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Supplementary Electronic Information

Pressure induced polymerization of acetylide anions in CaC_2 and 10^7 folds enhancement of electrical conductivity

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Materials and Methods

Sample Preparation. Both commercial sample and lab-synthesized sample were investigated in the research. For the commercial sample, a chunk of CaC_2 (Sigma-Aldrich, 98%) was ground to a fine powder in an agate mortar in a glove box (with moisture and oxygen content less than 10 ppm) for 30 min and the final powder was used in the experiments. It is mainly composed of CaC_2-I with minor impurities of CaO and CaC_2-II, similar as that reported in the literature.[1,2] CaO has phase transitions far above the pressure range presented in our research,[3] so it does not affect the investigation and can be used as a pressure marker in the diffraction experiment. It is difficult to avoid CaC_2-II, and it was identified in almost all of the related literatures to our knowledge,[1,2,4-6]as well as in our lab-synthesized sample. Our lab-synthesized sample was prepared by solid state reaction of stoichiometric Ca and graphite powder, which were sealed inside an evacuated tantalum tube in a glove box and then sealed inside an evacuated quartz tube. The sealed tube was heated at 1200° C for 12 hours. The sample is mainly composed of CaC_2-I with minor amount of CaC_2-II and CaO (Fig. S10). No significant difference between these two samples is observed in the X-ray diffraction (XRD) and Raman spectroscopy. Lab synthesized sample is used in Raman, infrared(IR), XRD and Gas Chromatography-Mass Spectrometry (GC-MS) experiment, and commercial sample is used in the neutron and impedance experiment.

Sample preparation for neutron pair distribution function (PDF) and GC-MS measurements. The CaC_2 samples recovered from high pressure are prepared at the Spallation Neutrons and Pressure Diffractometer (SNAP) beamline, at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) as well as in Center for High Pressure Science and Technology Advanced Research (HPSTAR). A VX3 Paris-Edinburgh cell equipped with double toroidal polycrystalline diamond anvils was used for applying pressure. The CaC_2 pellet was prepared in a glove box, loaded into the stainless steel gasket and sealed in several seconds. The series of samples for the PDF measurements were kept at the oil pressure of 400 bar, 600 bar, 800 bar, 1000 bar, 1200 bar, 1400 bar, 1650 bar and 1900 bar for 4 hours, which corresponds to 6 GPa, 8 GPa, 11 GPa, 14 GPa, 17 GPa, 20 GPa, 24 GPa, and 28 GPa respectively. The sample for the GC-MS was kept at approximately 26 GPa at the oil pressure of 1800 bar. All the pressures are estimated from pressure-load curves calibrated by our neutron diffraction results. For the samples synthesized by the diamond anvil cell (DAC) for the GC-MS measurements, CaC_2 raw materials were loaded in the glove box and the DAC with d_{culet} = 400 μm culet is used to apply pressure. The samples are kept at 30 GPa for 10 mins and five samples are collected for one GC-MS measurements. The pressure is calculated by the Ruby fluorescence.[7]

***In situ* XRD.** For the *in situ* high pressure XRD experiments, a symmetrical-style DAC fitted with diamonds polished to a culet diameter of d_{culet} = 400 μm was used to apply pressure. T301 stainless steel gaskets were pre-indented to a thickness of ~30 μm, and holes with diameter d = 200 μm were drilled in the center of the indentation to serve as the sample chambers. No pressure medium was used. The angle dispersive X-ray diffraction (ADXRD) data were collected up to ~30 GPa at the 16-BM-D beamline at the Advanced Photon Source (APS), Argonne National Laboratory with the transmission geometry. The monochromatic incident X-ray with a wavelength of 0.4246 Å was focused to approximately 10 um (Full-Width-Half-Maximum). The preliminary data reduction was performed using the Fit2D program.[8]

***In situ* Neutron Diffraction.** *In situ* neutron diffraction patterns were collected at the Spallation Neutrons and Pressure Diffractometer (SNAP) beamline, at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). A VX3 Paris-Edinburgh cell equipped with sintered diamond double toroidal anvils with a Titanium-Zirconium (TiZr) alloy gasket was used for applying pressure. The CaC_2 pellet was prepared in a glove box. It was loaded into the gasket and sealed in several seconds. No pressure medium was used. The pressure was calibrated with the equation of state of CaO.[3]

***In situ* Raman measurement.** *In situ* Raman spectroscopy under high pressure was measured on a Renishaw-inVia spectrometer with laser wavelength 488 nm. A symmetrical-style DAC fitted with diamonds with d_{culet} = 400 μm was used for applying pressure. A steel gasket pre-indented to a thickness of ~30 μm was used for sample chamber. No pressure medium was used. Ruby fluorescence was used for pressure calibration.[7]

***In situ* IR measurement.** *In situ* IR absorption experiment was measured on a Bruker 70V spectrometer equipped with a Hyperion microscope. The setting of the DAC is same as that used in Raman experiment except that type IIA diamonds are used.

Neutron PDF Measurements. The neutron PDF data of the samples recovered from various pressures were collected at the Nanoscale-Ordered Materials Diffractometer (NOMAD), SNS, ORNL. The recovered samples were grounded in the glove box, loaded in 2 mm quartz capillaries and sealed with epoxy glue for measurement. Neutron scattering up to $Q_{max} = 2\pi/d = 31.41$ Å^{-1} was used for PDF analysis, and the data were convoluted with the Lorch function to reduce the effect of fringes. The details of the data processing can be found on the website of NOMAD.

