Reversible pressure-induced polymerization of Fe(C₅H₅)₂ doped C₇₀

Wen Cui¹, Mingguang Yao¹, Zhen Yao¹, Fengxian Ma¹, Quanjun Li¹, Ran Liu¹, Bo

Liu¹, Bo Zou¹, Tian Cui¹, Bingbing Liu^{1,*}, Bertil Sundqvist^{1,2}

¹State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012,

China

²Department of Physics, Umea University, S-901 87 Umea, Sweden

*Corresponding author. Tel/Fax +00 86 431 85168256 E-mail address:
liubb@jlu.edu.cn (B.B. Liu)

Abstract

High pressure Raman, IR and X-ray diffraction (XRD) studies have been carried out on $C_{70}(Fe(C_5H_5)_2)_2$ (hereafter, “ $C_{70}(Fc)_2$ ”) sheets. Theoretical calculation is further used to analyze the Electron Localization Function (ELF) and charge transfer in the crystal and thus to understand the transformation of $C_{70}(Fc)_2$ under pressure. Our results show that even at room temperature dimeric phase and one dimensional (1D) polymer phase of C_{70} molecules can be formed at about 3 and 8 GPa, respectively. The polymerization is found to be reversible upon decompression and the reversibility is related to the pressure-tuned charge transfer, as well as the overridden steric repulsion of counter ions. According to the layered structure of the intercalated ferrocene molecules formed in the crystal, we suggest that ferrocene acts as not only a spacer to restrict the polymerization of C_{70} molecules within a layer, but also as charge reservoir to tune the polymerization process. This supplies a possible way for us to design the polymerization of fullerenes at suitable conditions.

1. Introduction

Fullerene C_{60} forms a variety of polymeric structures with dramatically different physical and chemical properties [1-3]. C_{60} can be polymerized by different methods, such as applying high pressure and temperature (HPHT) [4, 5], irradiation [6, 7] and doping [8, 9], resulting in 1D, 2D and 3D polymers. The C_{60} s in crystalline 3D polymer are linked by sp^3 -hybridized bonds to twelve adjacent molecules, and the polymers exhibit high hardness and electronic conduction [10, 11]. Recent research interest has been focusing on the effect(s) of confinement or intercalation by template or other molecules on the transformations of C_{60} s, towards controllable polymerization of fullerenes and creating new materials. Filling C_{60} molecules inside single wall carbon nanotubes produces linearly arranged C_{60} arrays in tube channels and the inserted C_{60} s can only form dimers or a single-chain polymer, depending on the pressure applied [12]. A reversible polymerization of bulk C_{60} was obtained by tuning the charge transfer interaction in ferrocene (Fc, $Fe(C_5H_5)_2$) doped C_{60} with the help of pressure [13]. In this case, the Fc molecules form a layered structure in the crystal and act as spacers that allow polymerization of C_{60} s only within a 2D layer. More interestingly, when C_{60} molecules are separated by m-xylene molecules, forming solvated C_{60} , the amorphized C_{60} cluster units formed by molecular collapse at high pressure can still be arranged in a crystalline structure with long range periodicity, which is superhard and indents diamond anvils [14]. Although much exciting progress has thus recently been made on C_{60} based material, less effort has been made on other fullerenes.

Another “heavy” fullerene easily available in significant quantities is C_{70} , which also exhibits many unique and outstanding physical properties. However, due to the special elliptical shape the polymerization of the C_{70} molecule becomes less efficient [15] since only the double bonds on the polar caps of the molecule are reactive, whereas the cyclic double bonds on the equatorial belt are ineffective in undergoing (2 + 2) cycloaddition reaction. This gives strict topological constraints on the formation of long-range ordered polymers of C_{70} s. Still, some attempts have been made to produce polymeric C_{70} . Several different forms of C_{70} dimers have been produced, such as C_{2h} C_{140} , C_{2v} C_{140} and C_1 C_{140} [15-17], and formation of polymeric zigzag chains in initially hexagonally close packed C_{70} single crystals is reported by Soldatov et al [18]. We also notice that when the rare-earth metal Sm is intercalated into C_{70} [19], the charge transfer between C_{70} s and Sm atoms results in Sm- C_{70} bonding in a 2D network structure, with a Sm atom as a bridge. Such an interesting physical phenomenon also indicates that charge transfer may play an important role in the polymerization of C_{70} and thus requires further investigations. Meanwhile, most of the early polymers were prepared under HPHT conditions and thus exploring methods for fullerene polymerization that do not rely solely on the HPHT treatment is also important.

