Supplementary Information

Realizing Long Range π-Conjugation in Phenanthrene and Phenanthrene-Based Molecular Crystals for Anomalous Piezoluminescence

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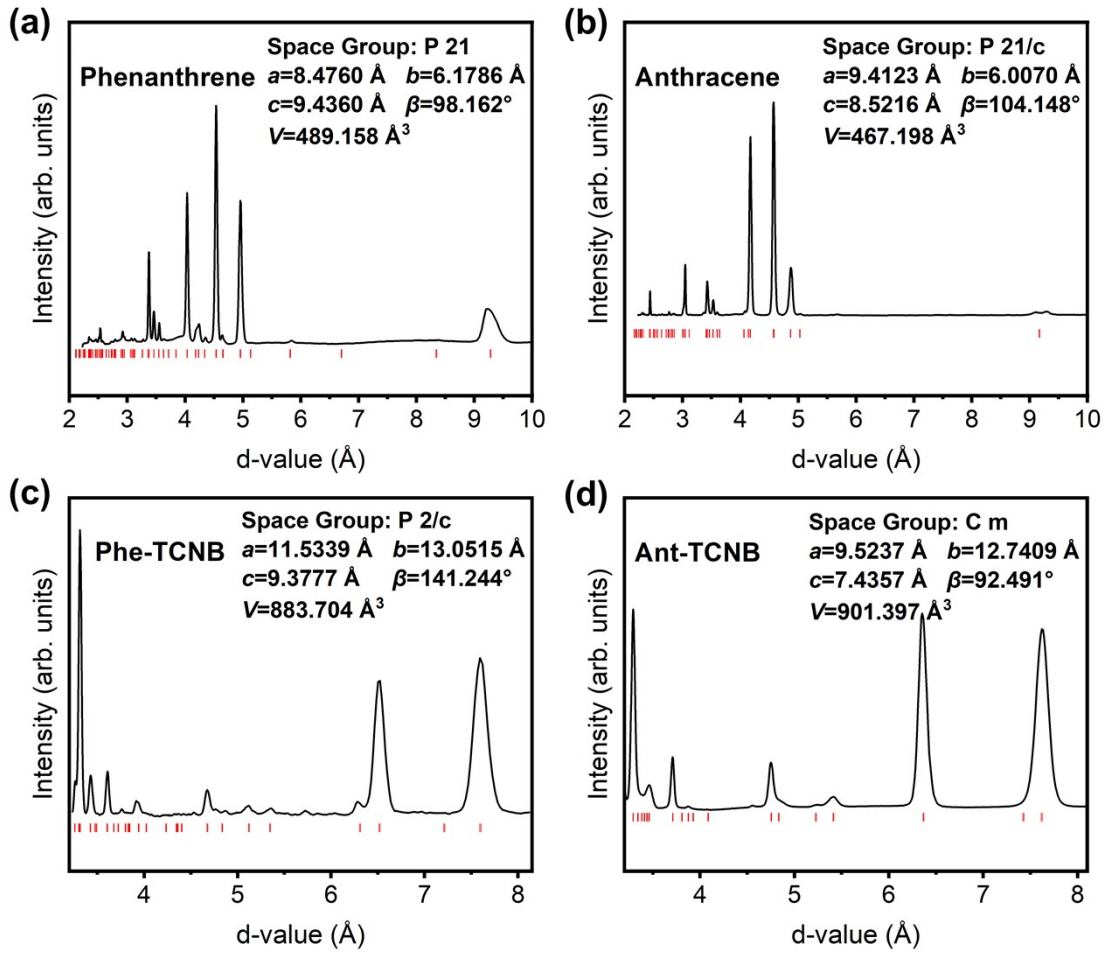

Figure S1. Experimental XRD patterns (λ = 1.5418 Å) of (a) phenanthrene crystal, (b) anthracene crystal, (c) Phe-TCNB cocrystal and (d) Ant-TCNB cocrystal at ambient pressure.

