Supporting Information

Pressure-induced Polymerization and Disproportionation of Li_2C_2 Accompanied with Irreversible Conductivity Enhancement

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Supplementary Information:

Materials and Methods

Supplementary Figures S1 to S5 and Table S1

Supplementary References

1. Materials and Methods

A Li_2C_2 sample was prepared from stoichiometric mixtures of Li metal and graphite powder, which were sealed inside a tantalum tube in a glove box. The tube was then sealed inside an evacuated quartz tube and heated at 800^{o}C for 12h. Phase analysis was performed by powder X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer (Cu K_α radiation) and no impurities were detected.

In situ XRD, Raman, and IR experiments under high pressure were carried out at room temperature in a diamond anvil cell (DAC), with a diamond culet size of 300 μm. The type II diamonds were used for the IR measurement. The T301 stainless steel gaskets were preindented to a thickness of 30 um and the center holes with 150 um diameters were drilled to act as the sample chamber. The Li_2C_2 powder was loaded in the glove box. No pressure transmitting medium was used. For the IR experiment, the KBr powder dried by the infrared lamp was introduced into the sample chamber to act as the diluents. The angle dispersive X-ray diffraction (ADXRD) data were collected up to ~40 GPa using a CCD detector calibrated with a CeO_2 standard sample at the 16-ID-B beamline at the Advanced Photon Source (APS), Argonne National Laboratory with transmission geometry. The wavelength of the incident X-ray was 0.4066 Å. The preliminary data reduction was performed using the Dioptas program.[1] In situ Raman spectra up to ~ 40 GPa were measured on a Renishaw inVia spectrometer with a 532 nm laser wavelength. The IR spectra were collected on a Bruker VERTEX 70v with a HYPERION 2000 microscope. A Globar was used as a conventional source. The spectra were collected in a transmission mode in the range of 500-5000 cm^{-1} with a resolution of 2 cm^{-1}. The diamond anvil absorption with the same setting was used as the background.

The impedance spectroscopy was measured by a Solartron 1260 impedance analyzer equipped with a Solartron 1296 dielectric interface. A symmetrical-style DAC was used to generate high pressure and the anvil culet was 300 μm in diameter. A steel supported Boron Nitride (BN) gasket was pre-indented to a thickness of 48 μm and a hole with d = 120 μm was drilled at the center of the indentation to act as the sample chamber. Pt foil with a thickness of fewer than 4 μm was cut to act as electrodes, and integrated as a parallel-plate capacitor. No pressure transmitting medium was used. The frequency range was between 0.1 Hz and 10 MHz and the applied ac voltage was 0.1-1V. The resistivity ρ was calculated by the formula $\rho=Rs/l$, where R (Ω), s (m^2) and l (m) are the resistance, electrode area, and sample thickness, respectively. The pressure was calculated by the

ruby fluorescence in the in situ XRD, Raman, IR, and impedance measurements.[2]

First principle calculations on the structural relaxation and spectrum properties (polarization, IR and Raman spectrum prediction) were carried out with the Density functional theory (DFT) as implemented in the CASTEP code.[3] The norm-conserving pseudopotential[4] was employed with an energy cutoff of 1200 eV of the plane wave basis. The electron-electron exchange interaction was described by the Local-density approximations (LDA) exchange-correlation function of Ceperley and Alder, as parameterized by Perdew and Zunger (CA-PZ).[5,6] A k-point separation of $2\pi\times0.03$ $Å^{-1}$ was assigned to generate the k-point grid using the Monkhorst-Pack grid parameters.[7] The phase of the Li_2C_2-*Cmcm*-armchair is built by replacing the zigzag chain to an armchair chain in the Li_2C_2-*Cmcm*-zigzag phase.[8]