Motivated by the progress with C_{60} fullerene, especially the unique polymerization behaviors and the novel structure of fullerenes obtained in the confined environment, we focused on the spatial confinement effect on the behavior of C_{70} under pressure. According to previous literature, $C_{70}(\text{Fc})_2$ is formed at ambient conditions by weak

charge transfer interaction between the two components [20]. High pressure serves as a powerful tool that is expected to tune the charge transfer between Fc and C₇₀ in the confinement environment created by the Fc molecules. (The structure is shown in Fig.S1(a) in Supporting Information.) Thus it might be possible to obtain various polymeric phases in C₇₀(Fc)₂ under moderate conditions. This study is promising for realizing the polymerization of C₇₀ in a controllable way and creating new polymeric structures, as well as to improve our understanding of the polymerization mechanism of confined C₇₀.

In this work, *in situ* Raman and IR spectroscopy as well as XRD are used to investigate the structural transitions of C₇₀(Fc)₂ under high pressure. We find that a dimeric phase and a 1D polymer are formed above 3 and 8 GPa, respectively. The polymerization is reversible when released from, at least, 20 GPa. To support our analysis we have also calculated the ELF and the charge transfer from C₇₀(Fc)₂ under pressure. The polymerization mechanisms are discussed in the framework of pressure-tuned changes in the charge transfer, the overridden steric repulsion of counterions and the unique layered structure of C₇₀(Fc)₂.

2. Experiment method

Crystalline C₇₀(Fc)₂ sheets are prepared by introducing 150 mg Fc into 3 ml of saturated C₇₀/toluene solution. After ultrasonication we then add 3 ml isopropyl alcohol (IPA) and the mixture is maintained at 10°C for 24 h for the growth of single crystalline C₇₀(Fc)₂ sheets. The morphologies of the obtained as-grown samples are

characterized by scanning electron microscopy (SEM, JEOL JSM-6700F) and X-ray diffraction (Rigaku D/max-RA, CuK α 1 radiation $\lambda = 1.5406 \text{ \AA}$). High pressure Raman measurements up to 35 GPa have been carried out using a Raman spectrometer (Renishaw inVia) with a 633 nm He-Ne laser line as excitation. High pressure IR measurements up to 20 GPa have been studied using a Bruker Vertex80 V FTIR spectrometer. *In situ* XRD measurements up to 28 GPa are performed at the Advanced Photon Source in the USA at ambient temperature ($\lambda = 0.4246 \text{ \AA}$). For all the high pressure experiments, samples are loaded in a gasketed Mao-Bell type diamond anvil cell (DAC). Silicone oil is used as pressure-transmitting medium in high pressure Raman and X-ray measurements, while liquid argon is used for high pressure IR measurement. All the measurements have been performed at room temperature.

3. Experiment results

SEM images of as-grown C₇₀(Fc)₂ sheets are shown in Figure 1. It is clear that the crystals have an hexagonal morphology with an average size of 4-5 μm and a thickness in the range 200-300 nm (Fig.1a, b). The XRD pattern in Figure 1(c) shows that the structure is monoclinic with lattice constants $a = 29.38 \text{ \AA}$, $b = 10.36 \text{ \AA}$, $c = 20.21 \text{ \AA}$ and $\beta = 127.31^\circ$, which is similar to those of the C₇₀(Fc)₂ crystals reported by Olmstead et al. [20]

Figure 1. SEM images of $C_{70}(Fc)_2$ at low (a) and high (b) magnification; (c) our experimental XRD pattern of $C_{70}(Fc)_2$.

3.1 Raman spectroscopy

Raman spectroscopy is a powerful tool to characterize C_{70} and C_{70} -based materials. For pristine C_{70} , 53 Raman active modes are predicted ($12A'_1 + 22E'_2 + 19E'_1$) from the D_{5h} point group according to group theory [21, 22]. Upon polymerization, one of the most characteristic feature is the split of the E'_2 Raman mode (located at 1567 cm^{-1} for pristine C_{70}) into two peaks due to the reduced symmetry [16, 18]. The Raman spectrum of the pristine sample is shown at the bottom of Figure 2; the single Raman peak centered at 1567 cm^{-1} indicates that the $C_{70}(Fc)_2$ sheets mainly contain monomeric C_{70} molecules. In addition to the peaks from C_{70} , two peaks at 310 and 1106 cm^{-1} from the vibrational modes of intercalated Fc molecules are observed. The two peaks are denoted as Fc(a) and Fc(b), respectively.

