Supporting Information

Molecular insertion regulates the donor-acceptor interactions in cocrystals for the design of piezochromic luminescent materials

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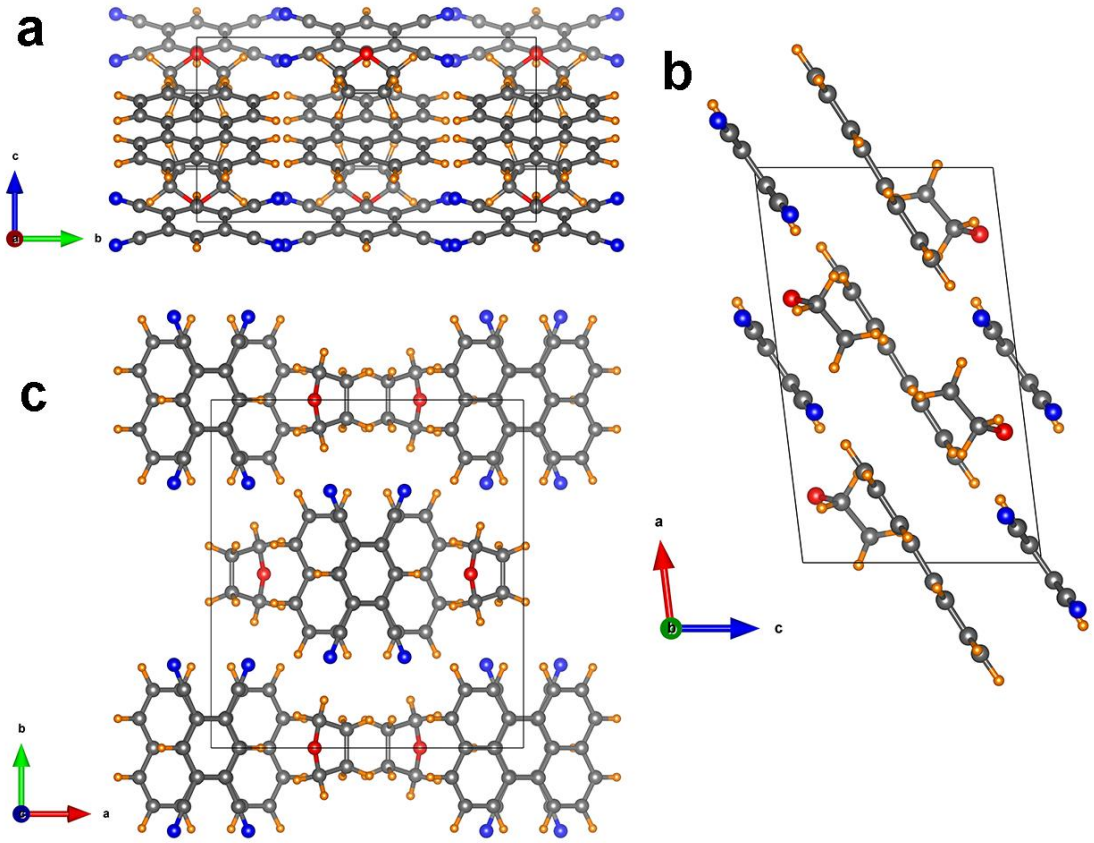
