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Supporting Information

Pressure-induced excimer formation and fluorescence enhancement of an anthracene derivative

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Author Contributions

‡Yuxiang Dai and Haichao Liu contributed equally to this work.

Experimental section

All the reagents and solvents used for synthesis were purchased from Aldrich and Acros and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, using tetramethylsilane (TMS) as the internal standard. The mass spectra (MS) were recorded using an ITQ1100 (Thermo Fisher). The compounds were characterized by a Flash EA 1112, CHNS elemental analysis instrument.

Single crystal X-ray diffraction (XRD)

Single crystals of 9-(5'-phenyl-[1,1':3',1''-terphenyl]-3-yl)anthracene (**PTA**) sample were grown by slow solvent evaporation from tetrahydrofuran (**THF**)/methanol solutions. Single crystals were prepared at room temperature. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-Kα and control software using the RAPID AUTO at 293 K. The crystal structure was solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS program.

Photophysical measurements

UV-Vis absorption spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Steady-state fluorescence spectra and fluorescence lifetimes were carried out with an FLS980 Spectrometer. Solutions were placed in 1-cm path length quartz cells, and crystals were fixed on the quartz plate for measuring steady-state fluorescence spectra and fluorescence lifetimes.

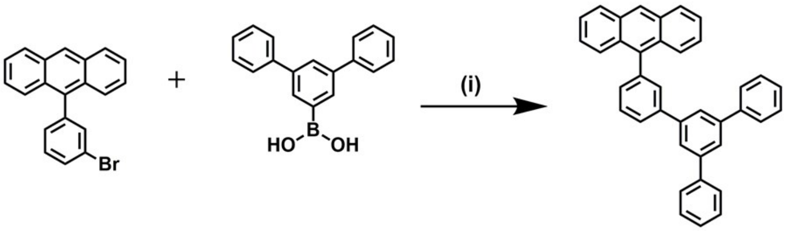
High pressure measurements

A 100-μm-diameter hole drilled in a pre-indented T301 stainless steel gasket was utilized as the sample chamber, which was placed in a symmetric diamond anvil cell (DAC). Pressure was measured using the standard ruby-fluorescence method.[1] Silicone oil was used as the pressure-transmitting medium (PTM) for the photoluminescence (PL) and UV-Vis absorption experiments and no PTM was used in the XRD or Raman experiments. All the high-pressure experiments were performed at room temperature. High-pressure PL and UV−Vis absorption spectra were measured with an optical fiber spectrometer (Ocean Optics, QE6500) and the 355 nm line of UV DPSS laser with a power of 10 mW was used as the excitation source for PL measurements. A spectrometer (iHR 550, Horiba Jobin Yvon) with a thermoelectrically cooled charge-coupled device (CCD, Horiba Jobin Yvon) was used to collect *in situ* high-pressure Raman spectra. The 785-nm laser was used as the excitation source for Raman measurements. *In situ* high-pressure XRD. The chromaticity coordinates are yielded from the emission spectra of the **PTA** crystal at different pressures. The fluorescence images were taken during the PL experiment. data were collected at beamline 12.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. Typical Bragg diffraction rings were integrated to generate the plots of intensity versus 2θ using the Fit2D software.[2] A second-order Birch−Murnaghan equation of state was used to fit the evolution in the unit cell volume as a function of pressure.

$$P(V) = \frac{3B_0}{2}[(\frac{V_0}{V})^{\frac{7}{3}} - (\frac{V_0}{V})^{\frac{5}{3}}]$$

where P is pressure, V_0 and V represent volumes at ambient pressure and high pressure, respectively. B_0 is the bulk modulus at ambient conditions.

Synthetic details



Scheme S1. A synthetic route to **PTA** ((i) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, H$_2$O, toluene and alcohol are refluxed under N$_2$ at 90 ˚C oil bath for 48 h).

Synthesis of 9-(5'-phenyl-[1,1':3',1''-terphenyl]-3-yl)anthracene (PTA)