High pressure Raman spectra recorded at room temperature up to 35 GPa are shown in Figure 2. From this figure, we find that as the pressure increases, the peaks at 226, 737 and 1182 cm^{-1} split and several new peaks appear at lower frequency at around 2-3 GPa. The peak of 1564 cm^{-1} shows two splits at about 2.6 and 7 GPa, respectively, marked by red arrows in Figure 2(c). Above 11 GPa, most of the peaks

become broad and weak. All these changes indicate the occurrence of transitions in the material which will be discussed later. Beside the changes in the Raman modes of C_{70} , the two modes from Fc molecules disappear with increasing pressures (see Fig.S2 for a more clear view). We further analyze the pressure dependence of several important modes in Figure 2(d), which shows that two obvious changes in the slopes of the pressure dependence of certain peaks can be observed at 2-3 and 8 GPa, respectively. This implies that two phase transitions may occur at the two corresponding pressure points. The pressure dependence of almost all Raman modes is also shown in Figure S3.

Figure 2. Raman spectra at low frequencies (a), intermediate frequencies (b) and high frequencies (c) for $C_{70}(\text{Fc})_2$ at different pressures, and the pressure dependence of the 1182 and 1564 cm^{-1} modes (d). The red arrows show the splits of the 1564 cm^{-1} mode.

3.2 IR spectroscopy

High pressure IR spectra were collected at room temperature up to 20 GPa and some selected spectra are presented in Figure 3. As we know, C_{70} has 31 infrared-active modes, out of which ten nondegenerate A_2'' and 21 doubly degenerate E_1'' modes are included at ambient conditions [23]. The IR spectrum of pristine $C_{70}(Fc)_2$ is shown at the bottom of Figure 3(a, b) and besides the IR modes from C_{70} , we can also observe two modes from Fc located at 1002 and 1107 cm^{-1} . We denote these two modes as Fc(1) and Fc(2), respectively.

From Figure 3, we can see that most peaks become weaker and broader as pressure increases. Remarkably, some new peaks appear at 600-800 and the 1430 cm^{-1} peak splits twice at about 2-3 and 8 GPa, respectively. The red arrows show the corresponding splits. All these splitted peaks finally merge into one broad peak at 20 GPa. Besides the peak from C_{70} , the Fc(1) mode also splits at about 3 GPa. The pressure evolutions for the frequencies of the most important modes 1430 cm^{-1} are shown in Figure 3(c). Also, the pressure dependence of most IR modes is shown in Figure S4. From the plotted curves, we can observe two transitions which occur at 2-3 and 6-8 GPa, respectively. These significant changes in the IR spectra further confirm that two phase transitions occur in our sample under high pressure.

Figure 3. IR spectra at low frequencies (a) and high frequencies (b) under different pressures and the pressure dependence of the 1430 cm^{-1} mode (c). The red arrows show the splits of the 1430 cm^{-1} mode.

The Raman and IR spectra at atmospheric pressure of the samples released from different pressures are shown in Figure 4. The IR spectrum of the sample released from 20 GPa shows identical features to those of pristine $\text{C}_{70}(\text{Fc})_2$. The Raman spectrum of the sample released from 35 GPa (Fig. 4b) shows that although most of the peaks from pristine $\text{C}_{70}(\text{Fc})_2$ disappear, the weak signals in the region of 700-800 and $1400\text{-}1600\text{ cm}^{-1}$, which should be from the remaining C_{70} in the released sample, can still be observed. These results indicate that the transitions observed in the samples under pressure are reversible up to at least 20 GPa while became partially reversible from 35 GPa. The irreversibility is mostly due to the amorphization of the

material at very high pressure.

Figure 4. IR (a) and Raman (b) spectra for $C_{70}(Fc)_2$ after decompression from the pressures indicated.