Electrical Resistance Measurement. *In situ* impedance spectroscopy was performed on an ac impedance spectroscopy system based on Zahner analyzer IM6.[9,10]A symmetrical-style DAC fitted with diamonds with d_{culet} = 500 μm was used for applying pressure. A steel-supported BN gasket was used that was pre-indented to a thickness of ~40 μm, and a hole with a diameter of ~200 μm was drilled in the indentation centre. Pt foils were cut to act as electrodes for the Van der Pauw setting. The applied ac voltage was 50 mV, in the frequency range 0.1 Hz-1 MHz. The intercept of low frequency on the *Z*' axis was recognized as the resistance ($R_{AB,\ CD,}$ $R_{AD,\ CB}$ as defined in the literature 11), and the resistivity is calculated by the equation $\exp(-\pi R_{AB,CD}\ d/\rho)+\exp(-\pi R_{AD,CB}\ d/\rho) = 1$,[11] where d is the thickness of the sample and ρ is the resistivity. No pressure medium was used. Ruby fluorescence was used for pressure calibration.[7]

Theoretical Calculation. To predict the structure and electronic properties of CaC_2 under external pressure, first-principle calculations based on density functional theory (DFT) were performed. The Cambridge Serial Total Energy Package (CASTEP) software was used.[12] During the calculation, the Broyden-Fletcher-Goldfarb-Shannon (BFGS) geometry optimization were performed on the phase I (*I*4/*mmm*) and phase VI (*I*2/*m*) CaC_2 models under different hydrostatic pressures, and the band structure calculations were followed. The plane-wave basis set was chosen for the expansion of valance-electron wave functions based on local density approximation (LDA), and the ultrasoft pseudopotentials constructed from the CASTEP database were selected. The k-point set was set as a Monkhorst-Pack grid with a reciprocal spacing of ~0.04 $Å^{-1}$. The energy cut-off of the plane-wave basis set was selected as 600 eV. The criterion for self-consistency was eigen-energy convergence within 10^{-8} eV/atom. For the geometry optimization, the criteria are selected as eigen-energy convergence within 10^{-7} eV/atom, net force convergence of atoms within 1×10^{-3} eV/Å, displacement convergence of atoms within 10^{-4} Å.

The phase transition pathway was explored by metadynamic method[13-15]in the supercell of 64 Ca atoms and 128 C atoms. CaC_2-VI structure was relaxed at 30 GPa as initial state and the simulation environment was set at 30 GPa and 300 K. The length of simulation was 500 fs for every meta-step and the whole procedure was made of more than 200 meta-steps (100 ps). The molecular dynamic calculation were performed using DFT within the Perdew-Burke-Ernzerhof (PBE) functional[16] in the framework of the all-electron projector augmented wave (PAW) method[17] as implemented in the VASP code.[18]

GC-MS measurements. The synthetic methods of the sample obtained from the PE cell and DAC are described above and they follow the same procedure to have the GC-MS measurement. The samples were sealed in the GC bottle in the glove box and a drop of deionized water was injected into the bottle. The generated gas was inhaled into a syringe and injected into the GC. The instrument used is an Agilent 7890A GC coupled to an Agilent accurate-mass 7200 quadrupole-time-of-flight-mass spectrometer (QTOF-MS) (Santa Clara, CA, USA), equipped with an electronic impact (EI) ionization source. Samples in gas phase was separated in a DB-5MS UI 30 m × 0.25 mm i.d., 0.25 μm film thickness capillary column and helium (99.999%) was used as carrier gas at a constant flow of 1.0 mL min^{-1}. 0.5 mL sample volume was injected manually in split mode (split ratio 50:1) at 250 °C. The GC oven was programmed from 30 °C (hold time 2 min) at 20 °C min^{-1} to 150 °C (hold time 2 min) and the transfer line was set at 250 °C. The 7200 QTOF detector was operated in single MS scan mode by EI ionization at 70 eV. The ion source and quadrupole temperatures were set at 250 and 150 °C, respectively. The acquisition rate was 5 spectra/s in 4 GHz high resolution mode and the mass resolution was 13000 at m/z 263.9866 (full width half maximum, FWHM). Mass-spectrometric grade perfluorotributylamine (PFTBA) was used for mass calibration. The scan spectra were recorded in the mass range m/z 20-500. Agilent MassHunter GC/MS Acquisition Software (Version: B.07.03) was used for the data acquisition. All qualitative data processing was performed using

Agilent MassHunter Qualitative Analysis Workstation Software (Version: B.07.00) and Wiley Registry 10th Edition/NIST 2014 EI library were used for the spectral library search.

GC-MS experiment for identifying benzene. This experiment was performed on an Agilent 7890B GC coupled to an Agilent 5977A mass spectrometer (Santa Clara, CA, USA), equipped with an electronic impact (EI) ionization source. The CaC_2 recovered from 26 GPa was sealed in the GC- bottle in the glove box and a drop of deionized water was injected into the bottle. The generated gas was inhaled into a syringe and injected into the GC. 0.5 mL of sample was injected manually in pulsed splitless mode at 250 °C and separated in a HP-5MS UI 30 m × 0.25 mm i.d., 0.25 μm film thickness capillary column. Helium (99.999%) was used as carrier gas at a constant flow of 1.0 mL min^{-1}. The GC oven was programmed from 30 °C (hold time 2 min) at 20 °C min^{-1} to 150 °C (hold time 2 min) and the transfer line was set at 280 °C. The 5977A mass spectrometer was operated in full scan mode by EI ionization at 70 eV. The ion source and quadrupole temperatures were set at 230 and 150 °C, respectively. Scan spectra were recorded in the mass range m/z 10-200. For the standard sample benzene, the benzene vapor was inhaled into a syringe and injected into the GC. All the measurement methods are same with the one described above. Agilent MassHunter GC/MS Acquisition Software (Version: B.07.00) was used for the data acquisition. All qualitative data processing was performed using Agilent MSD ChemStation Software (Version: F.01.00.1903).