9-(3-bromophenyl)anthracene was synthesized according to a previous report.[3] A mixture of 9-(3-bromophenyl)anthracene (166.62 mg, 0.50 mmol), [1,1':3',1''-terphenyl]-5'-ylboronic acid (191.89 g, 0.70 mmol), K$_2$CO$_3$ (2.48 g, 18.00 mmol), 6 mL distilled water, 9 mL toluene and 4.5 mL ethyl alcohol were degassed and recharged with nitrogen. Then Pd(PPh$_3$)$_4$ (23.11 mg, 0.02 mmol) was added to the mixture as a catalyst, and the mixture was degassed and recharged with nitrogen again. After being stirred and refluxed at 90 ℃ for 48 h under a nitrogen atmosphere, the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, filtered and concentrated in vacuum. It was purified via silica gel chromatography by the mixed petroleum ether and dichloromethane to afford the desired compound in 70% yield (169 mg). ^{1}H NMR (500 MHz, DMSO-d$_6$, 25 ℃, TMS): δ = 8.72 (s, 1H), 8.19 (d, J = 8.5 Hz, 2H), 8.14-8.08 (m, 1H), 7.99 (s, 2H), 7.94-7.84 (m, 5H), 7.78 (t, J = 7.7 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.57-7.37 (m, 12H); ^{13}C NMR (126 MHz, CDCl$_3$, 25 ℃, TMS): δ = 142.543 (C), 141.917 (C), 141.127 (C), 139.529 (C), 136.803 (C), 131.444 (C), 130.558 (CH), 130.306 (C), 130.140 (CH), 129.008 (CH), 128.875 (CH), 128.437 (CH), 127.603 (CH), 127.422 (CH), 126.881 (CH), 126.779 (CH), 126.388 (CH), 125.559 (CH), 125.416 (CH), 125.225 (CH); GC/MS, EI (mass m/z): 482.13 [M$^+$]; Anal. calcd for C$_{38}$H$_{26}$: C 94.57, H 5.43; found: C 94.61, H 5.64.

Table S1. Crystallographic data and structure refinement for **PTA**.

Color	colorless
Empirical formula	$C_{38}H_{26}$
Formula weight	482.59
T [K]	293(2)
Crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	24.582(2)
b [Å]	13.8071(8)
c [Å]	17.3300(11)
α [°]	90
β [°]	114.531(4)
γ [°]	90
V [Å^3]	5351.0(6)
Z	8
F(000)	2032
Density [g/cm^3]	1.198
μ [mm^{-1}]	0.068
Reflections collected	80489
Unique reflections	5490
R (int)	0.0723
GOF	1.026
R_1 [$I>2\sigma(I)$]	0.0499
ωR_2 [$I>2\sigma(I)$]	0.1263
R_1 (all data)	0.0874
ωR_2 (all data)	0.1564
CCDC	2025392

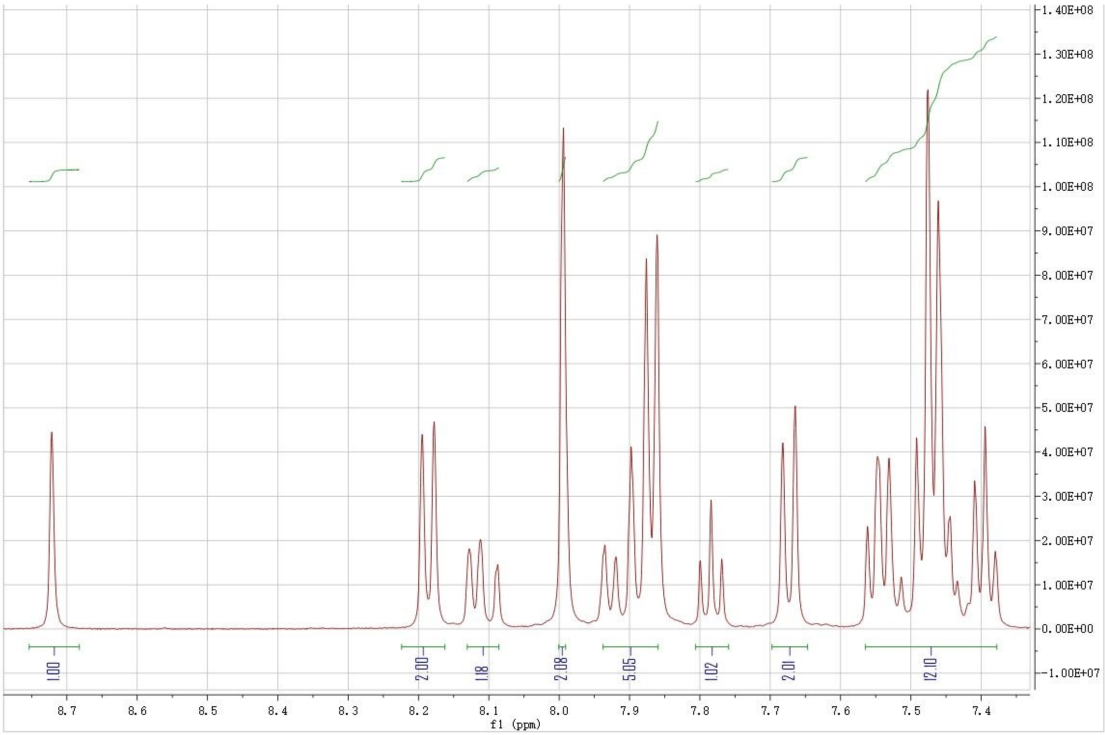


Fig. S1 ^{1}H NMR spectrum of the **PTA** compound.

