

## Supporting Information

### **Multiple responses of 1,6-Diphenyl-1,3,5-hexatriene to mechanical stimulation: emission enhancement, piezochromism and negative linear compressibility**

*Zhiyuan Fu,<sup>a</sup> Zhiqiang Yang,<sup>b</sup> Xinyi Yang,<sup>a</sup> Kai Wang,<sup>a,c\*</sup> Bo Zou<sup>a\*</sup>*

- a. State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, P. R. China. Email: [kaiwang@jlu.edu.cn](mailto:kaiwang@jlu.edu.cn); [zoubo@jlu.edu.cn](mailto:zoubo@jlu.edu.cn).
- b. State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
- c. Shandong Key Laboratory of Optical Communication Science and Technology, School of Physics Science and Information Technology, Liaocheng University, Liaocheng 252000, P. R. China.

Email: [kaiwang@jlu.edu.cn](mailto:kaiwang@jlu.edu.cn); [zoubo@jlu.edu.cn](mailto:zoubo@jlu.edu.cn)

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## Experimental Section

**Sample Preparation and High-Pressure Generation:** 1,6-Diphenyl-1,3,5-hexatriene was purchased from Sigma-Aldrich (1,6-Diphenyl-1,3,5-hexatriene, D208000), trans-Stilbene and trans,trans-1,4-Diphenyl-1,3-butadiene are purchased from Tokyo Chemical Industry (TCI, S0090, D0879) and used directly without purification. The high-pressure experiments were performed by the DAC. The sample was placed in the T301 gasket hole with a diameter of 150  $\mu\text{m}$  and a thickness of 45  $\mu\text{m}$ . And a small ruby ball was placed next to the sample for in-situ pressure calibration. In the high-pressure PL and ADXRD experiments, silicone oil (Aldrich) was used as the pressure-transition medium (PTM). KBr was used as the PTM in IR experiments.

**Optical Measurements:** In-situ high-pressure PL and absorption photos of the samples were shot by Canon Eos 5D mark II equipped with Nikon Eclipse TI-U microscope. The absorption spectra light source adopted deuterium-halogen light source, and the PL excitation source was the 266 nm laser, the fluorescence photo was shot excited by 355 nm. The Spectrometer adopted Ocean Optics QE series spectrometer. IR micro spectroscopy of DBTS was carried out on Nicolet iN10 microscope spectrometer (Thermo Fisher Scientific, USA) using a liquid-nitrogen-cooled detector. The excitation spectra and AIEE experiments measurements were carried out on Edinburgh FLS980. In-situ high-pressure Raman spectra on DPH crystal was carried out on self-made device with 785 nm laser.

**ADXRD Measurements:** In situ high-pressure powder ADXRD experiments were carried out with the support of 4W2 beamline at Beijing Synchrotron Radiation Facility with a wavelength of 0.6199  $\text{\AA}$ . The ADXRD patterns were collected for 300 s at each pressure and then were integrated with FIT2D program. The lattice parameters were analyzed by Materials Studio using ADXRD data.

**Computation Details:** Geometry optimization was performed for the DPH at different pressures, based on the first principles plane-wave pseudopotential density functional theory<sup>[1]</sup> as implemented in the CASTEP package.<sup>[2]</sup> The starting structure ZZZQNK05 (Deposition Number 693554) was obtained from the Cambridge Structure Database. The functional GGA and PBE was used in the calculation.<sup>[3]</sup> Using TS method for DFT-D correction.<sup>[4]</sup> The convergence levels for total energy, max force, max stress, max displacement, and SCF iterations were fine. Non-bond energy was performed by Materials Studio Forcite module, the forcefield chose COMPASS, charges used forcefield assigned, electrostatic chose Ewald and van der Waals chose atom based. Hirshfeld surfaces and contributions of intermolecular contacts to the Hirshfeld surface area were calculated by Crystal Explorer 17.5.<sup>[5-7]</sup> We also could get information about relative contributions of intermolecular contacts to the Hirshfeld surface area from it.