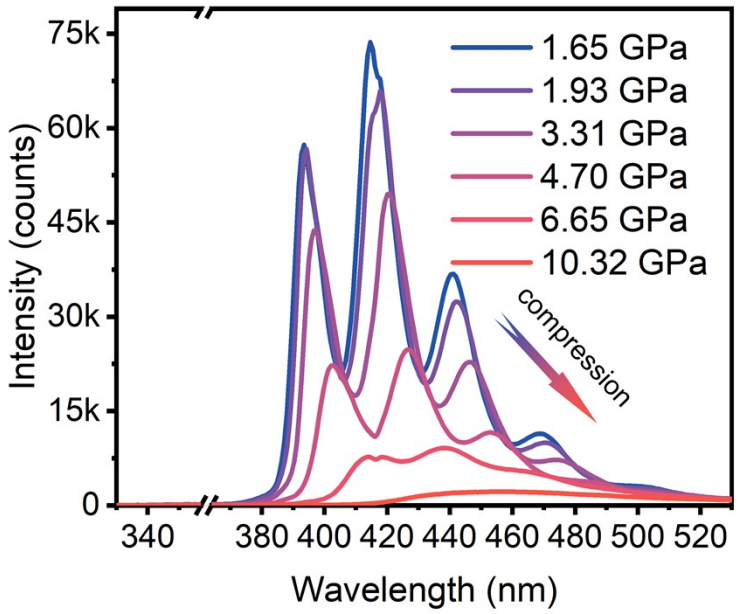

Figure S2. *In situ* PL spectra of phenanthrene crystal above 1.65 GPa

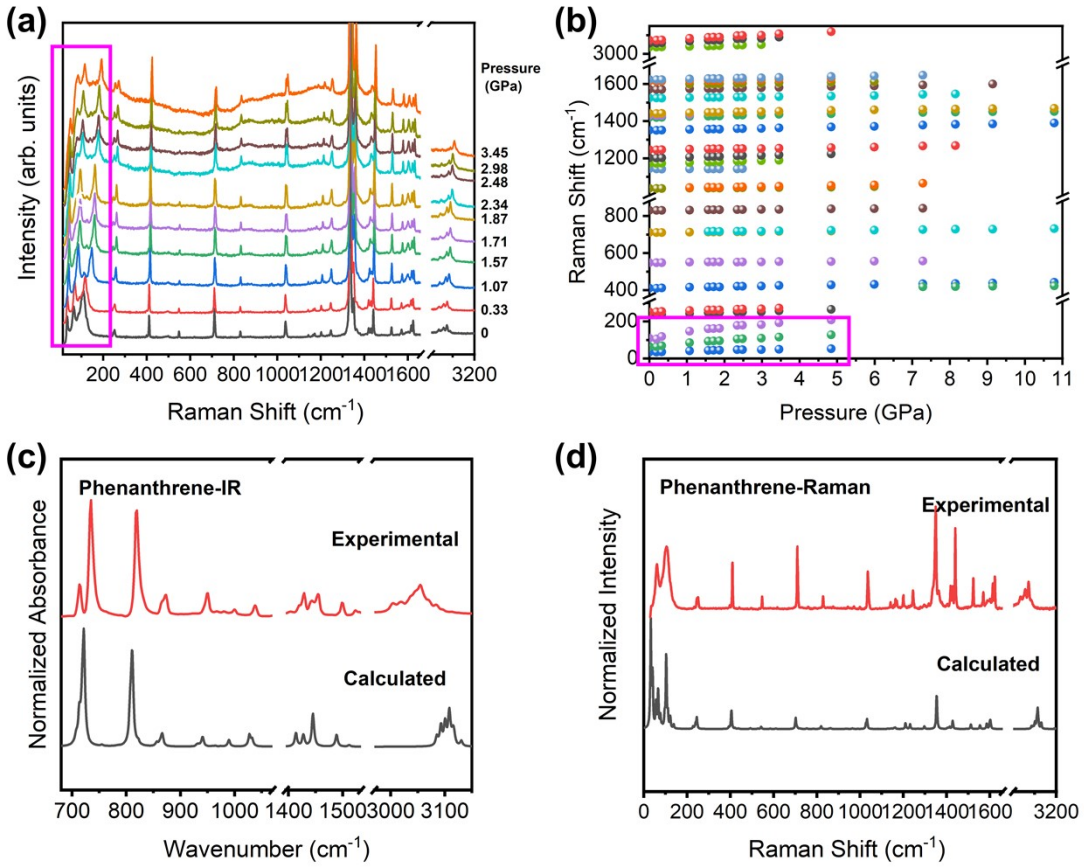

Figure S3. (a) *In situ* Raman spectra of phenanthrene crystal upon compression. (b) Pressure-dependent peak positions of observed Raman modes. The marked regions represent the intermolecular vibrational modes of phenanthrene. (c) Experimental (top) and calculated (bottom) IR spectra of phenanthrene. (d) Experimental (top) and calculated (bottom) Raman spectra of phenanthrene.