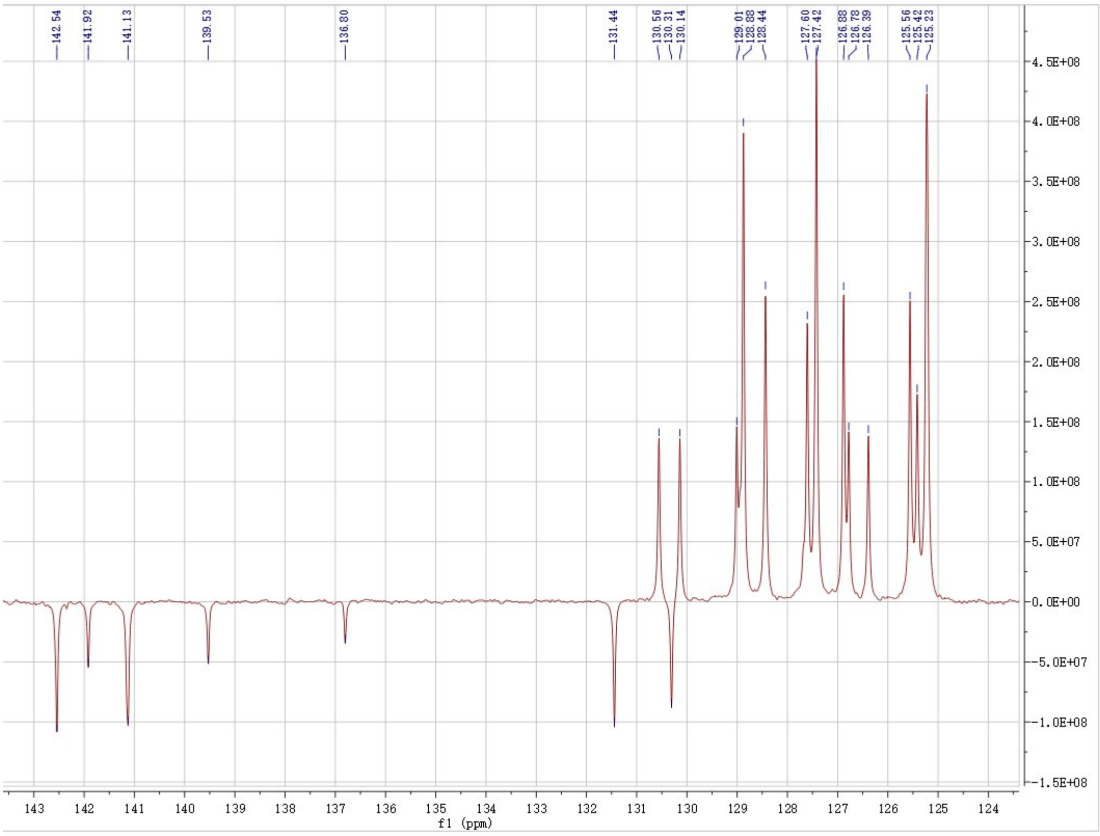


Fig. S2 ^{13}C NMR spectrum of the **PTA** compound.

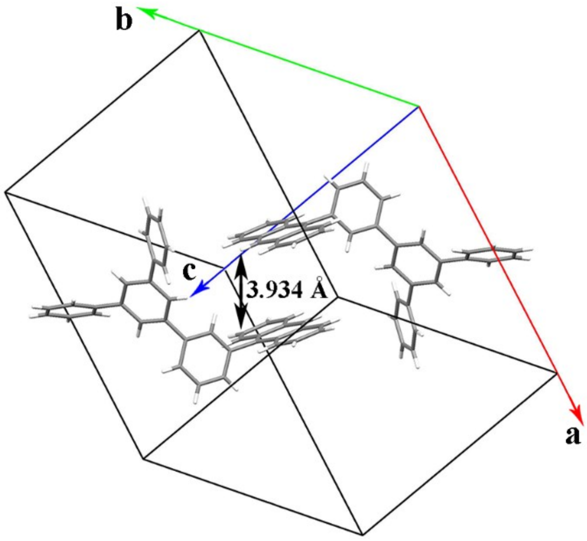


Fig. S3 A different viewing perspective from Figure 1 (left) that shows the crystal structure of **PTA**. The **AN** planes approach each other mainly along the *a*-axis, and the **AN** planes slide mainly along the *c*-axis.