The sample for the Gas Chromatography-Mass Spectrometry (GC-MS) measurement was prepared by the DAC with a diamond culet size of 300 um in diameter. The sample loading method was the same as the one described above. The Li_2C_2 was kept at 40 GPa for 10 mins and seven samples were collected for one GC-MS measurement. The pressure was calculated by the ruby fluorescence.[2] The samples were sealed in a GC bottle in the glove box and a drop of deionized water was injected into the bottle. The generated gas was drawn into a syringe and injected into the GC. The analytes were determined using a Thermo Scientific Q Exactive GC Orbitrap (QE-GC) system, equipped with an electronic impact (EI) ionization source. The samples were separated by a Thermo Scientific TRACE 1310 GC, furnished with a TG-5SilMS capillary column (30m × 0.25 mm i.d., 0.25 μm film thickness), and helium (99.999%) was used as carrier gas at a constant flow of 1.0 mL/min. The 0.5 mL gas sample was injected manually in the split mode of 20:1 (v/v) at 250 °C. The GC oven was programmed from 30 °C (maintained for 2 mins) at a rate of 20°C /min to 150 °C (maintained for 2 mins). The temperature of the transfer line was 280 °C. The Q Exactive GC system was tuned and calibrated by a calibration solution to achieve a mass accuracy of < 1 ppm root mean square (RMS). The system was operated in the EI mode at 70 eV using full scan at a resolving power of 60k (m/z 200). Scan spectra were recorded in the mass range m/z 50-500. The temperature of ion source was set at 250°C. The data were acquired using the Thermo Scientific TraceFinder 4.0 software. The components were recognized using Thermo Scientific deconvolution software in combination with the National Institute of Standards and Technology (NIST) 2014 and Wiley9 Data library.[9]

2. Supplementary Figures S1 to S5 and Table S1

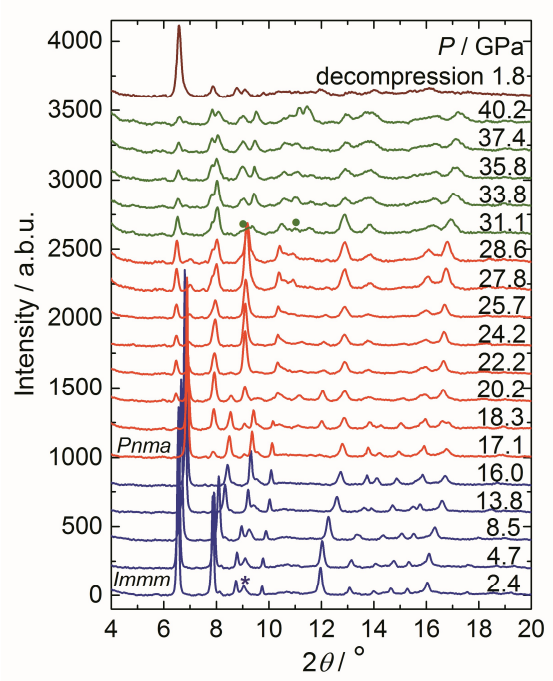

Figure S1. The selected X-ray diffraction patterns of Li_2C_2 under high pressure. The asterisk and dots represent the peak from Li_2O and the new peaks observed at 31.1 GPa, respectively.