3.3 XRD measurement

At ambient conditions, the XRD pattern from our sample (see Fig.1c) can be well indexed by a monoclinic structure, in good agreement with that reported in previous literature [20]. In this structured crystal, the fullerene C_{70} molecules are located among the layers of ferrocene molecules (see Fig.S1(a)). Some selected XRD patterns as a function of pressure at room temperature are shown in Figure 5(a). We can see that no significant change has been observed even up to 12.7 GPa. At higher pressure, most peaks become too weak to be observed and only a broad peak at 4.3 Å survives (the initially strongest peak in the pattern). The pressure evolutions of the lattice parameters are also shown in Figure 5(b). It is clear that two obvious changes in the slopes can be observed at 2.5 and 8 GPa, respectively. These transitions are in agreement with the results from Raman and IR studies, indicating that two phase

transitions may occur at the corresponding pressures. Note that the ambient pressure data presented here were obtained in our lab while the high pressure data were measured at the Synchrotron Radiation Station. However, based on a comparison with our previous data, the difference between the measured data from the two different experiments is quite small and acceptable. Thus the slope of the pressure dependence of the lattice parameters in the range 0-2 GPa is reasonable and consistent. We also show error bars in Figure 5(b) to show that the anomalies are much larger than the errors.

Figure 5. *In situ* XRD patterns of $C_{70}(Fc)_2$ at different pressures (a) and pressure dependence of the lattice parameters (b) of $C_{70}(Fc)_2$. The pressure dependence of d/d_0 is shown as an inset.

3.4 Theoretical calculation

To guide our interpretation of the experimental data, the structural evolutions of the crystal under pressure are simulated using Material Studio software and the calculation details are described in the Supporting Information (in the description of

Fig.S5). The ELF that can be used to search for possible bonding between neighboring C_{70} molecules has been calculated for our $C_{70}(Fc)_2$ under pressure. Figure 6 shows the results for the $C_{70}(Fc)_2$ crystal viewed from the (100) crystal plane obtained at 2, 3.5 and 8 GPa, respectively. In these figures, the Fc molecules which should be underneath the layer of C_{70} molecules are not shown (for better view) but all of them are taken into account in our simulations. From the figures, it is clear that the overlapping of ELF between C_{70} molecules increases with increasing pressure. At 2 GPa, no overlapping of the ELF between C_{70} molecules can be found and the ELF of two C_{70} s out of every four C_{70} molecules show overlapping at 3.5 GPa, while at 8 GPa, almost all the ELF of the C_{70} molecules in the crystal overlap. The overlapping of the ELFs strongly indicates that chemical bond formation is initiated between neighboring C_{70} molecules and the degree of polymerization is enhanced with increasing pressure. Several possible polymeric structures of C_{70} are shown in Figure S6 at pressures of 3.5 (a) and 8 GPa (b), respectively.

To further understand the effect of doping on the charge distribution in $C_{70}(Fc)_2$ under pressure, the iso-surface charge difference of the system is calculated by Density functional theory (DFT) simulations. In Table 1, we list the charge values on different atoms in $C_{70}(Fc)_2$ at three selected pressures and we can see that the values change with increasing pressure. The results suggest that the degree of the charge transfer from Fc to C_{70} molecules increases significantly by applying pressure.

Figure 6. ELF of the crystals viewed from the (100) plane at 2 GPa (a), 3.5 GPa (b) and 8 GPa (c). The green (or yellow) elliptical represents the ELF of each C₇₀ molecule.

P (GPa)	Charge value (e ⁻)		
	C(from C ₇₀)	Fe	C(from Fc)
2	-0.37	4.46	-8.61
3.5	-0.51	4.53	-8.39
8	-0.61	4.65	-8.13

Table 1. Charge values on different atoms in C₇₀(Fc)₂ at selected pressures.

4. Discussion

From high-pressure Raman, IR and XRD studies on the $C_{70}(Fc)_2$ sample, we suggest that two transitions take place in the material at around 2-3 and 8 GPa, respectively. Combined with our theoretical calculations, the transitions in the material can be demonstrated as follows.

4.1 Edge at 2-3 GPa

Around 2-3 GPa, there is an obvious change in the slopes of the pressure dependence for Raman and IR peaks. (see Fig.S3, 4) According to previous studies, similar changes were related to the orientational ordering transition from fcc to rhombohedral lattice structure or to a polymerization in the pristine C_{70} crystal [24-26]. In general, orientational phase transitions in C_{70} crystals only cause slope changes in some Raman or IR vibration modes, but in our case we also observe the splitting of some modes in the spectra, which can not be related to the orientational phase transition. Instead, the mode splitting in Raman and IR spectra always appears in C_{70} polymerization [16, 24]. For example, in pristine C_{70} , the chemical bond formation between C_{70} molecules results in spectroscopic changes with some new modes appearing at around 1 GPa [23]. We further compare the Raman and IR spectra of $C_{70}(Fc)_2$ at several selected pressures at around 2-3 GPa with that of the C_{70} dimer [16] in Figure S7. All the observed spectroscopic features (transitions) under pressure are quite similar to those of the C_{70} dimer [16], which strongly suggests the formation of C_{70} dimers in $C_{70}(Fc)_2$ above 2 GPa.