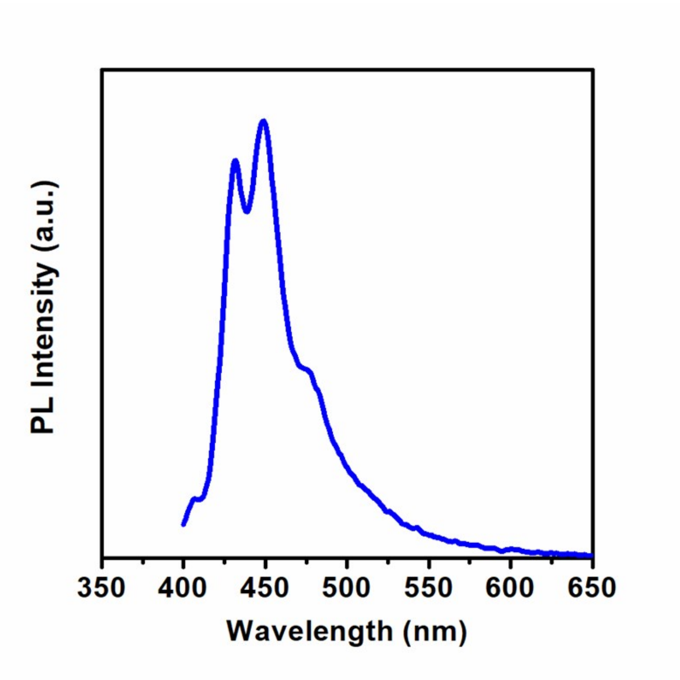


Fig. S4 Emission spectrum of **PTA** at ambient conditions, excited by a 355-nm laser.

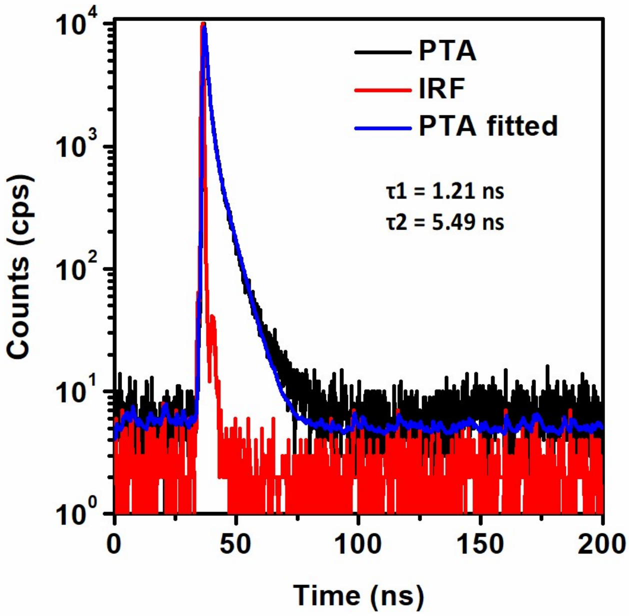


Fig. S5 Time-resolved spectrum of **PTA** at ambient conditions. (IRF: Instrument Response Function)

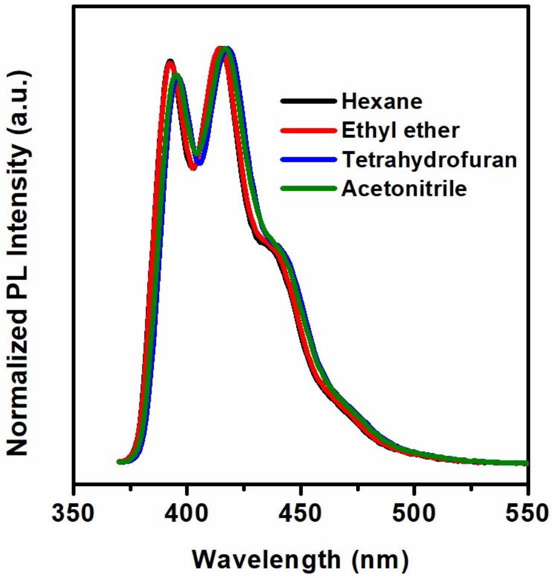


Fig. S6 Emission spectra of **PTA** in different solvents.

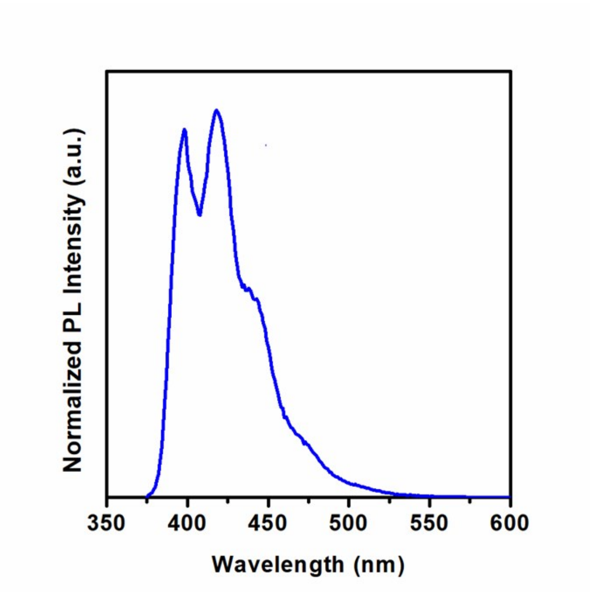


Fig. S7 Emission spectrum of a doped film with 1% weight of **PTA** in polymethyl methacrylate.