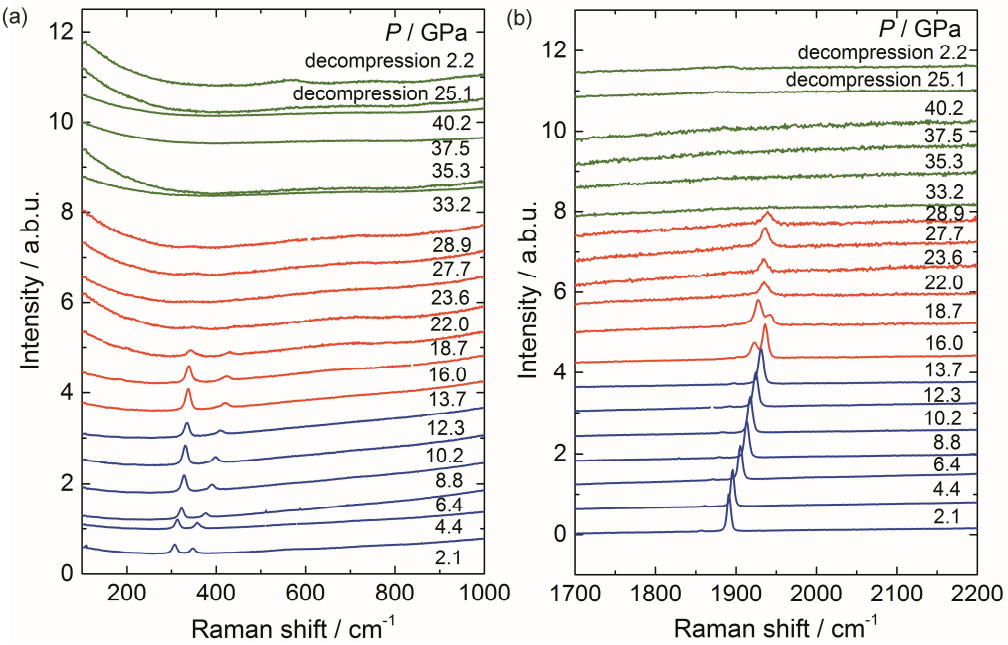

Figure S2. The selected Raman spectra of Li_2C_2 under high pressure; (a) the C_2 libration mode and (b) the C≡C stretching mode.

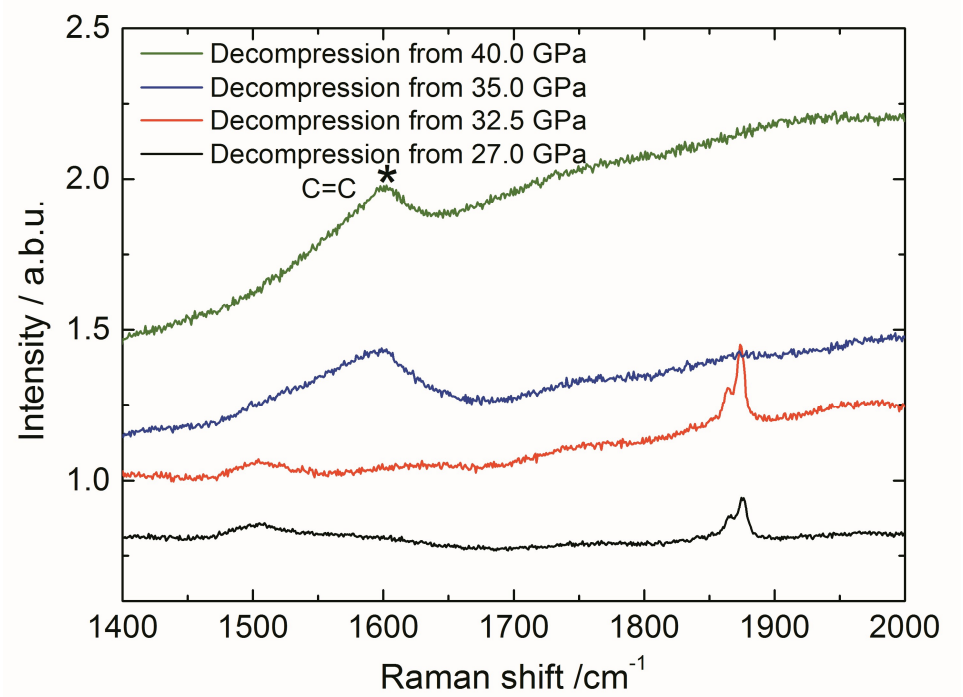

Figure S3. The Raman spectra of the sample recovered from 27 GPa, 32.5 GPa, 35 GPa, and 40 GPa at ambient pressure.