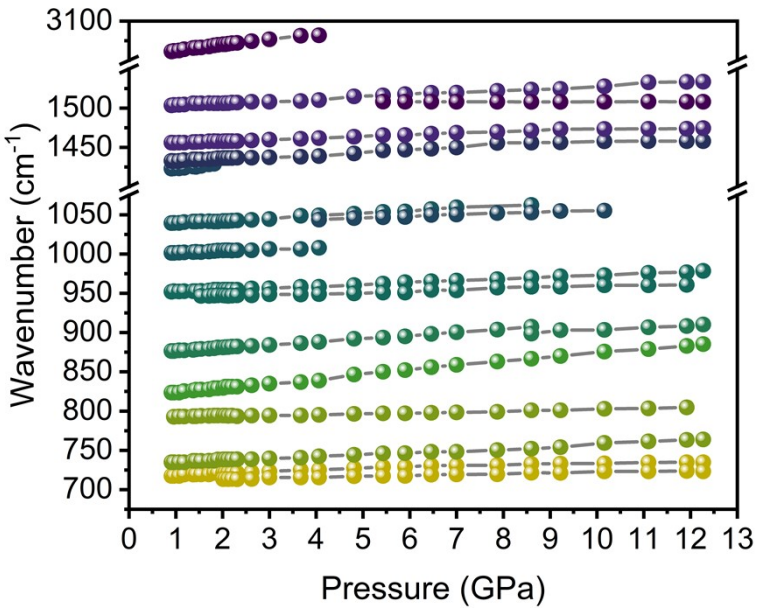

Figure S4. Pressure-dependent peak positions of observed IR modes.