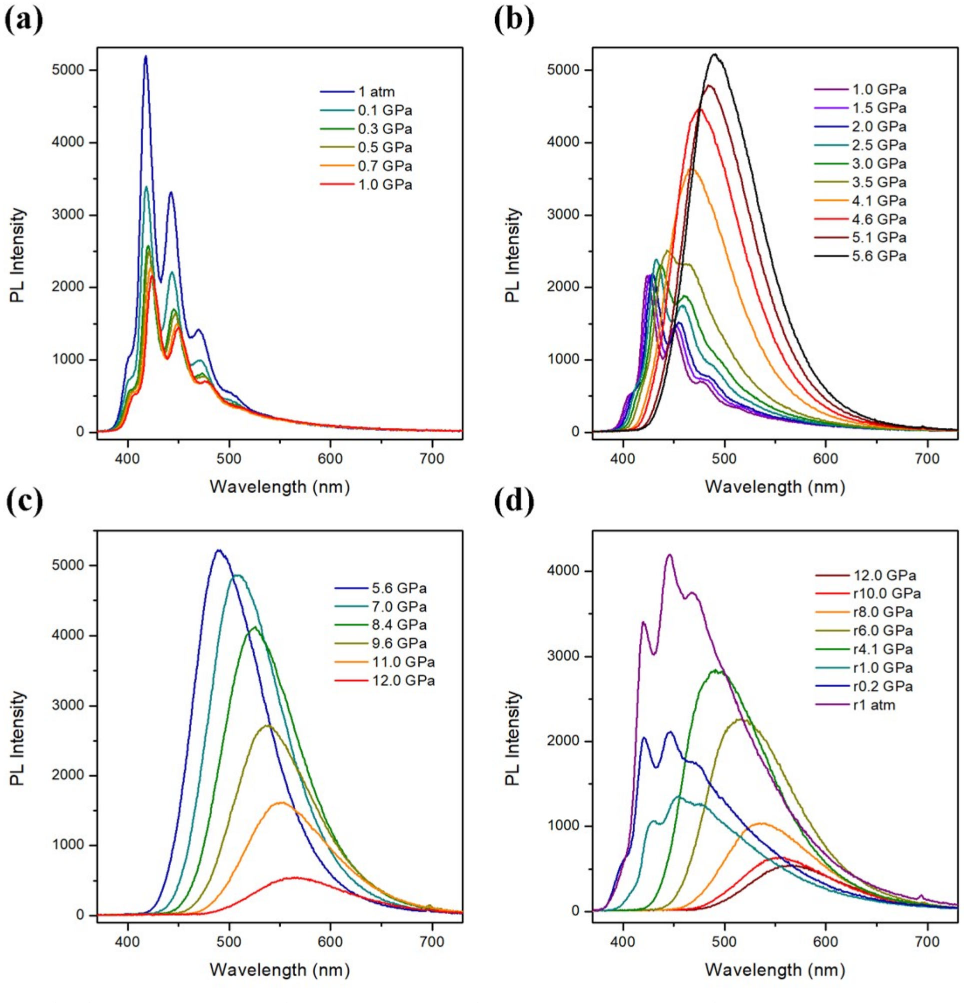


Fig. S8 Emission spectra of the **PTA** crystal at pressures ranging from (a) 1 atm to 1.0 GPa, (b) 1.0 to 5.6 GPa, (c) 5.6 to 12.0 GPa, and (d) 12.0 GPa to r1 atm (r represents releasing pressure).