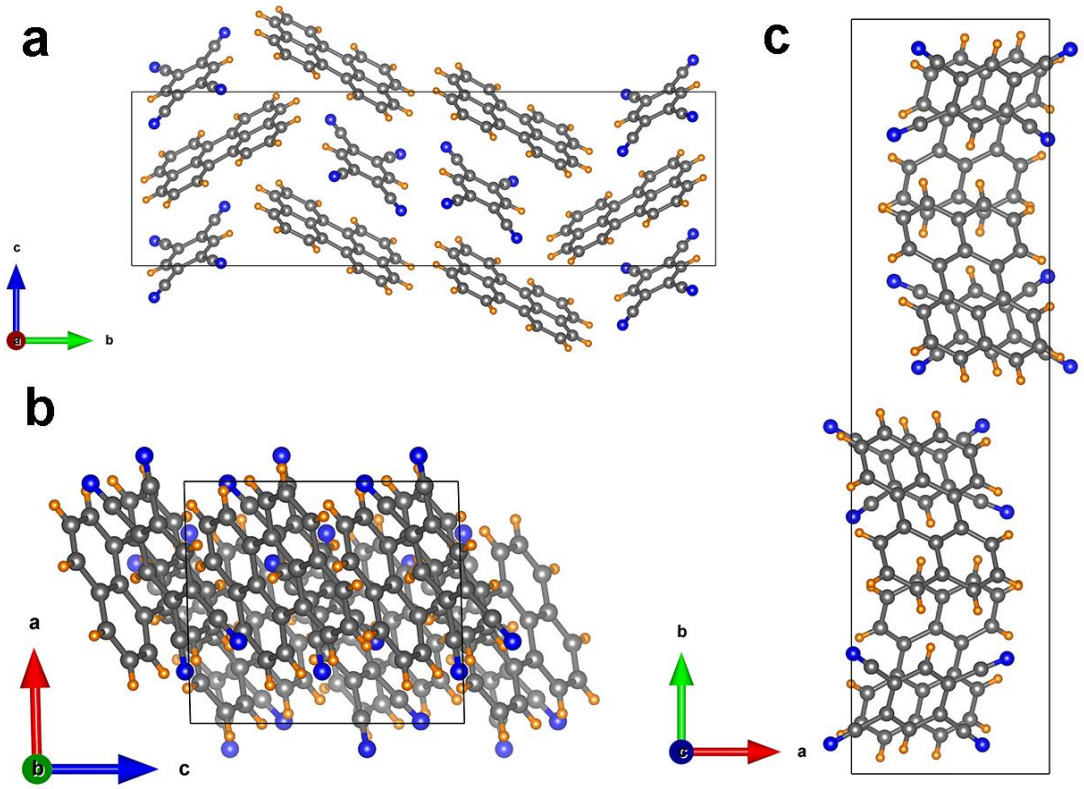
Compound Name	*PTCs*	*PTCs-THF*
Space Group	**P 21/c**	**C 2/M**
Cell Lengths(Å)	**a = 7.889**	**a = 13.205**
	b = 30.004	**b = 14.569**
	c = 8.936	**c = 7.9733**
Cell Angles (°)	**α = 90**	**α = 90**
	β = 91.493	**β = 97.083**