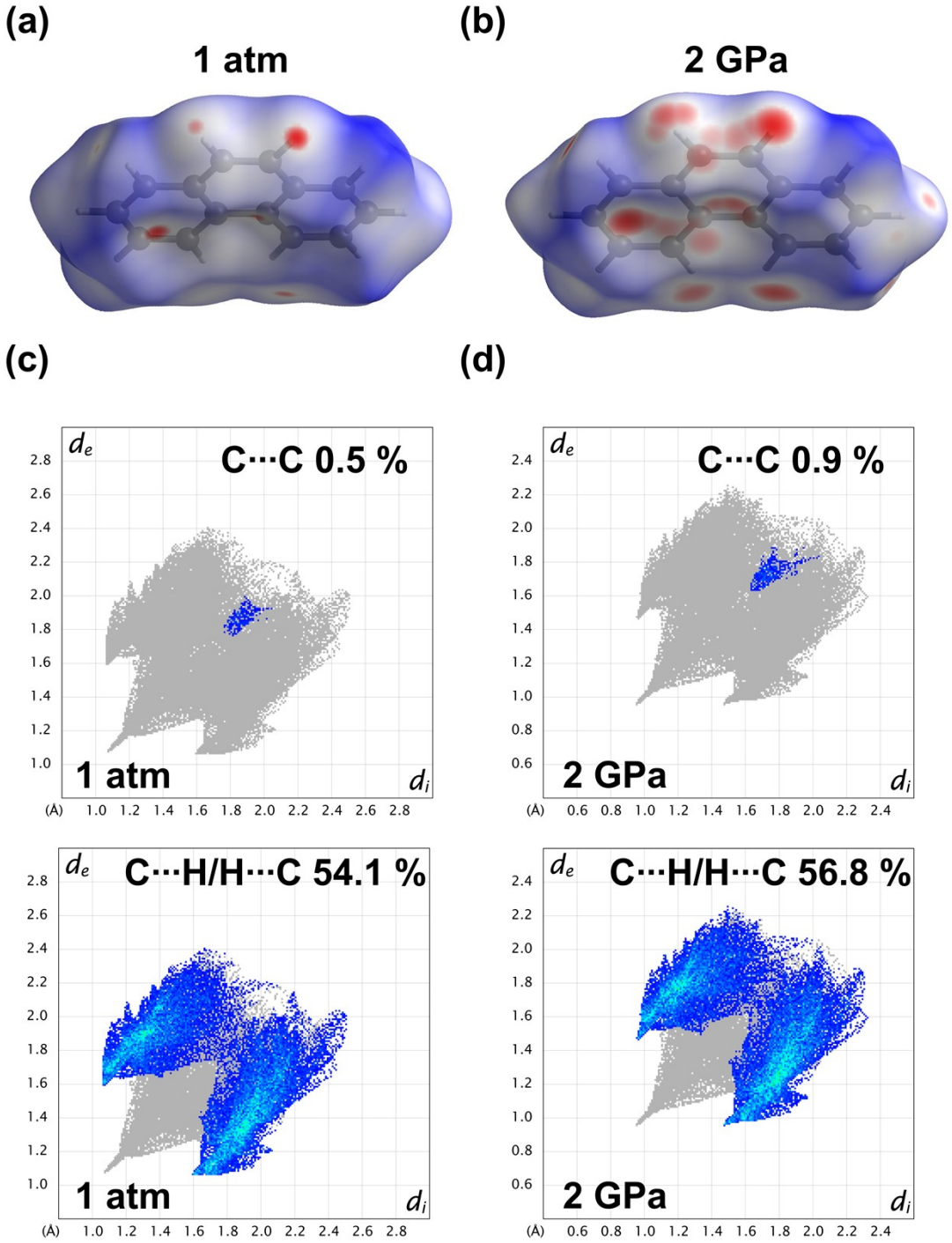

Figure S5. Hirshfeld Surface for the Calculated Structure at (a) 1 atm and (b) 2 GPa. Contribution of C···C and C···H/H···C interactions at (c) 1 atm and (d) 2 GPa is shown in the fingerprint plot diagram.

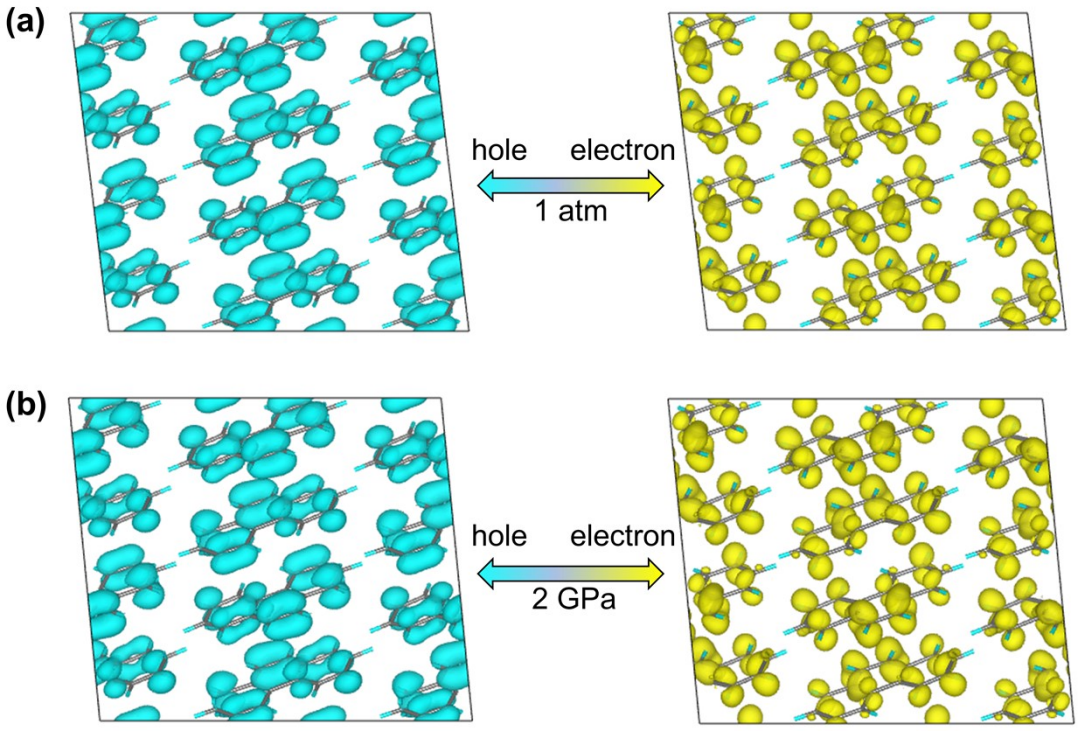

Figure S6. Wave functions of hole and electron for phenanthrene molecules at 1atm (a) and 2 GPa (b).