Quantitative experiments. The mixtures with volume ratio 1:100, 1:500 and 1:200 ($V_{benzene}$:$V_{acetylene}$) are used as the standard samples. The standard benzene/acetylene samples are prepared by quantitatively injecting benzene into acetylene containers. The quantitative experiment was performed on an Agilent 7890A GC/7200 QTOF-MS, equipped with a DB-5MS UI 30 m × 0.25 mm i.d., 0.25 μm film thickness capillary columns and operated in electron-impact (EI, 70 eV) mode. Helium (99.999%) was used as carrier gas at a constant flow of 1.0 mL min^{-1}. 0.002 mL sample was injected manually in split mode (split ratio 500:1) at 250 °C. The GC oven was programmed as follows: 30 °C (2 min), ramped at 20 °C min^{-1} to 150 °C (2 min). The temperature of transfer line was kept at 250 °C. The 7200 QTOF was operated in the extended dynamic range 2 GHz mode and the acquisition rate was 5.0 spectra/s. The source and quadrupole temperatures were set at 250 °C and 150 °C, respectively. The QTOF detector was operated in the single MS mode and the scan spectra were recorded in the m/z range from 20-500 units. The TOF mass analyzer was calibrated with a commercial solution of perfluorotributylamine (PFTBA). Agilent MassHunter GC/MS Acquisition Software (Version: B.07.03) was used for the data acquisition. All quantitative data processing was performed using Agilent MassHunter Quantitative Analysis Workstation Software (Version: B.07.00)

Table S1. Result of Rietveld refinement of the CaC_2 structure under external pressure

Pressure (GPa)	6.02	8.53	10.72	13.81	18.82
space group (number)	*I*4/*mmm* (139)				
a (Å)	3.76933(12)	3.72455(15)	3.68853(15)	3.64300(15)	3.5822(2)
c (Å)	6.272(4)	6.214(4)	6.203*	6.166*	6.121*
V ($Å^3$)	89.11(6)	86.20(6)	84.39(4)	83.44(4)	78.54(5)
Z	2				
density ($g \cdot cm^{-3}$)	2.39	2.47	2.52	2.55	2.71
R_p	0.0112	0.0114	0.0112	0.0103	0.0100
R_{wp}	0.0142	0.0155	0.144	0.0130	0.0123
R_{exp}	0.0065	0.0063	0.0064	0.0057	0.0053
GOF	2.18	2.45	2.24	2.29	2.31
z(C)	0.5988(4)	0.5999(5)	0.6025(5)	0.6001(6)	0.5900(12)
u(C)	0.0214(7)	0.0162(6)	0.0185(5)	0.0163(8)	0.0102(9)

*c-axis fixed at the value determined by XRD. C(0, 0, *z*), Ca(0, 0, 0), *u*(Ca) = 0.01

Table S2. Cell parameters and band gap of optimized CaC_2-I and CaC_2-VI.

P (GPa)	0	2	6	9	10	11	12	14	19
CaC_2-I (*I*4/*mmm*)									
a (Å)	3.7596	3.7165	3.6455	3.6014	3.5880	3.5752	3.5629	3.5396	3.4863
c (Å)	6.2737	6.2389	6.1763	6.1345	6.1213	6.1085	6.0961	6.0723	6.0171
V ($Å^3$)	88.68	86.17	82.08	79.57	78.81	78.08	77.38	76.08	73.13
Band gap(eV)	0.88	0.75	0.52	0.36	0.31	0.27	0.22	0.13	0
CaC_2-VI (in *I*2/*m*, for comparison with CaC_2-I)									
a (Å)	3.7967	3.7475	3.6708	3.6247	3.6105	3.5970	3.5840	3.5589	3.4965
b (Å)	3.7602	3.7178	3.6486	3.6065	3.5943	3.5827	3.5717	3.5519	3.5177
c (Å)	6.2837	6.2493	6.1882	6.1490	6.1370	6.1253	6.1140	6.0935	6.0502
β(°)	98.28	98.16	98.50	99.17	99.46	99.77	100.11	100.90	103.55
V ($Å^3$)	88.77	86.18	81.97	79.35	78.56	77.79	77.05	75.64	72.34
Band gap (eV)	1.30	1.14	0.90	0.76	0.72	0.68	0.65	0.58	0.45
E_{VI} - E_I *(eV, per unit cell)*	-0.010	-0.010	-0.011	-0.014	-0.015	-0.017	-0.019	-0.024	-0.043

Table S3. Identification of the peaks in the total ion chromatograms (TIC) of the gas phase of hydrolyzed CaC_2 recovered from 26 GPa.

Retention time (min)	Formula & Ion Species	*m/z*	*m/z* (Calculated)	Diff (ppm)[a]	Abundance %
1.275	C_3H_4	40.0311	40.0308	-8.76	97.58
1.591	C_5H_6	66.046	66.0464	6.17	100
1.658	C_5H_6	66.0461	66.0464	3.83	100
1.698	C_5H_4	64.0312	64.0308	-6.53	94.7
1.728	C_5H_6	66.0462	66.0464	2.75	100
1.901	C_5H_4	64.0309	64.0308	-3.04	100
2.154	$[C_6H_7]^+$	79.0539	79.0542	4.06	100
2.273[b]	C_5H_4	64.0307	64.0308	1.11	100
2.288[b]	C_6H_8	80.0609	80.0621	14.64	29.7
2.347	C_6H_6	78.0451	78.0464	16.69	23.92
2.397	$[C_6H_7]^+$	79.0537	79.0542	7.18	100
2.464	C_6H_8	80.0591	80.0621	36.95	12.16
2.497	C_6H_4	76.0311	76.0308	-4.72	100
2.521[c]	C_6H_8	80.0612	80.0621	10.68	53.88
2.539[c]	C_6H_6	78.0459	78.0464	6.89	100
2.577	C_6H_8	80.0609	80.0621	14.83	40.09
2.64	C_6H_6	78.0465	78.0464	-1.3	100
2.684	C_6H_4	76.0303	76.0308	5.42	100
2.757	C_6H_6	78.0458	78.0464	8.2	85.91
2.987	C_6H_8	80.0611	80.0621	12.47	45.11
3.077	C_6H_6	78.0465	78.0464	-0.65	100
3.273[d]	$[C_6H_5]^+$	77.0396	77.0386	-13.17	69.52
3.384[d]	C_6H_6	78.0475	78.0464	-13.55	59.53
3.45	C_6H_8	80.0613	80.0621	9.94	100
3.826	C_6H_6	78.046	78.0464	5.24	100
4.572	C_6H_6	78.046	78.0464	4.98	100
4.799	C_8H_7	103.0537	103.0542	5.31	100