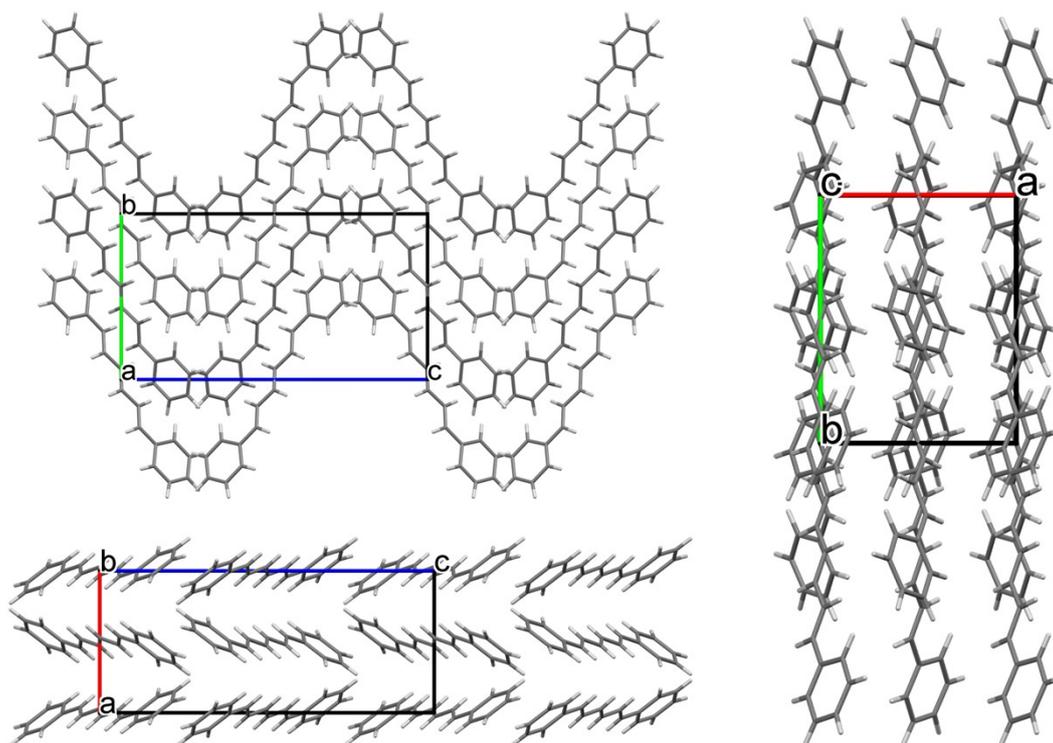


Figure S1 Packing arrangement of DPH crystal along different axes at ambient conditions.

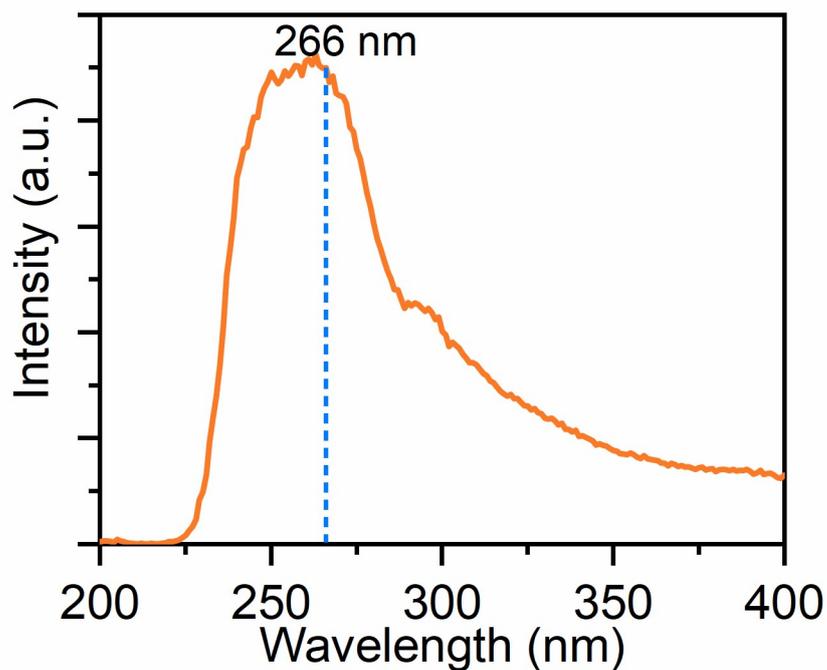


Figure S2 Excitation spectra of DPH,  $\lambda_{em}=450$  nm.