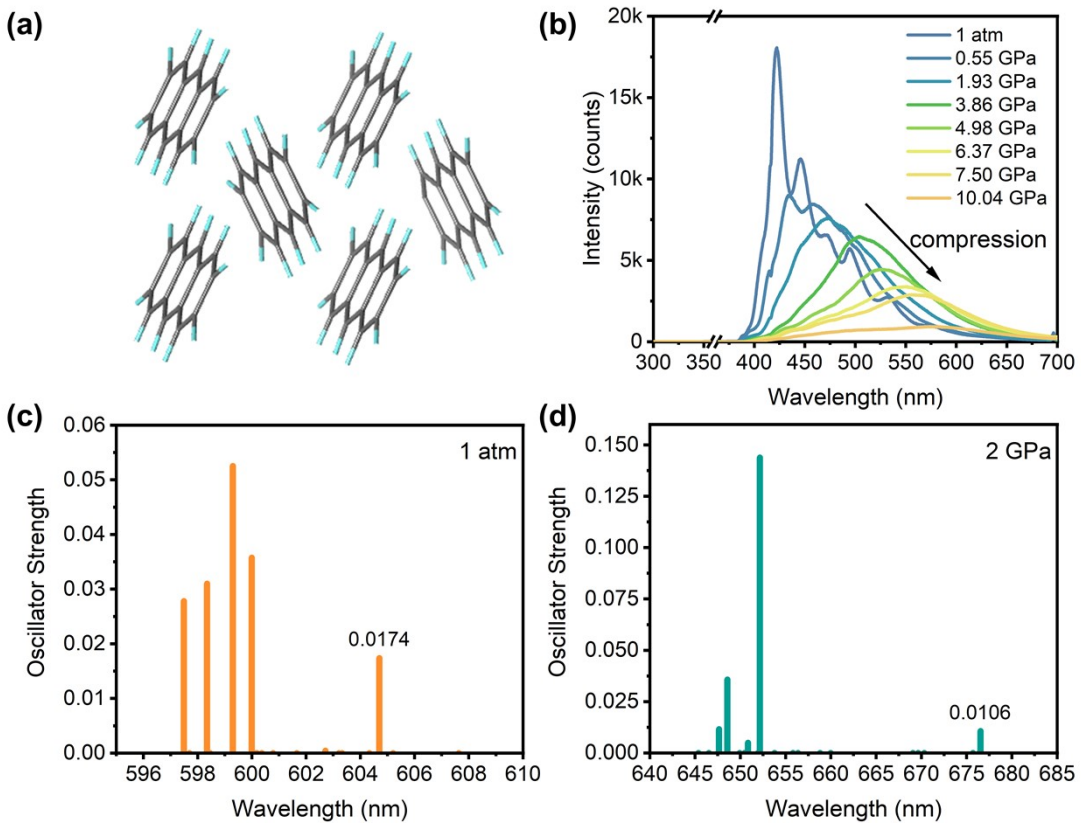

Figure S7. (a) The sketch map for molecular packing of anthracene. (b) The high-pressure PL spectra of anthracene. (c-d) The emission oscillator strength of anthracene at 1 atm and 2 GPa.