[a] The mass deviation between the calculated molecular weight and the measured one.

[b] The coelution peaks of the fraction corresponding to the peak whose retention time is 2.274 min.

[c] The coelution peaks of the fraction corresponding to the peak whose retention time is 2.534 min.
[d] The coelution peaks of the fraction corresponding to the peak whose retention time is 3.283 min.

Table S4. Identification of the peaks in the total ion chromatograms (TIC) of the liquid phase of hydrolyzed CaC_2 recovered from 26 GPa.

Retention time (min)	Formula & Ion Species	*m/z*	*m/z* (Calculated)	Diff (ppm)[a]	Abundance %
15.541	$C_{12}H_{10}$	154.0779	154.0777	-1.17	100
15.711	$C_{12}H_{10}$	154.0771	154.0777	3.73	24.49
15.978	$C_{12}H_{14}$	158.1097	158.1090	-4.33	52.69
16.022	$C_{12}H_{10}$	154.0771	154.0777	3.92	18.18
17.175	$C_{12}H_{10}$	154.0781	154.0777	-2.67	100
17.927	$C_{12}H_{12}$	156.0937	156.0934	-2.4	76.42
18.121	$C_{12}H_{10}$	154.0780	154.0777	-1.67	100
18.228	$C_{12}H_{10}$	154.0780	154.0777	-1.69	100
19.926	$C_{12}H_{10}$	154.0775	154.0777	1.23	65.09
20.136	$C_{12}H_{10}$	154.0776	154.0777	0.72	60.51
20.207	$C_{12}H_{10}$	154.0778	154.0777	-0.76	71.33
20.845	$C_{12}H_{10}$	154.0778	154.0777	-0.8	74.69

[a] The mass deviation between the calculated molecular weight and the measured one.

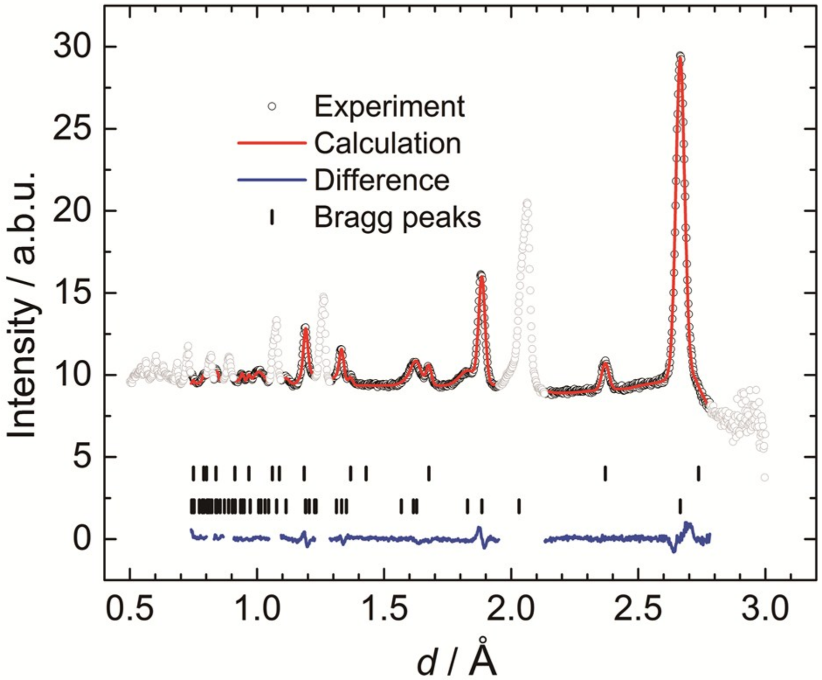

Fig.S1. Plot of Rietveld refinement of CaC_2 under 6 GPa. The circles are experimental data, with the peaks from diamond anvils are masked and shown in grey, the red lines are the calculated data, and the blue lines are the difference. The vertical bars are the Bragg positions of CaO (upper) and CaC_2 (lower).