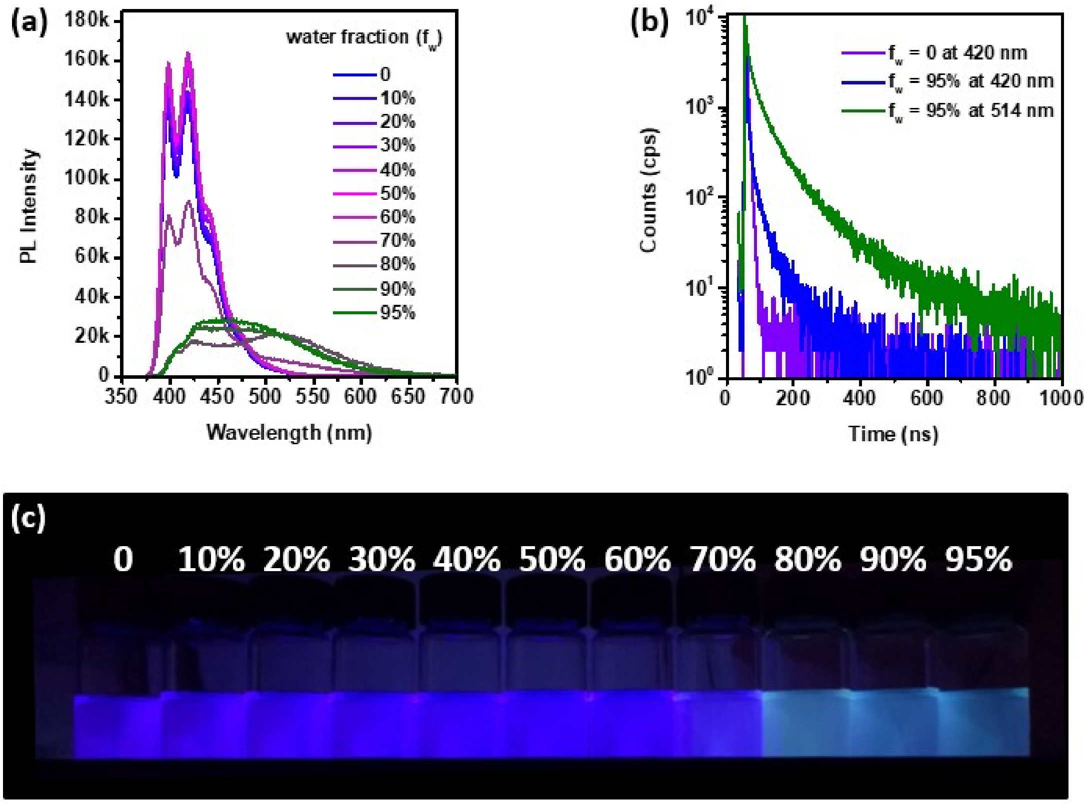


Fig. S9 (a) Emission spectra of **PTA** in mixed water-**THF** solutions with various water fractions (f_w). (b) Time-resolved spectra of **PTA** in mixed water-**THF** solutions with $f_w = 0$ and 95 (when $f_w = 0$ at 420 nm, $\tau = 5.281$ ns; when $f_w = 95\%$ at 420 nm, $\tau_1 = 3.292$ ns (41.09%), $\tau_2 = 15.80$ ns (42.77%), $\tau_3 = 69.26$ ns (16.14%); when $f_w = 95\%$ at 514 nm, $\tau_1 = 4.955$ ns (7.60%), $\tau_2 = 20.02$ ns (29.05%), $\tau_3 = 59.43$ ns (47.30%), $\tau_4 = 172.1$ ns (16.05%)). (c) Photographs of PTA in mixed water-THF solutions (the proportions of water are shown on the top) under 365 nm UV lamp irradiation.

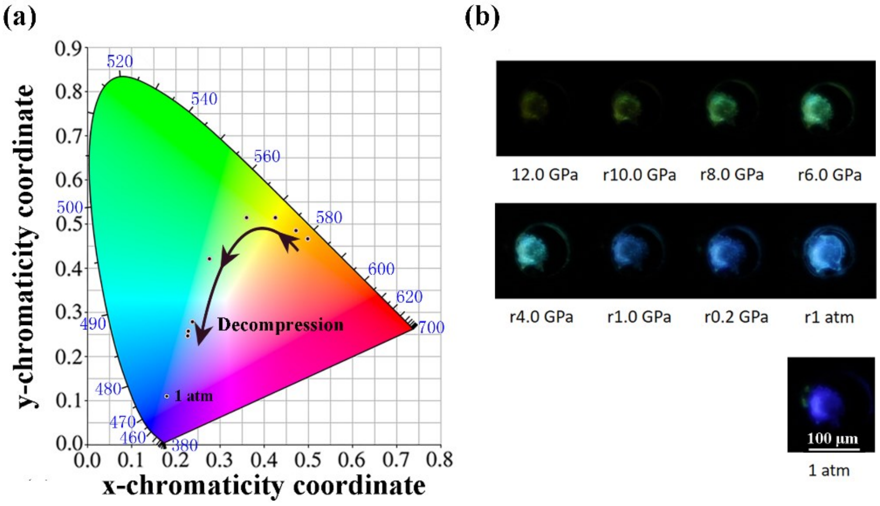


Fig. S10 (a) Pressure-dependent chromaticity coordinates of the emission spectra and (b) fluorescence images of the **PTA** crystal upon decompression from 12.0 GPa to 1 atm (r represents releasing pressure) with a comparison to the image of the starting material at 1 atm.