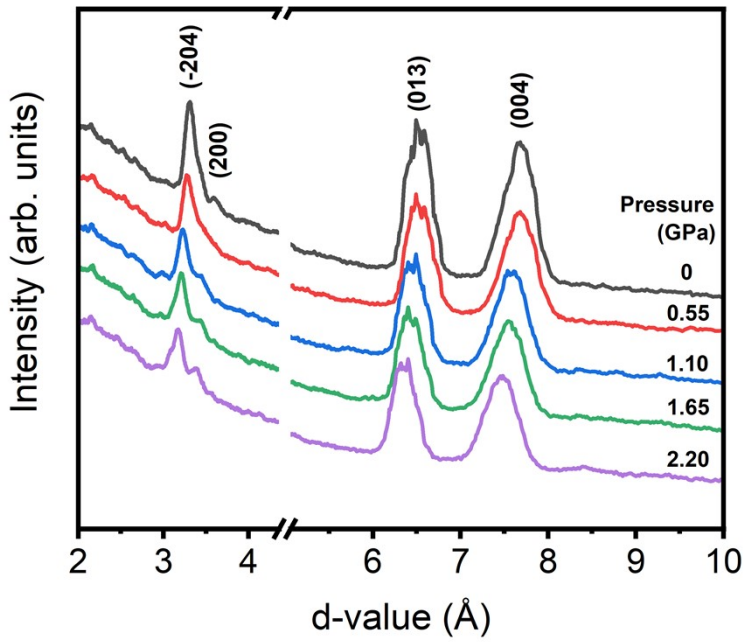

Figure S8. High-pressure XRD patterns of Phe-TCNB cocrystal below 2.2 GPa.