From the Figure S2, we can see that the optimal excitation wavelength of the DPH crystal is between 250-270 nm. In this paper, 266 nm was used as the excitation source for the in-situ high-pressure fluorescence spectra collection, and 355 nm was used as the excitation source for the corresponding in-situ fluorescence photos. The spectra corresponded very well to the photos, indicating that the change of the excitation spectra under high pressure would not affect the occurrence of fluorescence enhancement.

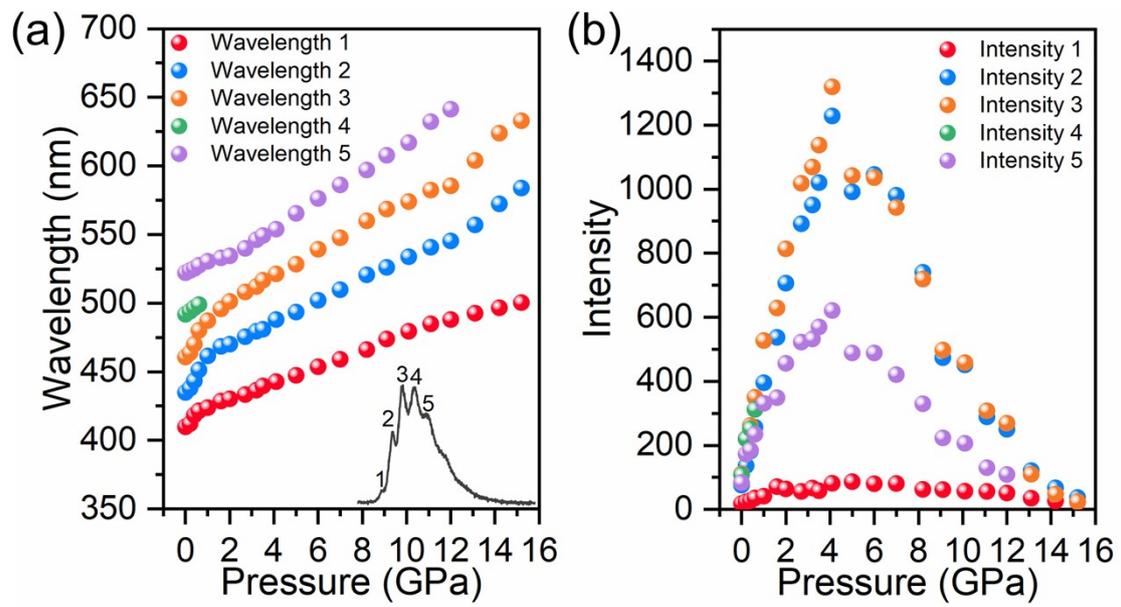


Figure S3 The plot of wavelength and intensity of DPH crystals as a function of pressure.