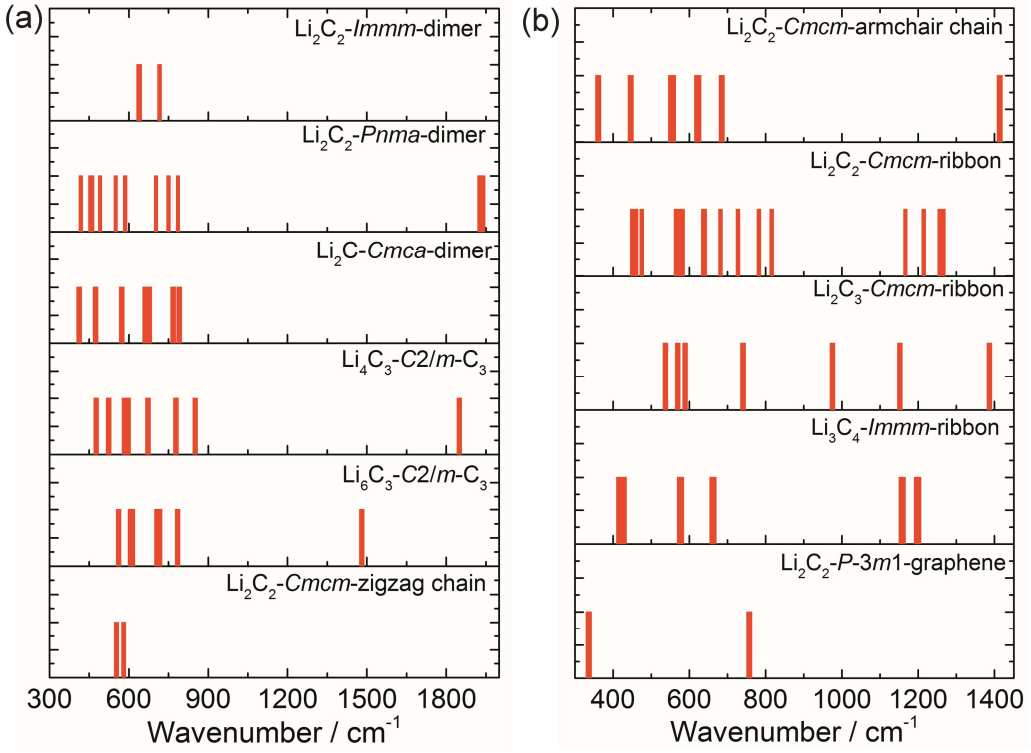

Figure S4. (a) and (b) the calculated IR modes (27 GPa) of all the phases that were predicted to be stable from 0-40 GPa.[8,10-11]

