed on the Tianhell supercomputer at the Chinese National Supercomputer Center in Guangzhou. The authors thank Dr. Joerg C. Neufeind for his helps in neutron PDF measurements and thank Dr. Qiaoshi Zeng and Dr. Yufei Meng for their helps on the reduction of X-ray PDF data and IR measurements.

Keywords: C₆H₆-C₆F₆ cocrystal • Hydrogenated-fluorinated graphane • Pressure-induced polymerization • Cycloadditions • High pressure crystal structure

- [1] a) Z. Zeng, L. Yang, Q. Zeng, H. Lou, H. Sheng, J. Wen, D. J. Miller, Y. Meng, W. Yang, W. L. Mao, H.-k. Mao, *Nat. Commun.* **2017**, *8*, 322; b) *The properties of natural and synthetic diamond* (Ed: J. E. Field), Academic Press, **1992**.
- [2] a) T. C. Fitzgibbons, M. Guthrie, E.-s. Xu, V. H. Crespi, S. K. Davidowski, G. D. Cody, N. Alem, J. V. Badding, *Nat. Mater.* **2015**, *14*, 43-47; b) X. Li, M. Baldini, T. Wang, B. Chen, E.-s. Xu, B. Vermilyea, V. H. Crespi, R. Hoffmann, J. J. Molaison, C. A. Tulk, M. Guthrie, S. Sinogeikin, J. V. Badding, *J. Am. Chem. Soc.* **2017**, *139*, 16343-16349; c) X. Li, T. Wang, P. Duan, M. Baldini, H.-T. Huang, B. Chen, S. J. Juhl, D. Koeplinger, V. H. Crespi, K. Schmidt-Rohr, R. Hoffmann, N. Alem, M. Guthrie, X. Zhang, J. V. Badding, *J. Am. Chem. Soc.* **2018**, *140*, 4969-4972; d) M. M. Nobrega, E. Teixeira-Neto, A. B. Cairns, M. L. A. Temperini, R. Bini, *Chem. Sci.* **2018**, *9*, 254-260.
- [3] a) P. Pruzan, J. C. Chervin, M. M. Thiéry, J. P. Itié, J. M. Besson, J. P. Forgerit, M. Revault, *J. Chem. Phys.* **1990**, *92*, 6910-6915; b) F. Cansell, D. Fabre, J.-P. Petit, *J. Chem. Phys.* **1993**, *99*, 7300-7304; c) L. Ciabini, M. Santoro, R. Bini, V. Schettino, *J. Chem. Phys.* **2002**, *7*, 2928-2935; d) B. R. Jackson, C. C. Trout, J. V. Badding, *Chem. Mater.* **2003**, *15*, 1820-1824.
- [4] M. V. Kondrin, N. A. Nikolaev, K. N. Boldyrev, Y. M. Shulga, I. P. Zibrov, V. V. Brazhkin, *CrystEngComm*, **2017**, *19*, 958-966.
- [5] B. Chen, R. Hoffmann, N. W. Ashcroft, J. Badding, E. Xu, V. Crespi, *J. Am. Chem. Soc.* **2015**, *137*, 14373-14386.
- [6] A. Y. Rogachev, X. D. Wen, R. Hoffmann, *J. Am. Chem. Soc.* **2012**, *134*, 8062-8065.
- [7] a) J. S. W. Overell, G. S. Pawley, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1966-1972; b) J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1655-1657; *Angew. Chem.* **1992**, *104*, 1666-1669.
- [8] Y. Wang, L. Wang, H. Zheng, K. Li, M. Andrzejewski, T. Hattori, A. Sano-Furukawa, A. Katrusiak, Y. Meng, F. Liao, F. Hong, *J. Phys. Chem. C* **2016**, *120*, 29510-29519.
- [9] L. Ciabini, M. Santoro, F. Gorelli, R. Bini, V. Schettino, S. Raugel, *Nat. Mater.* **2007**, *6*, 39-43.
- [10] T. Hattori, A. Sano-Furukawa, H. Arima, K. Komatsu, A. Yamada, Y. Inamura, T. Nakatani, Y. Seto, T. Nagai, W. Utsumi, T. Iitaka, H. Kagi, Y. Katayama, T. Inoue, T. Otomo, K. Suzuya, T. Kamiyama, M. Arai, T. Yagi, *Nuclear Instrum. Methods Phys. Res., Sect. A* **2015**, *780*, 55-67.
- [11] *Graphite and Precursors* (Ed: P. Delhaes), CRC Press, **2001**, ISBN 90-5699-228-7.