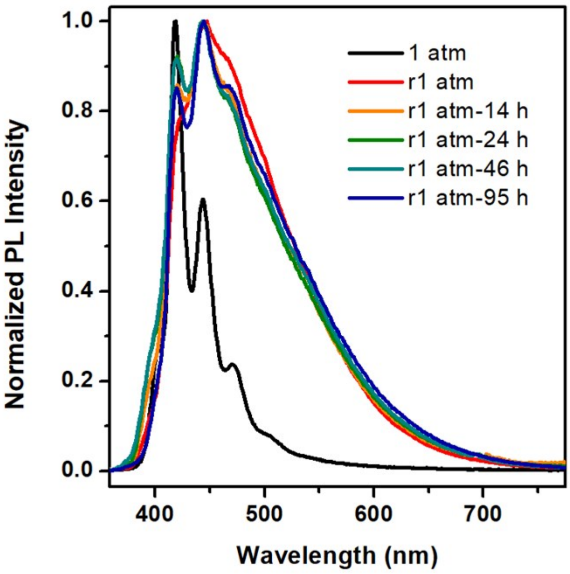


Fig. S11 Emission spectra of the recovered **PTA** held at ambient conditions for many hours. The spectra did not change after 14 hours and demonstrate partial fluorescent color was retained at ambient conditions (r represents releasing pressure).

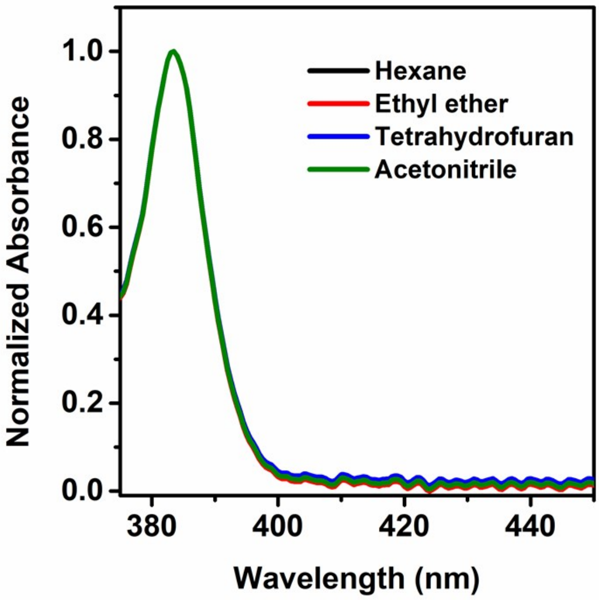


Fig. S12 UV-Vis absorption spectra of **PTA** in different solvents.

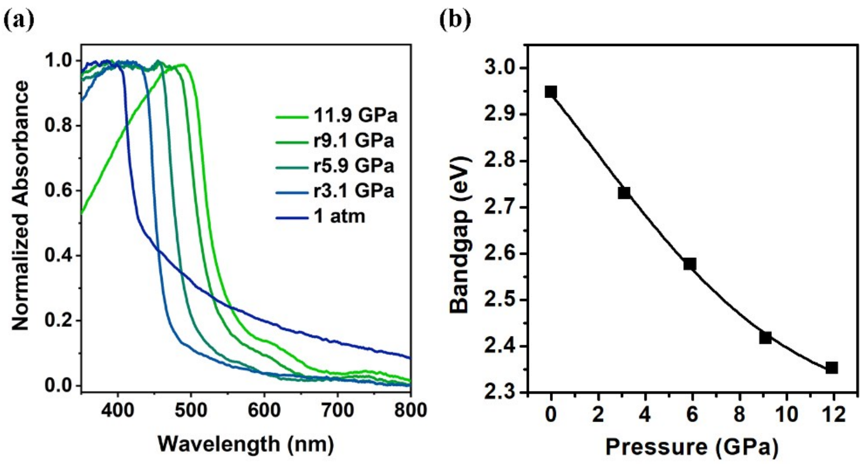


Fig. S13 (a) UV-Vis absorption spectra and (b) band gap evolution of the **PTA** crystal upon decompression from 11.9 GPa back to 1 atm (r represents releasing pressure).