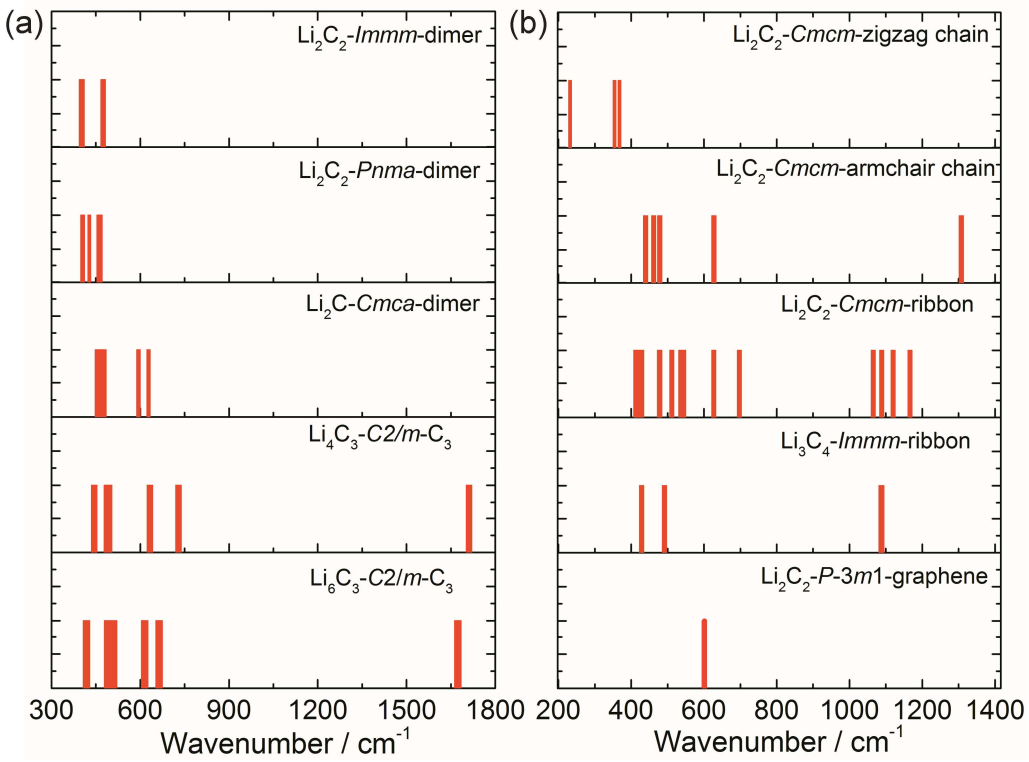

Figure S5. (a) and (b) the calculated IR modes (1 GPa) of all the phases that were predicted to be stable from 0-40 GPa.[8,10-11]

Table S1. Selected high-resolution mass spectrum results obtained by deconvolution.

No.	RT(min)	Formula	m/z(Da)	Δppm	Percent%	Name(NIST and Wiley)	Fitting score
1	2.88	C_6H_8	80.06207	0.227	12.9	1,3-Cyclohexadiene	93
						2-Hexen-4-yne	92
						1,3-Cyclopentadiene, 5-methyl-	92
2	3.00	C_6H_8	80.06205	-0.18	5.9	Allylidenecyclopropane	95
						3-Methylenecyclopentene	93
						2-Hexen-4-yne	92
8	4.20	C_8H_8	104.06210	0.463	0.5	4-Ethynyl-1-vinylcyclobutene	90
9	4.22	C_7H_{12}	96.09341	0.604	0.4	Cyclohexene, 4-methyl-	91
10	4.41	C_8H_{10}	106.07774	0.359	4.8	Benzene, ethyl-	98
						1-allyl-2-cyclopropylacetylene	95
						Benzene, 1,2-dimethyl-	95
11	4.57	C_8H_8	104.06201	-0.402	4.6	4-Ethynyl-1-vinylcyclobutene	92
						Cyclooctatetraene	92
						Styrene	92
13	4.93	C_8H_8	104.06206	0.078	0.5	4-Ethynyl-1-vinylcyclobutene	91
14	5.02	C_8H_8	104.06205	-0.018	2.8	Styrene	95
						1,3,5,7-Cyclooctatetraene	95
						Benzocyclobutane	95
15	5.04	C_8H_{10}	106.07776	0.548	0.9	Ethylbenzene	92
						Benzene, 1,3-dimethyl-	91
						Benzene, 1,2-dimethyl-	91
16	5.21	C_8H_{10}	106.07773	0.265	1.5	Bicyclo[4.2.0]octa-1(8),2-diene	90
18	5.35	C_8H_6	102.04643	0.277	1.2	1-Phenylethyne	94

						1,4-diethynylcyclobutene	94
19	5.51	C_8H_8	104.06205	-0.018	9.1	Tetracyclo[3.3.0.0(2,4).0(3,6)]oct-7-ene	93
						4-Ethynyl-1-vinylcyclobutene	91
						Styrene	92
22	5.79	C_8H_8	104.06203	-0.210	3.7	Styrene	95
						1,3,5,7-Cyclooctatetraene	95
						Benzocyclobutane	94
23	5.80	C_8H_{10}	106.07774	.0.359	1.1	Ethylbenzol	96
						Cyclobutene, 2-propenylidene-	94
26	5.97	C_8H_8	104.06203	-0.210	1.9	Styrene	90
						Tetracyclo[3.3.0.0(2,4).0(3,6)]oct-7-ene	90
29	6.28	C_8H_8	104.06207	0.175	1.0	Styrene	92
						1-Ethynyl-2-methyl-3-methylene-1-cyclobutene	91
30	6.37	C_8H_8	104.06207	0.175	1.3	Tetracyclo[3.3.0.0(2,4).0(3,6)]oct-7-ene	94
						Styrene	93
						1,3,5,7-Cyclooctatetraene	93

3. Supplementary References

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