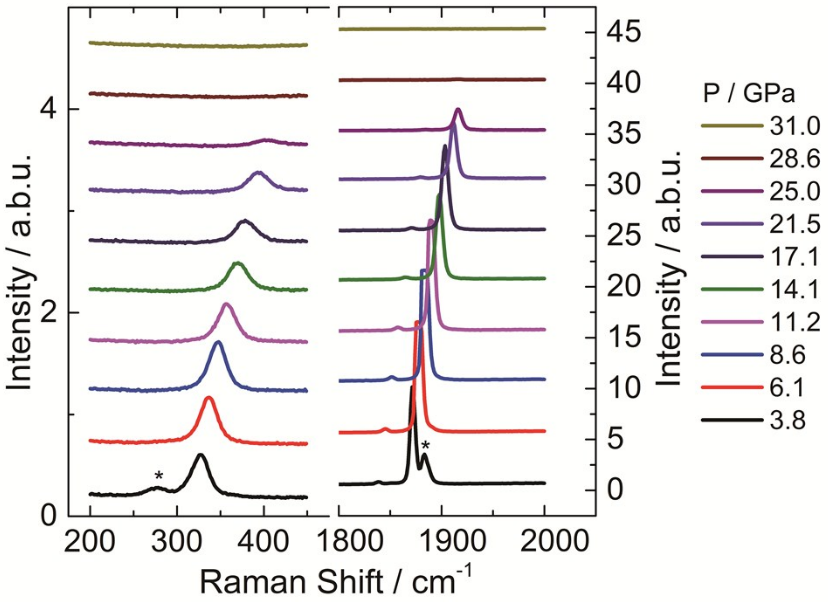

Fig.S2. Selected Raman peaks of the C-C stretching and libration modes of CaC_2 under high pressure. The peaks marked by star are from CaC_2-II, a phase that cannot be avoided during the synthesis.

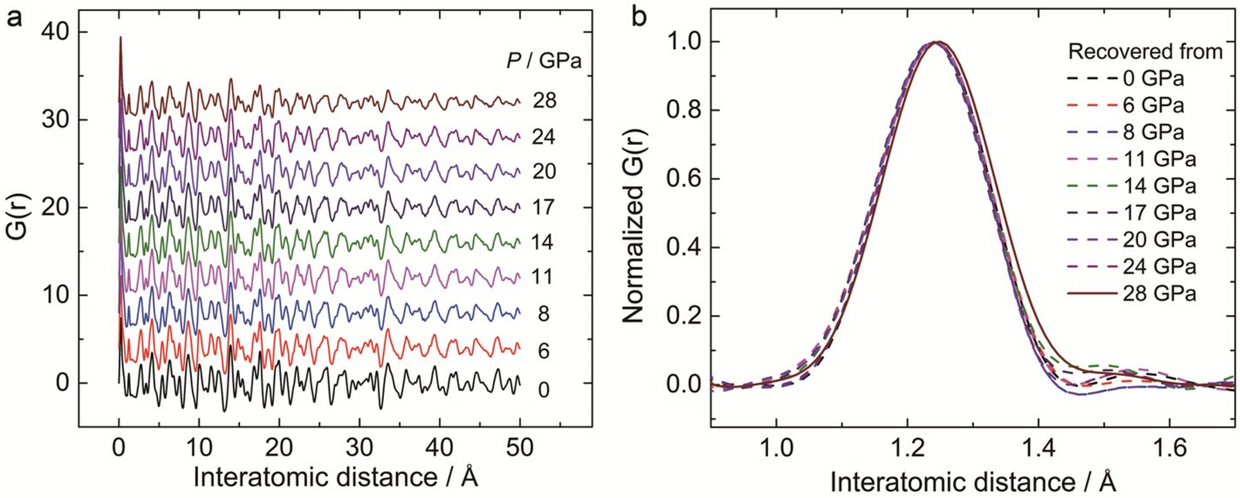

Fig.S3. (a) Neutron pair distribution function (PDF) (G(r)) patterns of recovered CaC_2. (b) Normalized first peak after background subtraction.

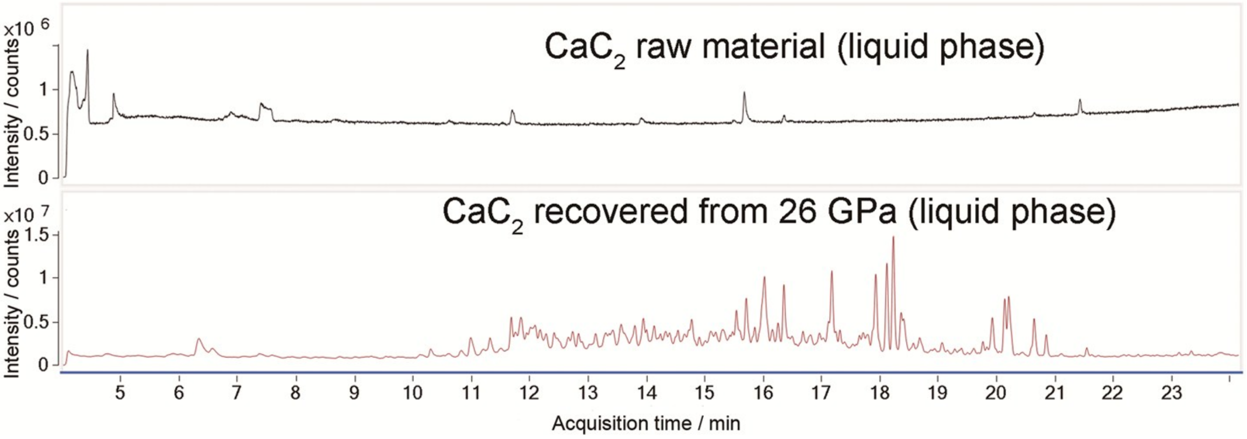

Fig.S4. Total ion chromatograms (TIC) of hydrolyzed product (in the liquid phase) of CaC$_2$(upper) and CaC$_2$ recovered from 26 GPa. The peaks in the plot of CaC$_2$ raw materials result from the silanes of the GC-column.