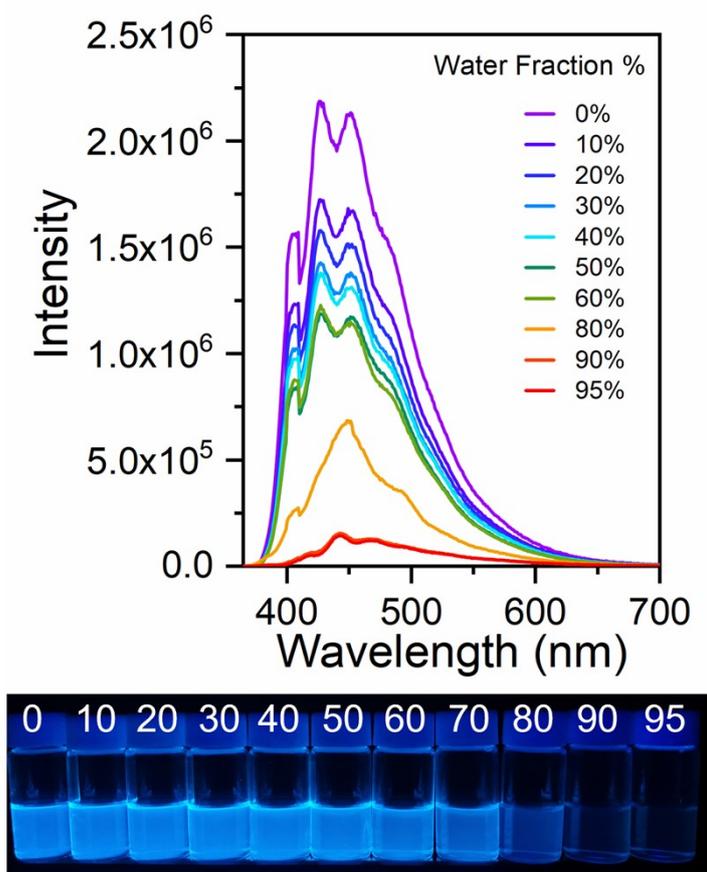


Figure S4 PL spectra of DPH ( $5 \times 10^{-5}$  mol/L) in the THF-H<sub>2</sub>O mixed solvent medium at different water fractions. ( $\lambda_{\text{ex}} = 355$  nm) and its corresponding photos.

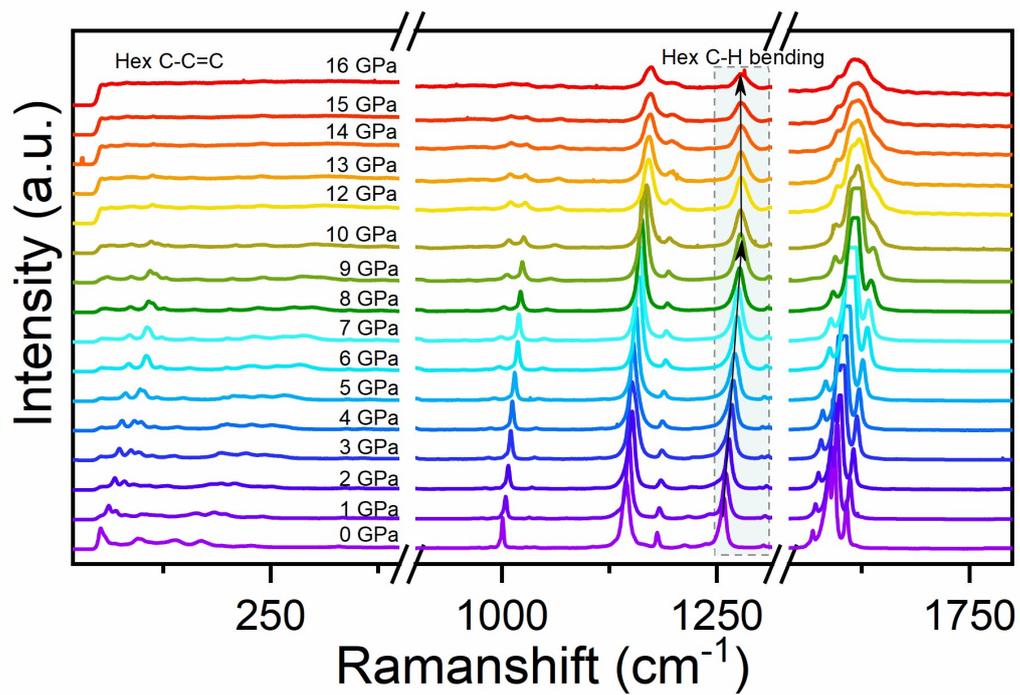


Figure S5 (a) In-situ high-pressure Raman spectra of DPH at different pressures.