The ELF results shown in Figure 6(b) further support the formation of a dimer phase in $C_{70}(Fc)_2$ at about 3.5 GPa due to the overlapping of the electron cloud around the molecules. Two possible structures of the C_{70} dimer structure are proposed in Figure S6(a). For both structures, neighboring molecules are linked by four-membered rings in a (2+2) cycloaddition between double bonds close to polar pentagons on the C_{70} cages. These structures have also been studied in previous work by different methods (HPHT treatment or separation by high performance liquid chromatography) [16, 17]. In contrast to the dimer of C_{60} , C_{70} dimers can have several different structures due to its special elliptical molecular shape.

The observed changes in all the lattice constants and the dominant diffracted peaks of the crystal from XRD measurement at 2-3 GPa, with no significant change in the recorded XRD patterns, is generally consistent with that of the reported XRD data on fullerene dimerization in previous work. For example, in the studies of dimerization of C_{60} , the XRD pattern can still be described by a fcc structure without significant change in the diffracted pattern [27, 28]. Thus, the phase transition observed in our sample can be assigned to the dimerization of C_{70} molecules.

4.2 Edge at 8 GPa

The second transition is observed at about 8 GPa in both Raman and IR measurements. The change in the slopes (see Fig.S3, 4) and the split of the dominant peaks have not been observed in pristine C_{70} at similar pressures at room temperature. As mentioned above, the splitting of spectroscopic modes may be due to the

polymerization of C_{70} molecules which cause a symmetry decrease and the formation of new bonds [16, 18]. In Figure S8 we compare the Raman spectra of $C_{70}(Fc)_2$ at several selected pressures around 7-9 GPa with that of the C_{70} zigzag chain-like polymer phase [18]. All the features and changes are very similar to those of 1D zigzag chain-like C_{70} polymer. Also, the IR spectrum for the long chain polymer C_{70} [18] exhibits characteristic patterns at 700-800 and 1414-1442 cm^{-1} , which are similar to those observed for our $C_{70}(Fc)_2$ at 7-9 GPa.

Our ELF calculations on the crystal (Fig.6c) further support the idea that a long range polymerization may take place in the material above 8 GPa, due to the further increase of the overlapping of the ELF of the molecules. Although this overlap can be observed within the whole layer of C_{70} s, the most probable polymer structure is the 1D polymer. The 1D zigzag chain-like polymer structure of $C_{70}(Fc)_2$ which is matched with our experimental studies is sketched in Figure S6(b). In this case, the neighboring molecules are connected by double bonds close to the polar pentagons of the dimerized C_{70} cages. This structure can be formed naturally from dimer structure 1, while such long chain polymerization is unfavorable from dimer structure 2 due to the inserted Fc molecular spacer, which limits the space arrangement of C_{70} molecules. In general, the one-dimensional C_{70} polymers can only be obtained either by applying simultaneous HPHT conditions or by doping [18, 19]. Compared to the case of C_{60} polymerization, the various configurations in C_{70} polymer phases can be related to the special elliptical shape and the fact that reactive double bonds exist only on the polar caps of the molecules. These reasons, together with the layer-like arrangement of Fc

molecules in $C_{70}(Fc)_2$ and the charge transfer between C_{70} and Fc, results in the different polymer phases in $C_{70}(Fc)_2$. In contrast to the polymer in Sm doped C_{70} , for which the bonding is formed between C_{70} s by a metal atom bridge, the 1D polymer in $C_{70}(Fc)_2$ is formed by the direct bonding between C_{70} molecules (C_{70} - C_{70}) under pressure, due to the enhanced charge transfer between C_{70} and Fc molecules as well as the restrictions imposed by the layers of Fc spacer molecules.