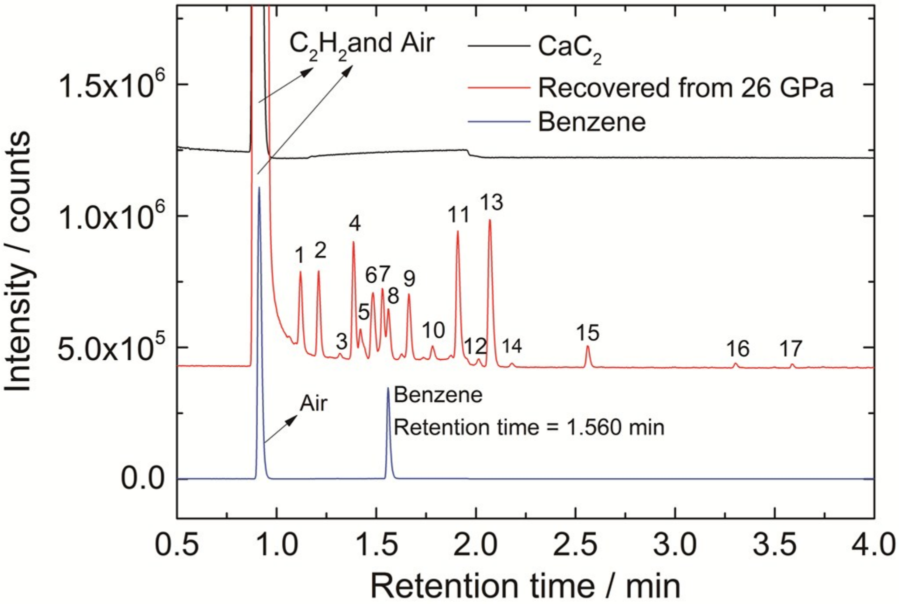

Fig.S5. Total ion chromatograms (TIC) of hydrolyzed product of CaC$_2$ and CaC$_2$ recovered from 26 GPa, and the standard sample benzene.

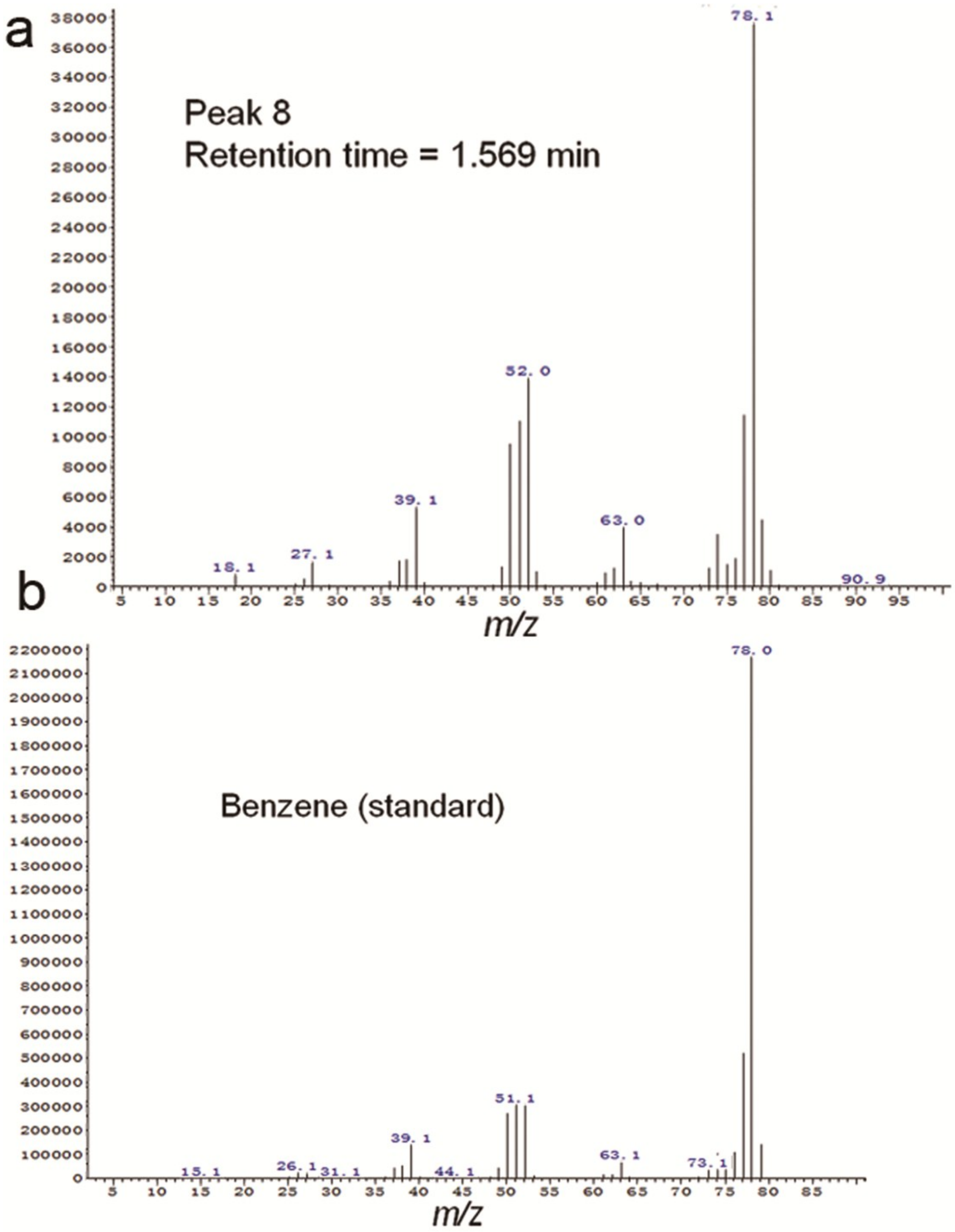

Fig.S6. The mass spectra of peak 8 in Fig.S5(a) and the standard sample benzene (b).