	γ = 90	**γ = 90**
Cell Volume(Å^3)	**2114.5**	**1522.2**

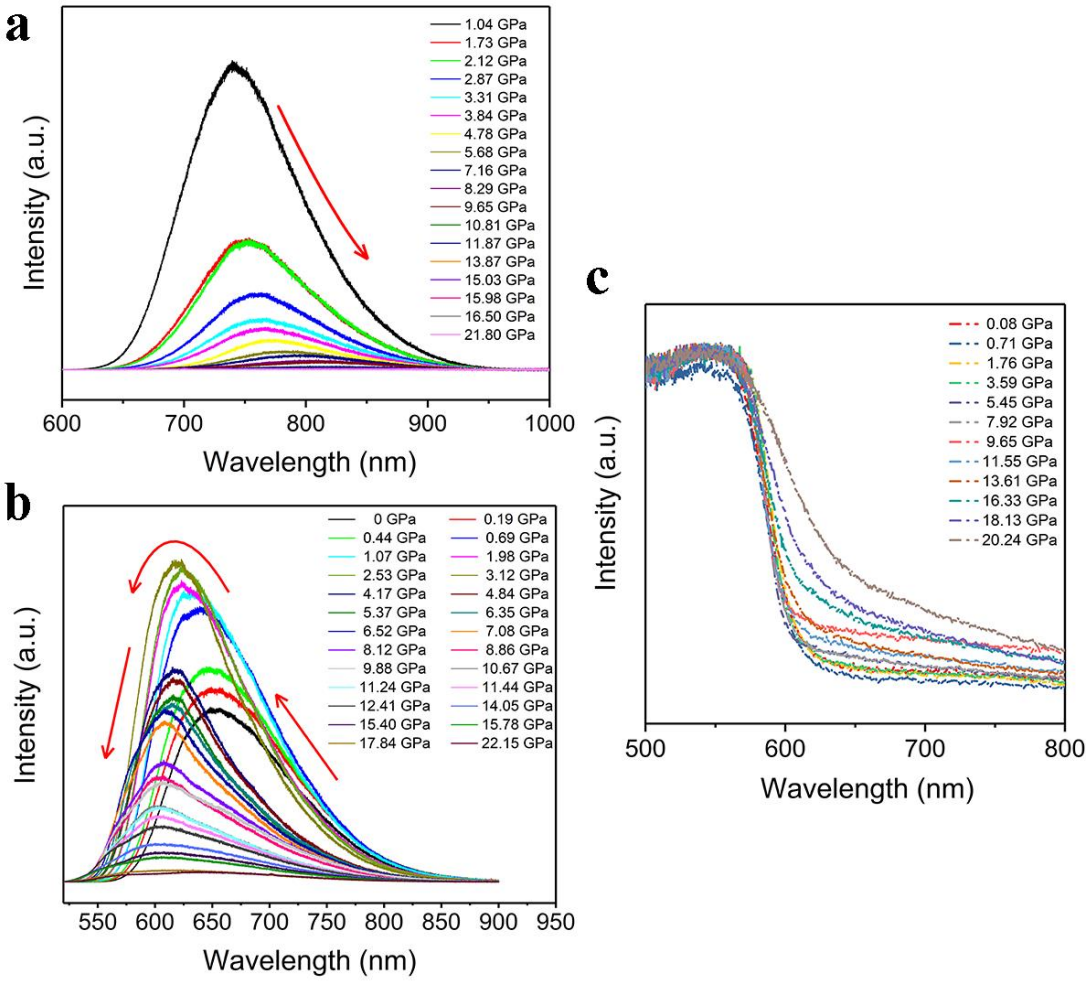
Supplementary Table 1. Crystallographic data for PTCs and PTCs-THF obtained from our experiments.



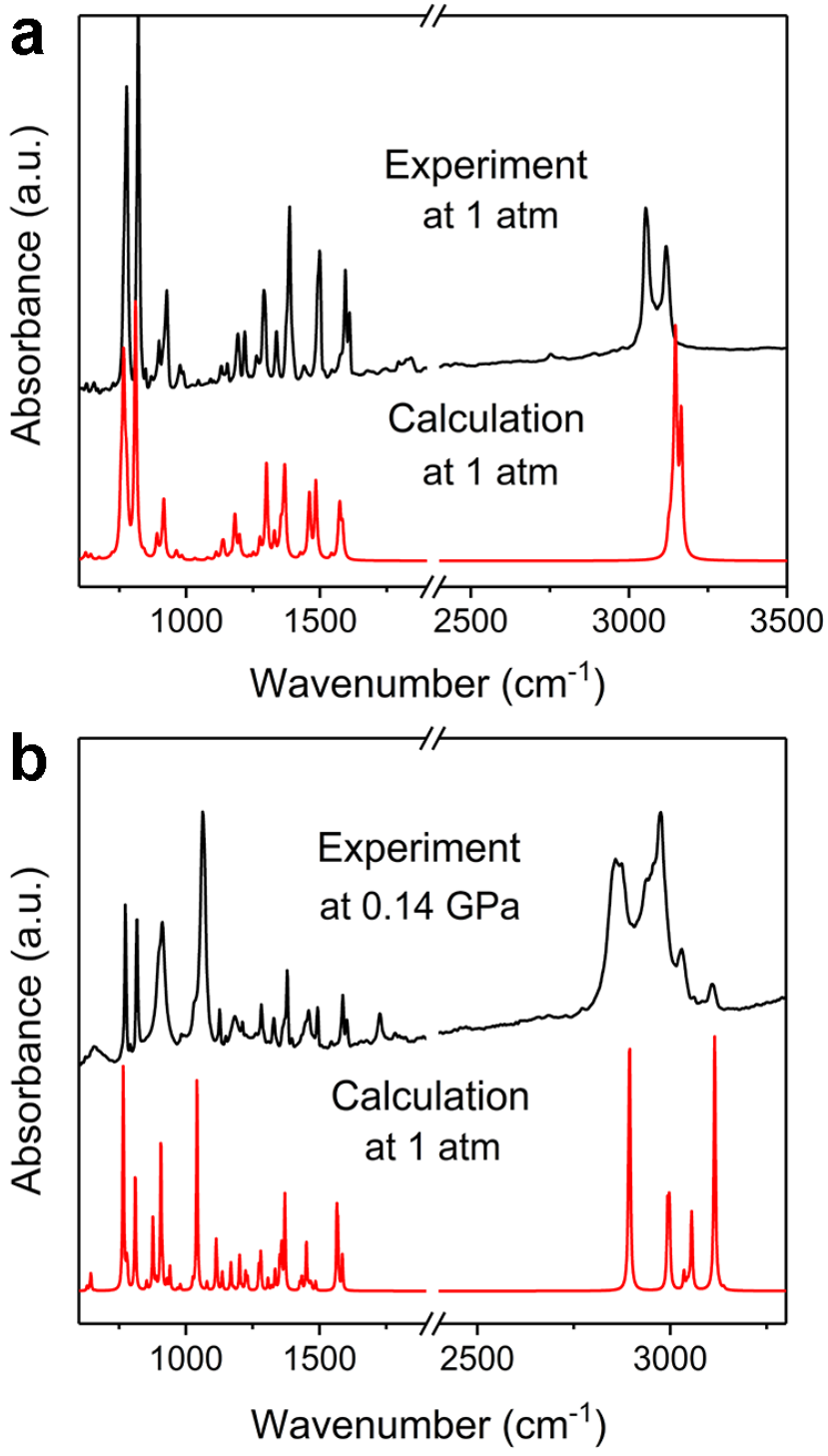