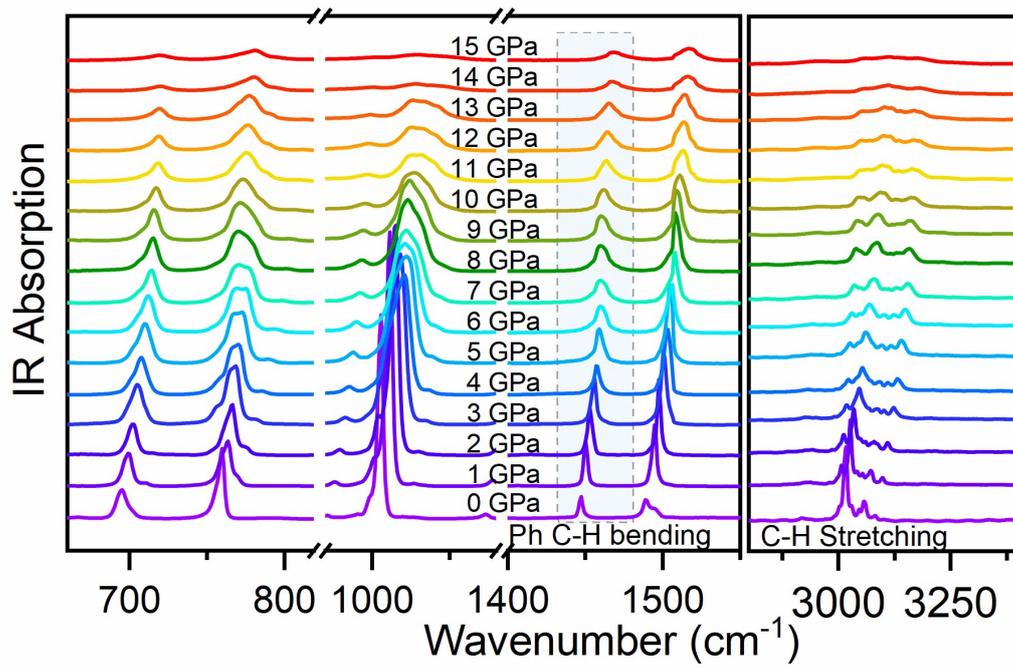


Figure S6 In-situ high-pressure IR spectra of DPH at different pressures.