The simulated XRD patterns (see Fig.S5) show that the sample preserves the starting structure even after the polymerizations, which is in good agreement with our high pressure XRD measurements. The changes observed in the b and c parameters at the pressures where the polymerizations occur (see Fig.5b) can be well understood by the polymeric structures formed in the $C_{70}(Fc)_2$ crystal. The starting structure of the $C_{70}(Fc)_2$ crystal can be viewed as close-packed layers of C_{70} molecules stacked directly one above the other, parallel to the (100) crystal plane (see Fig.S1). The spatial separation of the C_{70} layers prevents the formation of interlayer polymeric bonds in the a-axis direction, only allowing polymerization within the C_{70} layers in the $C_{70}(Fc)_2$ crystal. Thus, C_{70} molecules can form a 1D zigzag chain-like polymer in the (100) plane, which results in a lower compressibility of the b-axis and c-axis within the layer than that of the a-axis between the layers.

4.3 Others

In addition to the Raman changes observed for the C_{70} molecules, obvious spectroscopic changes for the Fc molecules have been observed at low pressure (see

Fig.S2). In our previous study on pristine Fc [13], we observed that the Fc(a) mode arising from the ring-metal stretch [29] splits into two peaks already at low pressure. In contrast, no obvious splitting of this mode is observed in $C_{70}(Fc)_2$. Also, the Fc(b) mode, which corresponds to the ring breathing in Fc [29], can persist at least up to 24 GPa in pristine Fc, whereas in $C_{70}(Fc)_2$, this mode shows a significant softening at 3 GPa and disappears at higher pressure. These transformations of Fc in $C_{70}(Fc)_2$ are similar to those of Fc in $C_{60}(Fc)_2$ [13]. For the latter case the unusual softening of the Fc modes was explained by an increasing interaction between C_{60} and Fc under pressure. Indeed, our theoretical analysis of $C_{70}(Fc)_2$ clearly shows that the charge transfer between the two molecules increases with increasing pressure, which should be related to the observed transformations in the Fc molecules in $C_{70}(Fc)_2$. Such enhanced interaction (charge transfer) between C_{70} and Fc caused by applying pressure consequently favors the polymerization of fullerene molecules and thus the formation of the dimer and long chain polymer structures in our sample at suitable pressures.

The reversible polymerization behavior of $C_{70}(Fc)_2$ observed from our IR and Raman studies under pressure is very different from the irreversible polymerization of pure C_{70} by HPHT [18]. A similar reversible polymerization has also been observed in $C_{60}(Fc)_2$ under pressure in our previous report [13], in which the steric repulsion of the counter ions can be overridden at high pressure, resulting in reversible polymerization. Similar to $C_{60}(Fc)_2$, $C_{70}(Fc)_2$ is formed by a weak charge transfer interaction between C_{70} and Fc molecules at ambient conditions. The interaction between C_{70} and Fc can

be enhanced by applying pressure, which favors the polymerization of C_{70} even at room temperature. This can be understood by the fact that the pressure could induce a redistribution of the electron cloud between C_{70} and the Fc molecules and thus favor the polymerization of C_{70} molecules. The stability of the polymerization is controlled by the steric repulsion of counter ions which can be overridden at high pressure and eventually returns to the initial state when pressure is released, leading to reversible polymerization. However, compared with the study on $C_{60}(Fc)_2$, due to the great difference in the molecular morphology between C_{60} and C_{70} the polymerization of C_{70} is difficult and the deformation of C_{70} should be more significant. However, our results clearly show that intercalation by Fc or other molecules is an important way to tune the polymerization of fullerenes, and may be expanded to other fullerene materials, such as larger fullerene.

5. Conclusion

In situ Raman spectra, IR spectra and XRD patterns are recorded to investigate the phase transitions of single crystalline $C_{70}(Fc)_2$ under high pressure. The experimental measurements coupled with theoretical calculation enabled us to elucidate the role of the pressure-tuned interaction (charge transfer) between the Fc and C_{70} molecules on the polymerization of fullerenes in the crystal. A dimer phase and a 1D zigzag chain-like polymer of C_{70} molecules are found to be formed from about 3 and 8 GPa, respectively. Both the dimer and the 1D polymer phases exhibit spectroscopic characteristic similar to those for pure C_{70} dimer and polymer. Several possible

dimer/polymer structures have been further proposed, which can only form within single layers due to the special layered structure in the $C_{70}(Fc)_2$ sheets. The observed polymerization is reversible upon decompression and can be related to the overridden steric repulsion of counter ions at high pressure, as well as the reduction of charge transfer as pressure is decreased.