Supplementary Figure 1. Molecular packing of PTCs-THF perpendicular to the **a)** *a*-, **b)** *b*-, and **c)** *c*-axis.



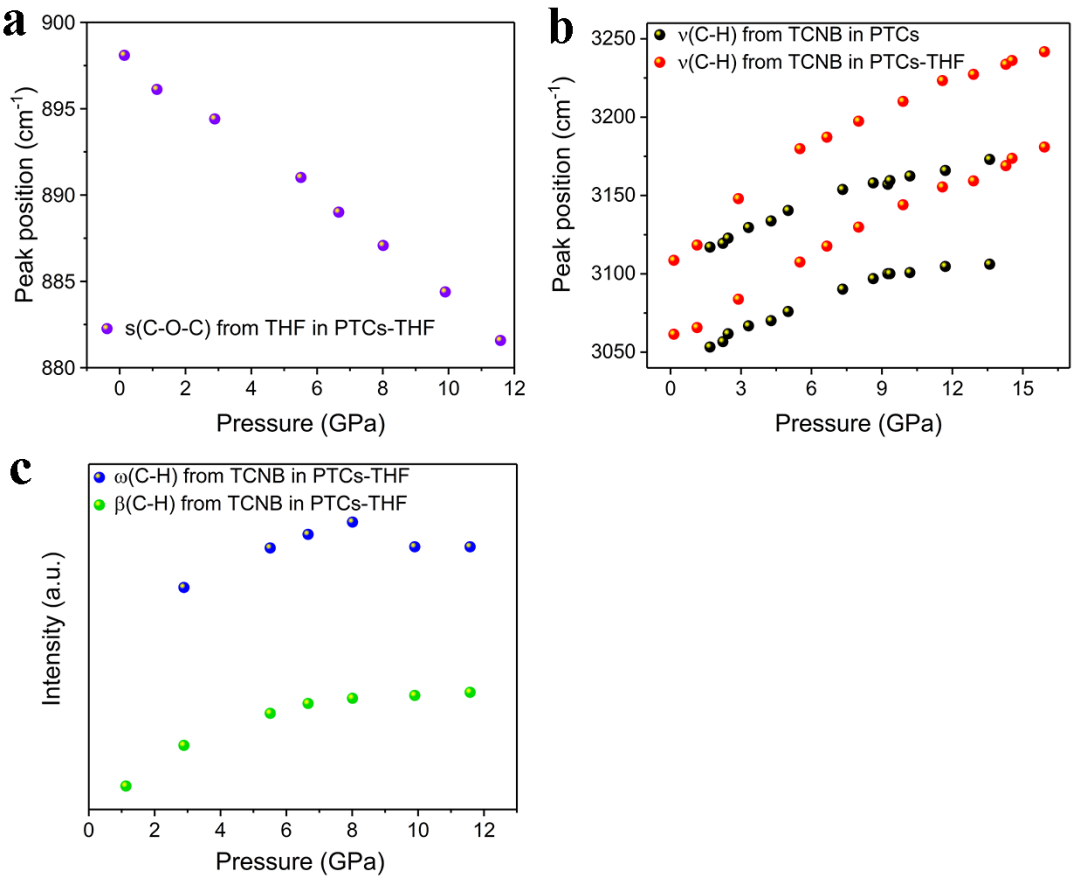
Supplementary Figure 2. Molecular packing of perylene-TCNB cocrystals (PTCs) perpendicular to the **a)** *a*-, **b)** *b*-, and **c)** *c*-axis.