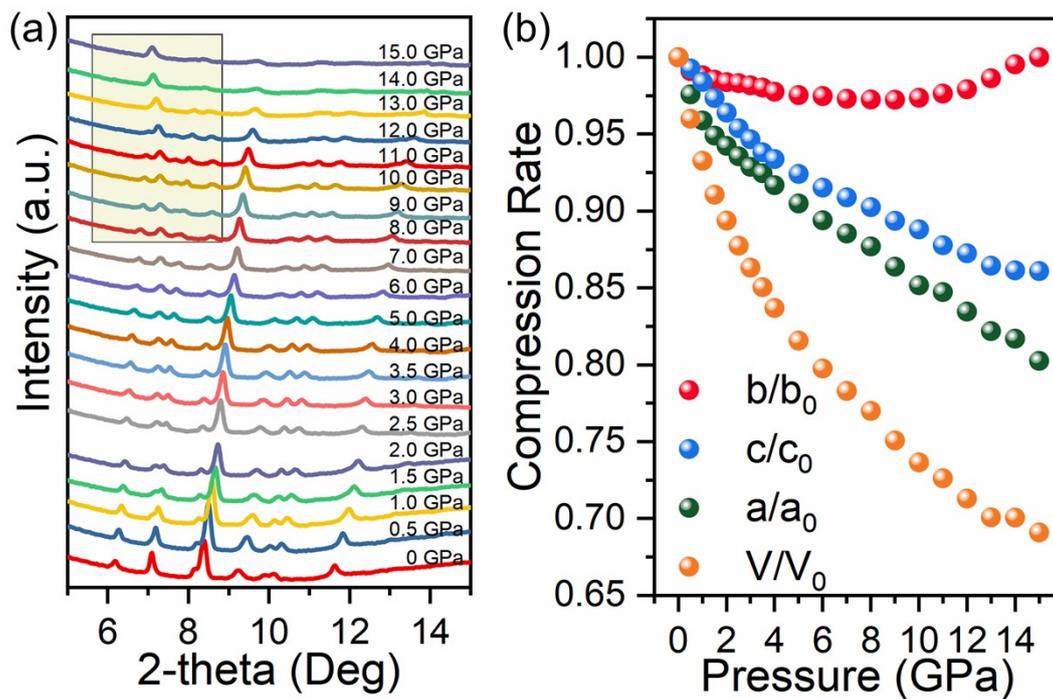


Figure S7 (a) ADXRD patterns of DPH crystals under different pressures. (b) Compression rate of the DPH lattice at pressures.

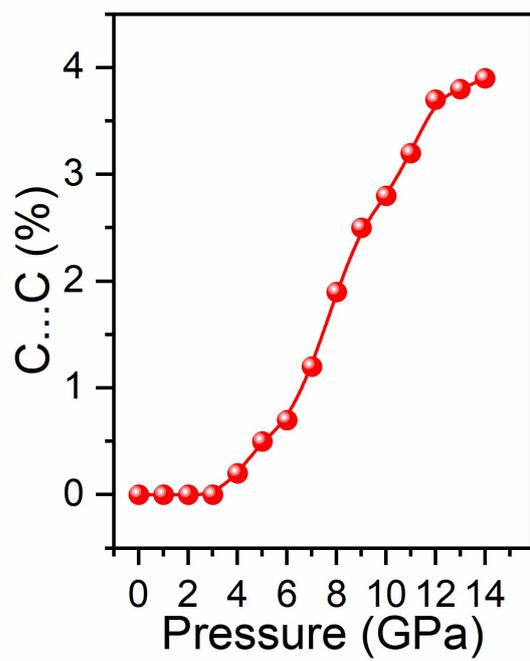


Figure S8 Contribution rate of C...C interactions to the Hirshfeld surface area versus pressure.

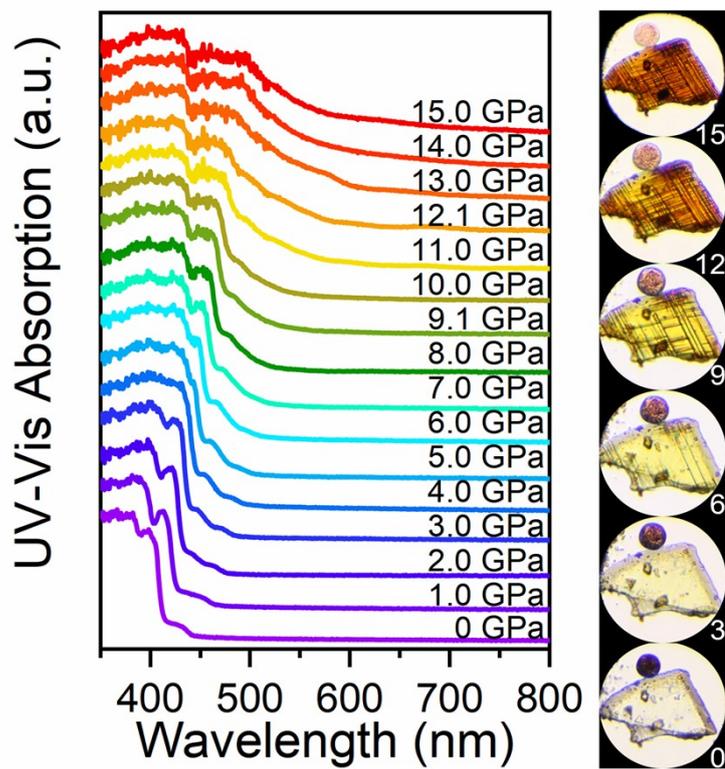


Figure S9 UV-Vis absorption spectra and photos of DPH crystal at different pressures. The white figures on photos represent the pressure (unit: GPa).