Acknowledgements

This work was supported financially by the National Basic Research Program of China (2011CB808200), the NSFC (10979001, 51025206, 51032001, 21073071, 11004075, 11104105) and the Cheung Kong Scholars Programme of China, and also by the Swedish Research Council (grant 621-2010-3732).

Appendix A. Supplementary data

The Supporting Information Section provides detailed figures showing Raman and IR spectra, as well as sketches of the possible polymer structures and additional analysis of the calculation results.

References

- [1] Rao AM, Eklund PC. C₆₀ Polymers. Mater. Sci. Forum 1996; 232: 173-206.
- [2] Sundqvist B. Polymeric Fullerenes Phases Formed Under Pressure. Struct. Bond. 2004; 109: 85-126.
- [3] Liu BB, Hou YY, Wang L, Liu DD, Yu SD, Zou B, et al. High pressure and high temperature induced polymeric C₆₀ nanocrystal. Diamond Relat Mater. 2008; 17(4-5): 620-623.
- [4] Iwasa Y, Arima T, Fleming RM, Siegrist T, Zhou O, Haddon RC, et al. New Phases of C₆₀ Synthesized at High Pressure. Science 1994; 264(5165): 1570-2.
- [5] Bashkin IO, Rashchupkin VI, Gurov AF, Moravsky AP, Rybchenko OG, Kobelev NP, et al. A new phase transition in the T-P diagram of C₆₀ fullerite. J. Phys.: Condens. Matter 1994; 6(36): 7491-7498.
- [6] Rao AM, Eklund PC, Hodeau JL, Marques L, Nunez-Regueiro M. Infrared and Raman studies of pressure-polymerized C₆₀s. Phys. Rev. B 1997; 55(7): 4766-4773.
- [7] Eklund PC, Rao AM, Zhou P, Wang Y, Holden JM. Photochemical transformation of C₆₀ and C₇₀ films. Thin Solid Films 1995; 257(2): 185-203.
- [8] Wågberg T, Sundqvist B. Raman study of the two-dimensional polymers Na₄C₆₀ and tetragonal C₆₀. Phys. Rev. B 2002; 65(15): 155421-7.
- [9] Pekker S, Janossy A, Mihaly L, Chauvet O, Carrard M, Forro L. Single-Crystalline (KC₆₀)_n: A Conducting Linear Alkali Fulleride Polymer. Science 1994; 265(5175): 1077-1078.
- [10] Okada S, Saito S, Oshiyama A. New Metallic Crystalline Carbon: Three

Dimensionally Polymerized C₆₀ Fullerite. Phys. Rev. Lett. 1999; 83(10): 1986-1989.

[11] Yamanaka S, Kini NS, Kubo A, Jida S, Kuramoto H. Topochemical 3D Polymerization of C₆₀ under High Pressure at Elevated Temperatures. J. Am. Chem. Soc. 2008; 130(13), 4303-4309.

[12] Zou YG, Liu BB, Wang L, Liu DD, Yu SD, Wang P, et al. Rotational dynamics of confined C₆₀ from near-infrared Raman studies under high pressure. PNAS 2009; 106(52): 22135-22138.

[13] Cui W, Yao MG, Liu DD, Li QJ, Liu R, Zou B, et al. Reversible Polymerization in Doped Fullerenes Under Pressure: The Case Of C₆₀(Fe(C₅H₅)₂)₂. J. Phys. Chem. B 2012; 116(9); 2643-2650.

[14] Wang L, Liu BB, Li H, Yang WG, Ding Y, Sinogeikin SV, et al. Long-Range Ordered Carbon Clusters: A Crystalline Material with Amorphous Building Blocks. Science 2012; 337(6096): 825-828.

[15] Rao AM, Menon M, Wang KA, Eklund PC, Subbaswamy KR, Cornett DS, et al. Photoinduced polymerization of solid C₇₀ films. Chem. Phys. Lett. 1994; 224(1-2): 106-112.

[16] Lebedkin S, Hull WE, Soldatov A, Renker B, Kappes MM. Structure and Properties of the Fullerene Dimer C₁₄₀ Produced by Pressure Treatment of C₇₀. J. Phys. Chem. B 2000; 104(17): 4101-4110.

[17] Forman GS, Tagmatarchis N, Shinohara H. Novel Synthesis and Characterization of Five Isomers of (C₇₀)₂ Fullerene Dimers. J. Am. Chem. Soc.

2002; 124(2): 178-179.