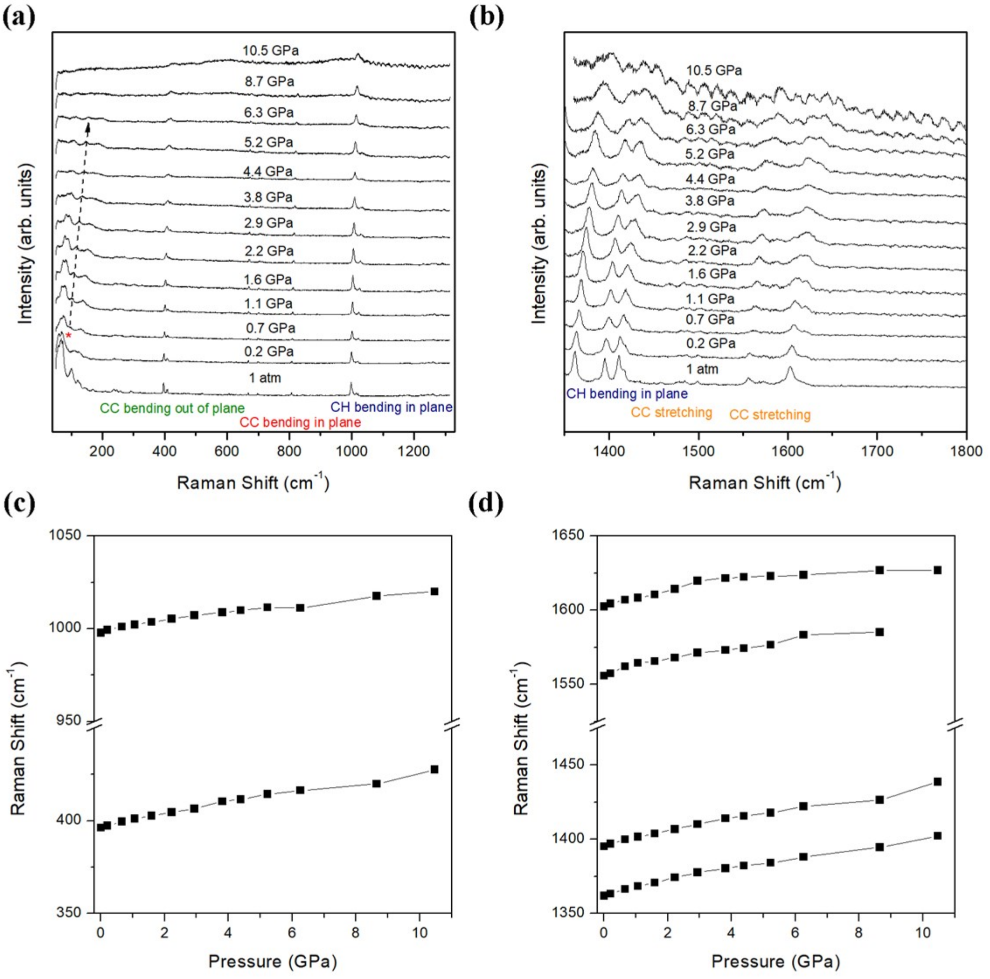


Fig. S14 (a, b) Raman spectra of **PTA** at selected pressures, (c, d) Pressure dependence of Raman shifts of selected modes in **PTA**. Assignment of major regions of Raman peaks: CC bending out of plane < 700 cm^{-1}; CC bending in plane < 1000 cm^{-1}; CH bending in plane from 1000 to 1500 cm^{-1}; CC stretching from 1300 to 1650 cm^{-1}.

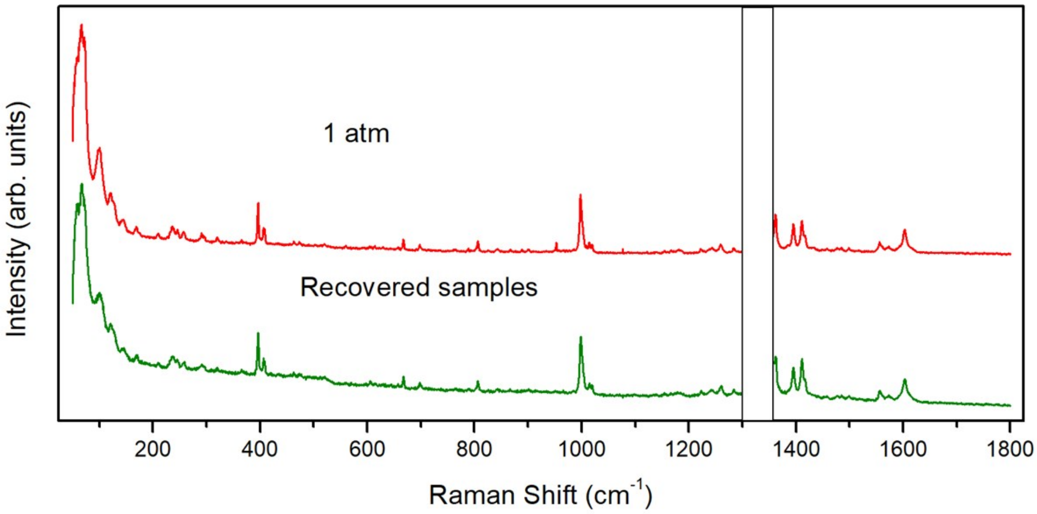


Fig. S15 Comparison of the Raman spectra of the recovered sample after fully releasing pressure and the starting sample.

References

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[2] A. Hammersley, S. Svensson, M. Hanfland, A. Fitch, D. Hausermann, *High Pressure Res.* **1996**, *14*, 235.
[3] H. Liu, D. Cong, B. Li, L. Ye, Y. Ge, X. Tang, Y. Shen, Y. Wen, J. Wang, C. Zhou and B. Yang, *Cryst. Growth Des.*, **2017**, *17*, 2945.