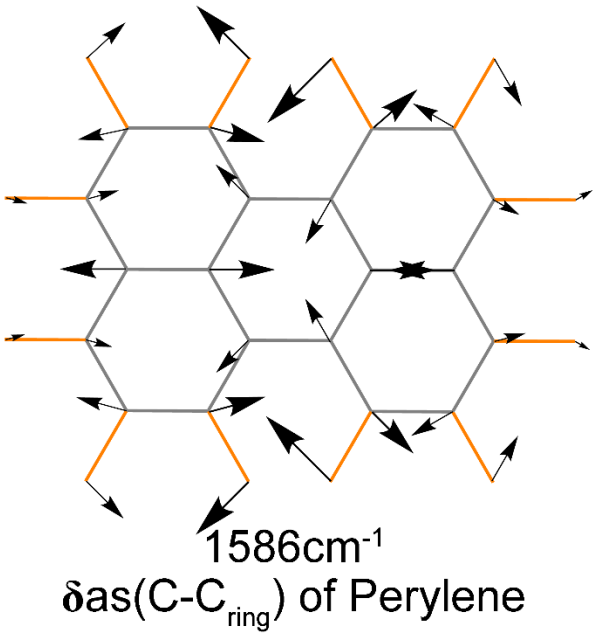
Supplementary Figure 3. a) PL spectra of PTCs under pressure up to 21.80 GPa. **b)** PL spectra of PTCs-THF up to 22.15 GPa. **c)** *In situ* UV-vis absorption spectra of PTCs-THF up to 20.24 GPa.