[18] Soldatov AV, Roth G, Dzyabchenko A, Johnels D, Lebedkin S, Meingast C, et al. Topochemical Polymerization of C₇₀ Controlled by Monomer Crystal Packing. Science 2001; 293(5530): 680-683.

[19] Chi DH, Iwasa Y, Uehara K, Takenobu T, Ito T, Mitani T, et al. Pressure-induced structural phase transition in fullerides doped with rare-earth metals. Phys. Rev. B 2003; 67(9): 094101-9.

[20] Olmstead MM, Hao L, Balch AL. Organometallic C₇₀ chemistry. Preparation and crystallographic studies of (η^2 -C₇₀)Pd(PPh₃)₂ • CH₂Cl₂ and (C₇₀) • 2{(η^5 -C₅H₅)₂Fe}. J. Organomet. Chem. 1999; 578(1-2): 85–90.

[21] Dresselhaus MS, Dresselhaus G, Satio R. Carbon fibers based on C₆₀ and their symmetry. Phys. Rev. B 1992; 45(11): 6234-6242.

[22] Jishi RA, Mirie RM, Dresselhaus MS, Dresselhaus G, Eklund PC. Force-constant model for the vibrational modes in C₇₀. Phys. Rev. B 1993; 48(8): 5634-5642.

[23] Thirunavukkuarasu K, Long VC, Musfeldt JL, Borondics F, Klupp G, Kamarás K, et al. Rotational Dynamics in C₇₀: Temperature-and Pressure-Dependent Infrared Studies. J. Phys. Chem. C 2011; 115(9): 3646–3653.

[24] Premila M, Sundar CS, Sahu P. Ch, Bharathi A, Hariharan Y, Muthub DVS. Pressure induced dimerization of C₇₀. Solid State Commun. 1997; 104(4): 237-242.

[25] Chandrabhas N, Sood AK, Muthu DVS, Sundar CS, Bharathi A, Hariharan Y, et al. Reversible Pressure-Induced Amorphization in Solid C₇₀: Raman and

- Photoluminescence Study. Phys. Rev. Lett. 1994; 73(25): 3411-3414.
- [26] Christides C, Thomas IM, Dennis TJS, Prassides K. Pressure and Temperature Evolution of the Structure of Solid C₇₀. Europhys. Lett. 1993; 22(8): 611-618.
- [27] Lepoittevin C, Alvarez-Murga MA, Marques L, Mezouar M, Hodeau JL. Structural characterization of corrugated anisotropic graphene-based carbons obtained from the collapse of 2D C₆₀ polymers. Carbon 2013; 52: 278-287.
- [28] Moret R, Launois P, Wågberg T, Sundqvist B, Agafonov V, Davydov VA, et al. Single-crystal structural study of the pressure-temperature-induced dimerization of C₆₀. Eur. Phys. J. B 2004; 37: 25 – 37.
- [29] Bodenheimer J, Loewenthal E, Low W. The Raman spectra of ferrocene. Chem Phys Lett 1969; 3(9): 715-716.

Captions:

Figure 1. SEM images of $C_{70}(Fc)_2$ at low (a) and high (b) magnification; (c) our experimental XRD pattern of $C_{70}(Fc)_2$.

Figure 2. Raman spectra at low frequencies (a), intermediate frequencies (b) and high frequencies (c) for $C_{70}(Fc)_2$ at different pressures, and the pressure dependence of the 1182 and 1564 cm^{-1} modes (d). The red arrows show the splits of the 1564 cm^{-1} mode.

Figure 3. IR spectra at low frequencies (a) and high frequencies (b) under different pressures and the pressure dependence of the 1430 cm^{-1} mode (c). The red arrows show the splits of the 1430 cm^{-1} mode.

Figure 4. IR (a) and Raman (b) spectra for $C_{70}(Fc)_2$ after decompression from the pressures indicated.

Figure 5. *In situ* XRD patterns of $C_{70}(Fc)_2$ at different pressures (a) and pressure dependence of the lattice parameters (b) of $C_{70}(Fc)_2$. The pressure dependence of d/d_0 is shown as an inset.

Figure 6. ELF of the crystals viewed from the (100) plane at 2 (a), 3.5 (b) and 8 GPa (c). The green (or yellow) elliptical represents the ELF of each C_{70} molecule.

Table 1. Charge values on different atoms in $C_{70}(Fc)_2$ at selected pressures.