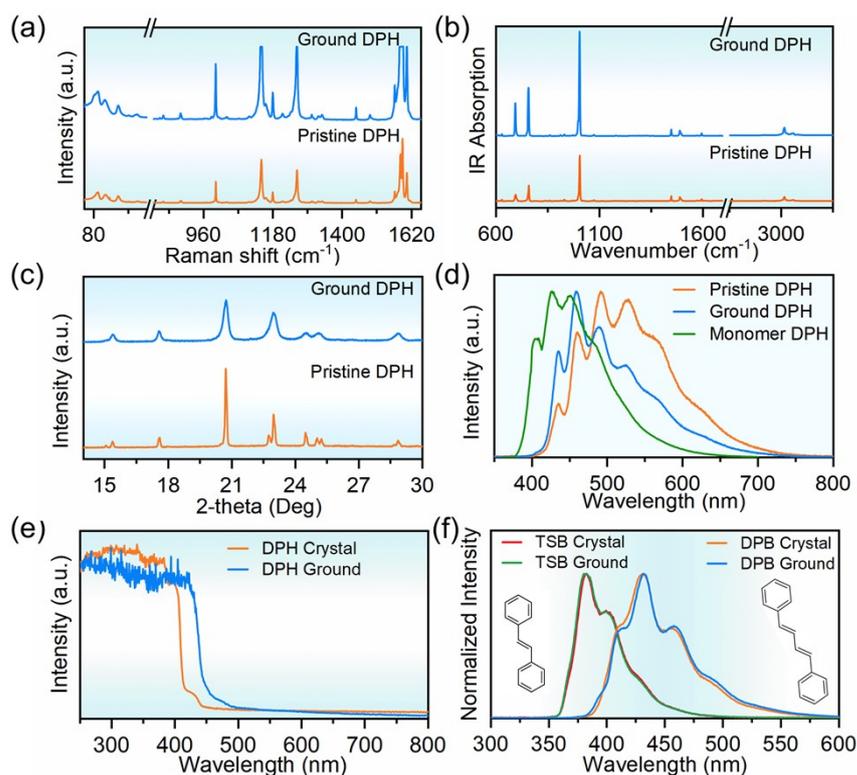


Figure S10 The spectra (a) Raman spectra, (b) IR spectra and (c) XRD before and after DPH grinding. (d) Comparison of the emission spectra before and after grinding with the emission spectra in the single-molecule state. The single-molecule state: DPH was dissolved in THF solvent at a concentration of  $5 \times 10^{-5}$  mol/L. (e) The UV-Vis absorption of DPH before and after grinding. (f) The fluorescence spectra of trans-Stilbene (TSB) and trans,trans-1,4-Diphenyl-1,3-butadiene (DPB) before and after grinding.

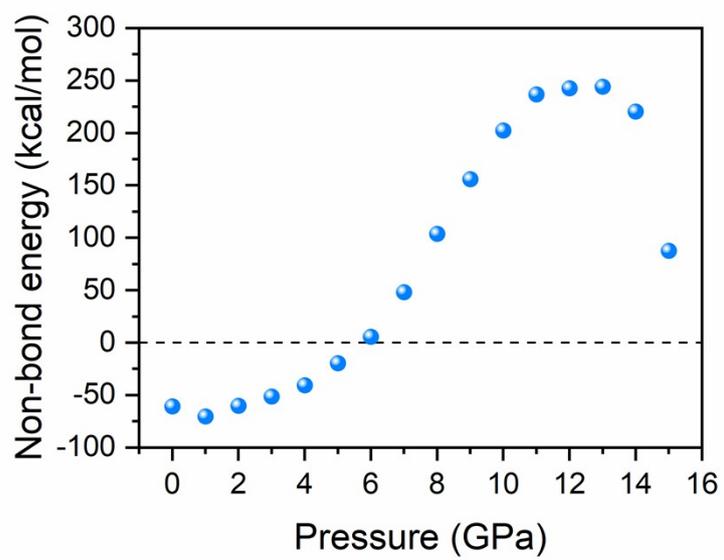


Figure S11 The calculated non-bond energy by COMPASS forcefield.