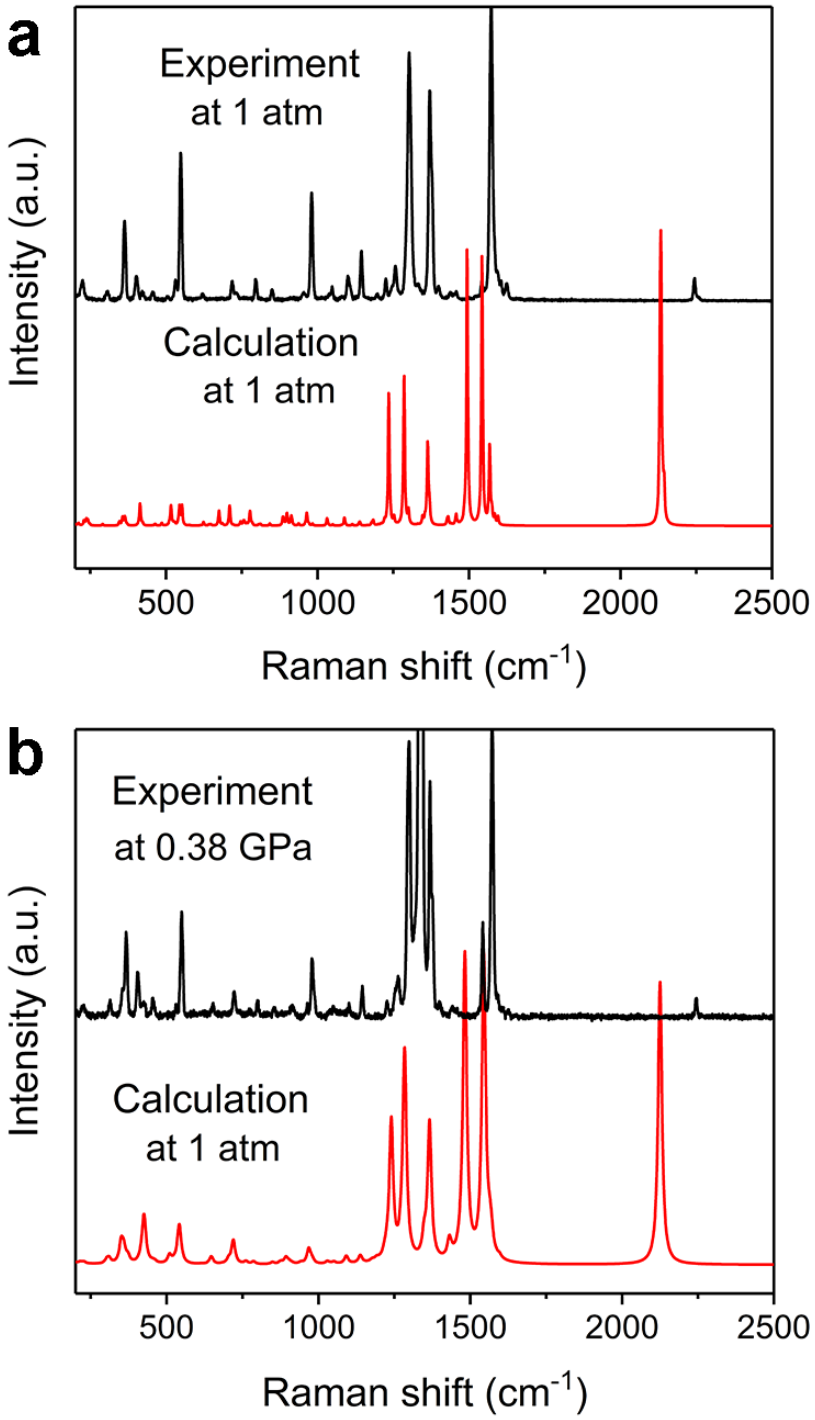
Supplementary Figure 4. a) Experimental (top) and calculated (bottom) IR spectra of PTCs. **b)** Experimental (top) and calculated (bottom) IR spectra of PTCs-THF.