- [12] a) J. Rohrer, P. Hylgaard, *Phys. Rev. B* **2011**, *83*, 165423; b) V. E. Antonov, I. O. Bashkin, A. V. Bazhenov, B. M. Bulychev, V. K. Fedotov, T. N. Fursova, A. I. Kolesnikov, V. I. Kulakov, R. V. Lukashev, D. V. Matveev, M. K. Sakharov, Y. M. Shulga, *Carbon* **2016**, *100*, 465-473; c) X. D. Wen, R. Hoffmann, N. W. Ashcroft, *J. Am. Chem. Soc.* **2011**, *133*, 9023-9035.
- [13] a) K. Guérin, J. P. Pinheiro, M. Dubois, Z. Fawal, F. Masin, R. Yazami, A. Hamwi, *Chem. Mater.* **2004**, *16*, 1786-1792; b) V. Pischedda, S. Radescu, M. Dubois, C. Cavallari, N. Batisse, F. Balima, *Carbon* **2018**, *127*, 384-391.
- [14] a) H. Peelaers, A. D. Hernández-Nieves, O. Leenaerts, B. Partoens, F. M. Peeters, *Appl. Phys. Lett.* **2011**, *98*, 051914; b) Y. Liu, R. L. Vander Wal, V. N. Khabashesku, *Chem. Mater.* **2007**, *19*, 778-786; c) Y. Sato, S. Shiraiishi, Z. Mazej, R. Hagiwara, Y. Ito, *Carbon* **2003**, *41*, 1971-1977.
- [15] Z. Sofer, P. Šimek, V. Mazánek, F. Šembera, Z. Janoušek, M. Pumera, *Chem. Commun.* **2015**, *51*, 5633-5636.
- [16] a) E. R. Lippincott, T. E. Kenney, *J. Am. Chem. Soc.* **1962**, *84*, 3641-3648; b) J. O. Jensen, *J. Mol. Struct-Theochem.* **2004**, *680*, 227-236.
- [17] a) Spectral Database for Organic Compounds, SDBS, Free site organized by National Institute of Advanced Industrial Science and Technology (AIST), Jpn, <http://sdb.sdb.aist.go.jp>; b) J. C. Berridge, A. Gilbert, G. N. Taylor, *J. Chem. Soc., Perkin Trans.1* **1980**, *38*, 2174-2178.
- [18] E. R. Blout, M. Fields, R. Karplus, *J. Am. Chem. Soc.* **1948**, *70*, 194-198.
- [19] a) N. C. Craig, E. A. Entemann, *J. Chem. Phys.* **1962**, *36*, 243-248; b) R. F. Waldron, A. C. Barefoot, D. M. Lemal, *J. Am. Chem. Soc.* **1984**, *106*, 8301-8302; c) B. E. Roberts, G. D. Goldman, D. M. Lemal, *J. Fluor. Chem.* **1990**, *48*, 353-360.
- [20] H. Zheng, K. Li, G. D. Cody, C. A. Tulk, X. Dong, G. Gao, J. J. Molaison, Z. Liu, M. Feyngenson, W. Yang, I. N. Ivanov, L. Basile, J.-C. Idrobo, M. Guthrie, H.-k. Mao, *Angew. Chem. Int. Ed.* **2016**, *55*, 12040-12044; *Angew. Chem.* **2016**, *128*, 12219-12223.
- [21] C. L. Bull, N. P. Funnell, M. G. Tucker, S. Hull, D. J. Francis, W. G. Marshall, *High Press. Res.* **2016**, *36*, 493-511.
- [22] Y. Wang, C. Bull, K. Li, H. Zheng, Y. Wang, STFC ISIS Facility, **2017**, 1620149, doi:10.5286/ISIS.E.84424559.

COMMUNICATION

Short range ordered H,F-substituted graphane was obtained by compressing benzene and hexafluorobenzene cocrystal. By using neutron diffraction and gas chromatography-mass spectrum, we figured out the reaction process and elementary reaction. The reaction process contains [4+2]Diels-Alder, retro-Diels Alder, and 1-1' coupling, and the Diels-Alder reaction is the key reaction in the polymerization process.

Yajie Wang, Xiao Dong, Xingyu Tang, Haiyan Zheng,* Kuo Li,* Xiaohuan Lin, Leiming Fang, Guang'ai Sun, Xiping Chen, Lei Xie, Craig L. Bull, Nicholas P. Funnell, Takanori Hattori, Asami Sano-Furukawa, Jihua Chen, Dale K. Hensley, George Cody, Yang Ren, Hyun Hwi Lee, Ho-kwang Mao

Page No. – Page No.

Pressure-Induced Diels-Alder Reactions in C₆H₆-C₆F₆ Cocrystal towards Graphane Structure