The high-resolution quadrupole-time of flight (Q-TOF) data shows that nine isomers with the molecular formula C_6H_6 were present in the product of CaC_2 recovered from 26 GPa after reacting with water (Fig.7). The GC-MS with unit mass resolution was employed to confirm the presence of benzene. The TIC plot is similar with the Q-TOF result (Fig.S5). As shown in Fig. S5 and S6, the fraction corresponding to peak 8 has the same retention time of the chromatogram and mass spectra as benzene. That means the cyclic molecules benzene is one of the product of CaC_2 recovered from 26 GPa after reacting with water. That may result from cyclic polycarbide anions precursor.

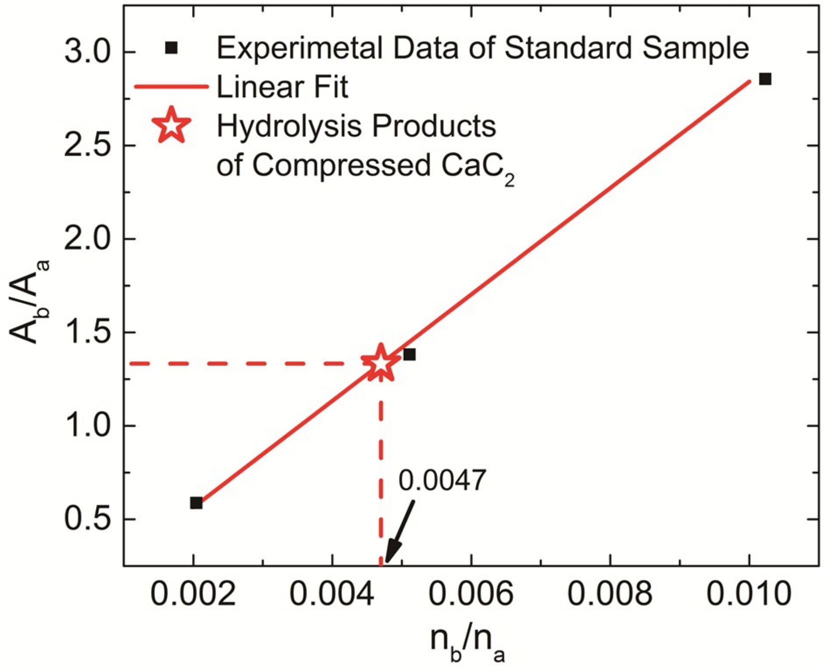

Fig.S7. Working curve for quantitative analysis of benzene and acetylene. n_b/n_a stands for the molar ratio of benzene and acetylene, and A_b/A_a stands for the ratio of their peak areas in the TIC.

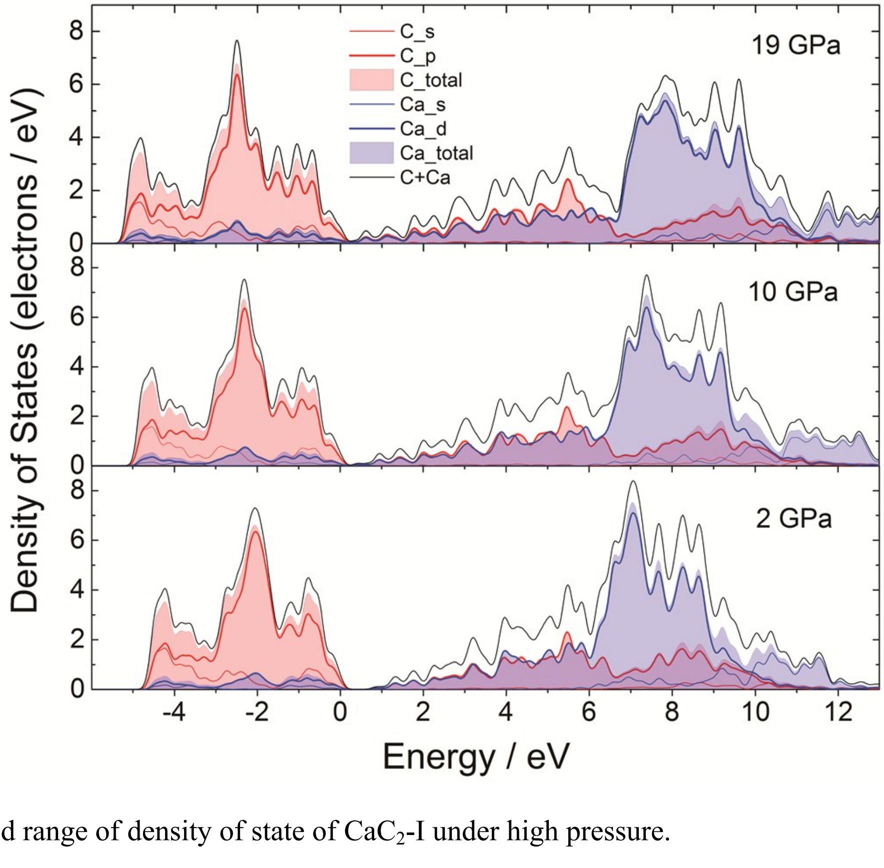

Fig.S8. Selected range of density of state of CaC$_2$-I under high pressure.