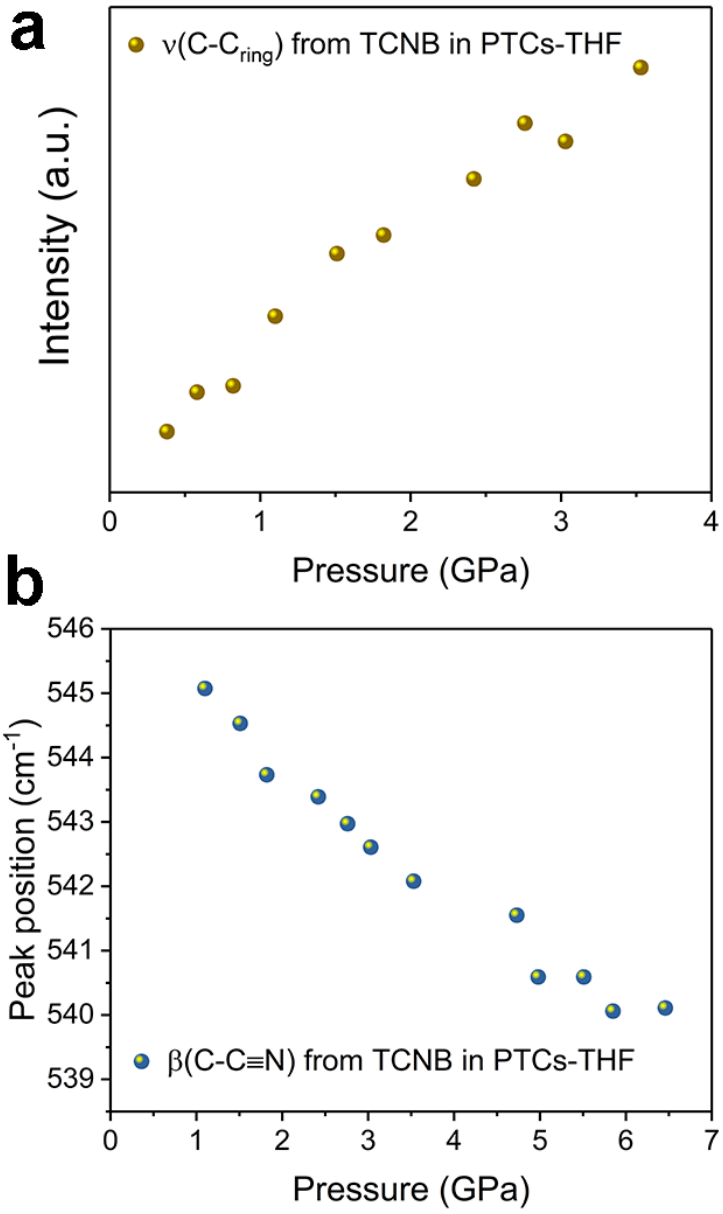
Supplementary Figure 5. The pressure dependence of the peak positions and intensities for some selected IR modes for PTCs-THF and PTCs. The pressure dependence of the peak position for **a)** C-O-C symmetrical stretching vibration s(C-O-C) from THF in PTCs-THF; **b)** C-H stretching vibration ν(C−H) from TCNB; **c)** the pressure dependence of peak intensity for C-H wagging vibrations