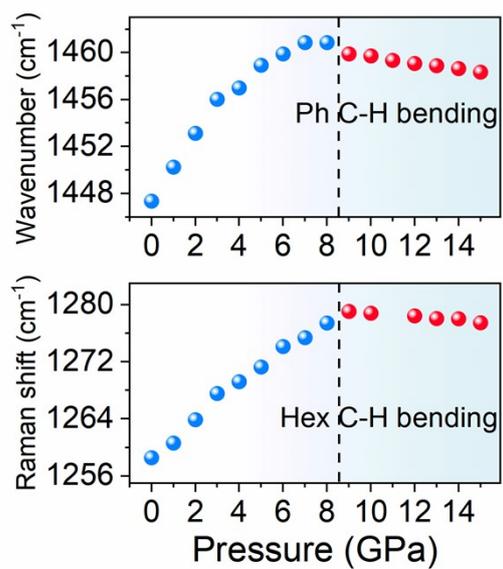


Figure S12 The vibrational spectra of C-H bonds. The upper part is the IR spectra of Ph C-H, and the lower part is the Raman spectra of Hex C-H. Ph represent phenyl ring, and Hex represent hexatriene, which are all part of DPH.

## Nanoindentation Experiments:

The nanoindentation experiments were measured on an Agilent Nano Indenter G200, and a Berkovich diamond indenter was used. The test method was set as “G-Series CSM Standard Hardness, Modulus and Tip Cal”. The temperature was 25 °C.

The diamond indenter diameter was about 150-180  $\mu\text{m}$ , and the experiment required multiple acquisitions (more than 10 times) at one crystal surface. During the test, we prepared 5 larger single crystals. One of the single crystals failed due to its size being close to the indenter diameter. Three samples were only able to perform 2- or 3-times acquisition process and failed due to their relatively small size on the next run. In the end only one single crystal was able to make 4 acquisitions, which results were listed in Table S1 and Figure S13.

Table S1 The results of nanoindentation experiments

Test	Avg Modulus (100-200 nm)/ GPa	Avg Hardness (100-200 nm)/ GPa
1	3.1	0.18
2	2.4	0.14
3	5.7	0.23
4	4.4	0.27
Mean	3.9	0.2

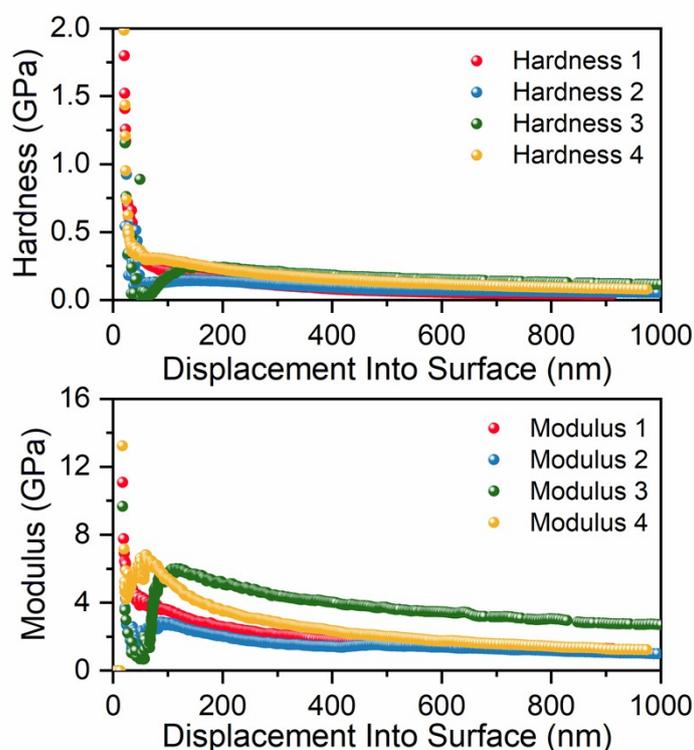


Figure S13 Results of hardness and modulus acquisitions in the same DPH crystal.

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