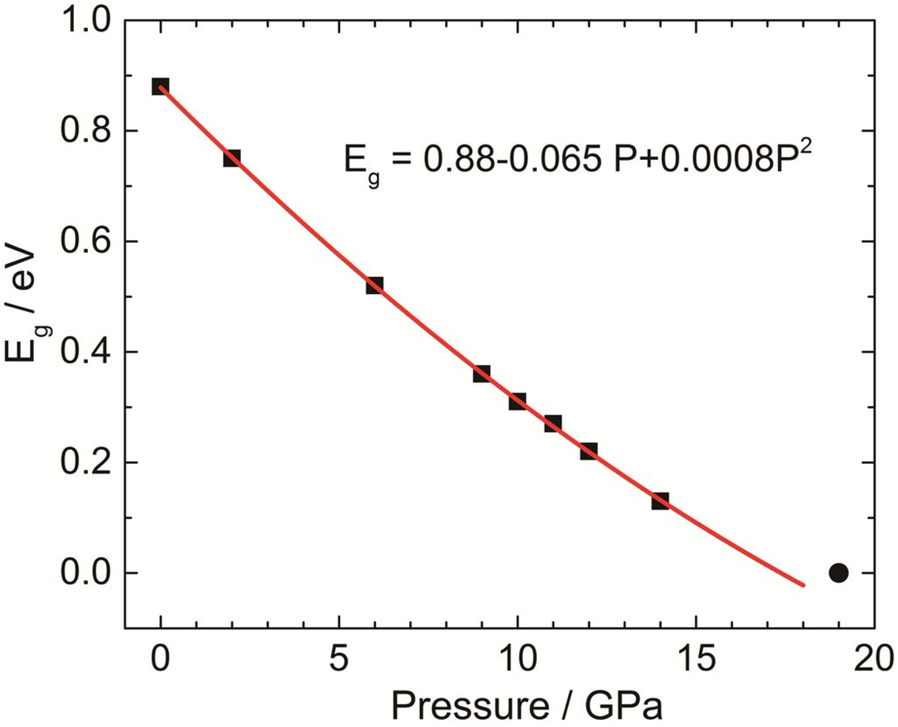

Fig.S9. Band gap of CaC_2 -I under high pressure. The red line is fitted polynomial as guide for eyes.

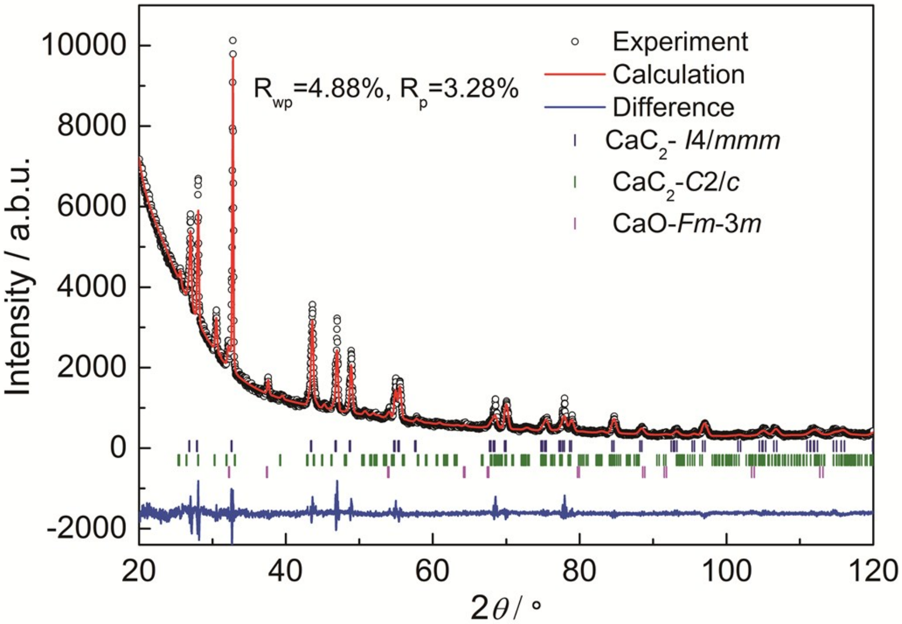

Fig.S10. Rietveld refinement of synthesized CaC_2.

References:

1 J. Nylen, S. Konar, P. Lazor, D. Benson and U. Haussermann, *J. Chem. Phys.* 2012, **137**, 224507.

2 I. Efthimiopoulos, G. V. Vajenine, E. Stavrou, K. Syassen, St. Liebig, U. Ruschewitz and M. Hanfland, *Acta Cryst.* 2010, **A66**, s197.

3 J. F. Mammone, H. K. Mao and P. M. Bell, *Geophys. Res. Lett.* 1981, **8**, 140-142.

4 N. -G. Vannerberg, *Acta Chem. Scand.*1962, **16**, 1212-1220.

5 N. -G. Vannerberg, *Acta Chem. Scand.*1961, **15**, 769-774.

6 M. Knapp, and U. Ruschewitz, *Chem. -Eur. J.*2001, **7**, 874-880.

7 H.-k.Mao,J.Xu, and P. M. Bell, *J. Geophys. Res.-Sol. Ea.*1986, **91**, 4673.

8 A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, *High Pressure Res.* 1996, **14**, 235-248.

9 K. Li, H. Zheng, I. N. Ivanov, M. Guthrie, Y. Xiao, W. Yang, C. A. Tulk, Y. Zhao, and H.-k. Mao, *J. Phys. Chem. C,* 2013, **117**, 24174−24180.

10 I. Ivanov, et al. Carbon Nanotube Assemblies for Transparent Conducting Electrodes. Nanoscale Applications for Information and Energy Systems. Springer Press, New York, p 117-148, 2013.

11 L. J. van der Pauw, *Philips Res. Rep.,*1958, **13**, 1-9.

12 M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *Phys. :Condens. Matter*, 2002, **14**, 2717-2744.

13 R. Martonak, A. Laio and M. Parrinello, *Phys. Rev. Lett.* 2003, **90**, 075503

14 R. Martonak, A. Laio, M. Bernasconi, C. Ceriani, P. Raiteri, F. Zipoli and M. Parrinello, *Zeitschrift f. Kristallogr.* 2005, **220**, 489.

15 R. Martonak, D. Donadio, A. R. Oganov and M. Parrinello, *Nat. Mat.* 2006, **5**, 623.

16 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.

17 P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.

18 G. Kresse and J. Furthmueller, *Comput. Mat. Sci.* 1996, **6**, 15-50.