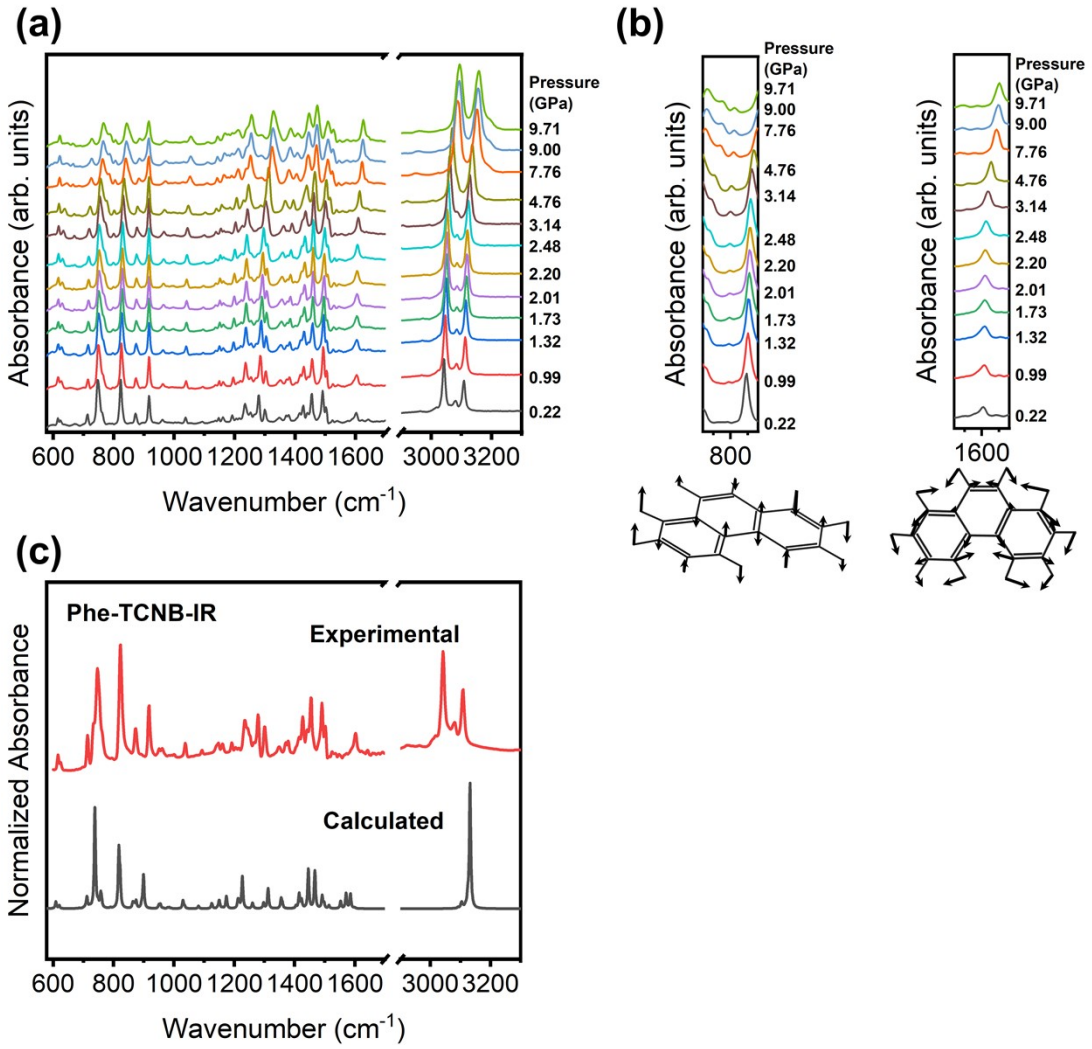

Figure S9. (a) *In situ* IR spectra of Phe-TCNB cocrystal upon compression. (b) The IR peak around 796 cm^{-1} and 1602 cm^{-1} and the sketch maps for the corresponding vibration modes. (c) Experimental (top) and calculated (bottom) IR spectra of Phe-TCNB.

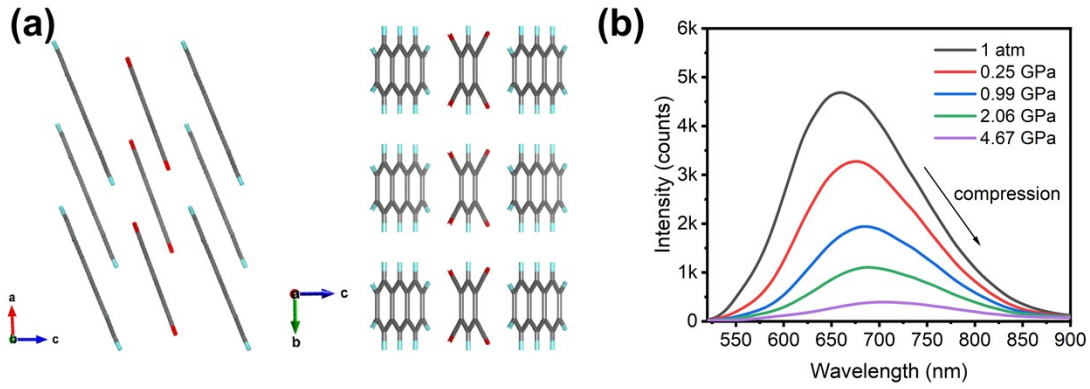

Figure S10. (a) The sketch map for molecular packing of Ant-TCNB. (b) The high-pressure PL spectra of Ant-TCNB.

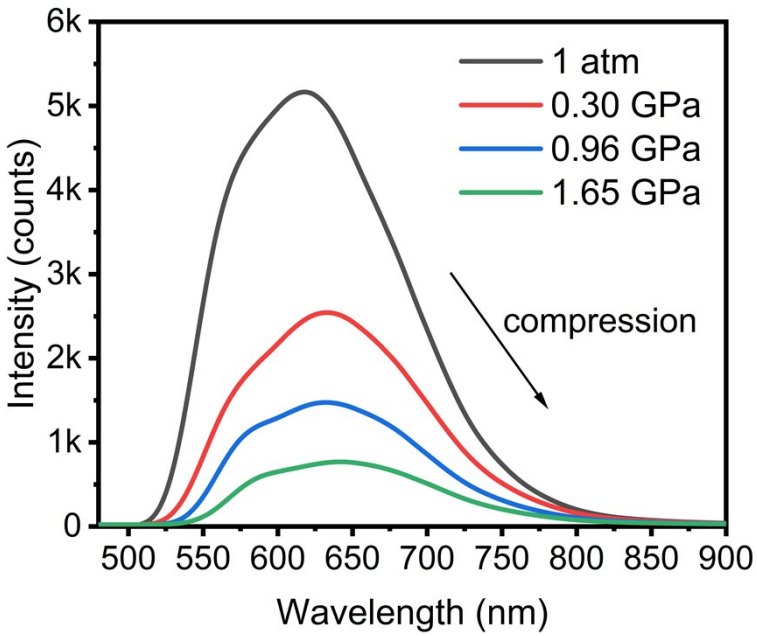

Figure S11. *In situ* PL spectra of $Ant_{0.5}$-$Phe_{0.5}$-TCNB cocrystals upon compression.