ω(C-H) and C-H bending vibrations β(C-H) from TCNB in PTCs-THF.



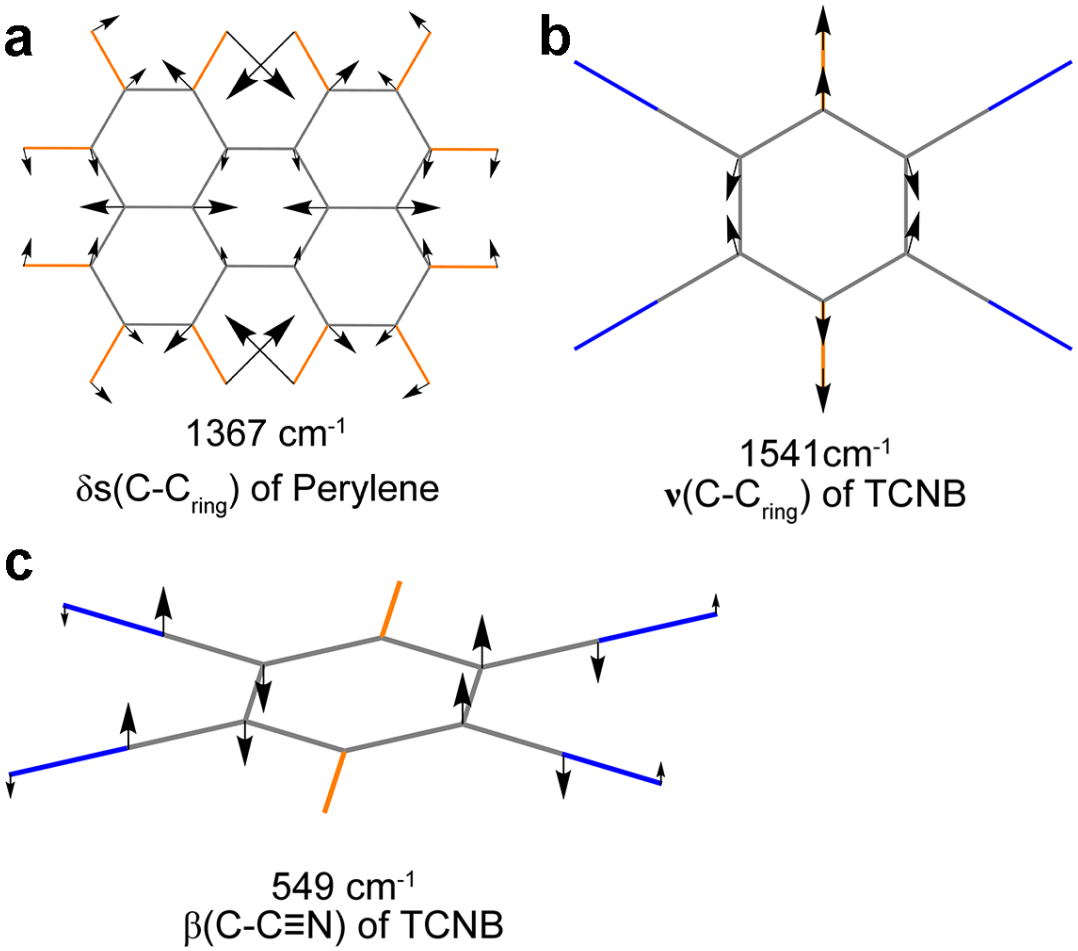
Supplementary Figure 6. The IR vibration at 1586 cm^{-1} is from the asymmetrical deformation vibrations δas(C-C_{ring}) of perylene. The size of the arrow represents the amplitude of the vibration.



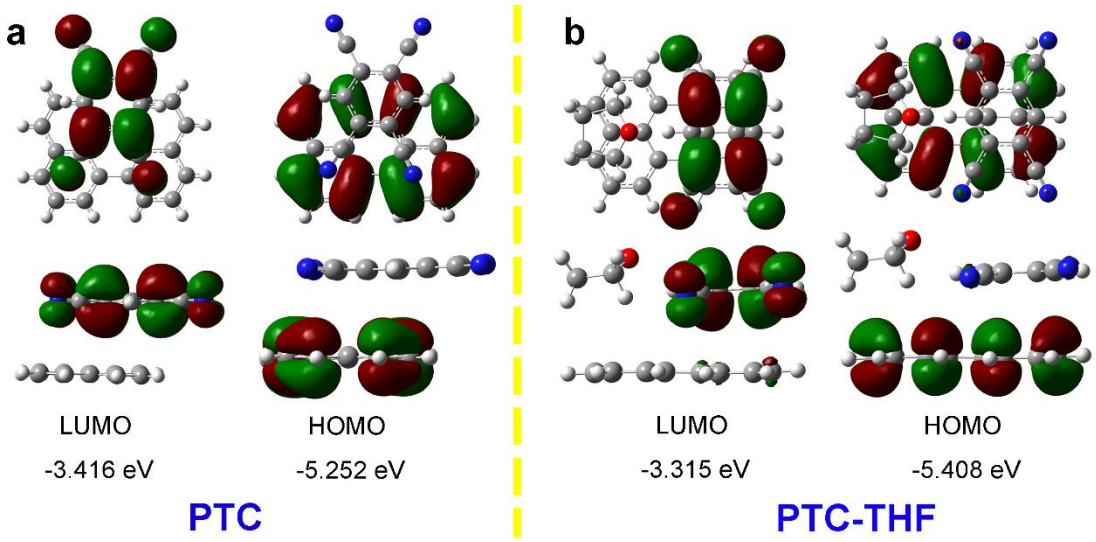
Supplementary Figure 7. a) Experimental (top) and calculated (bottom) Raman spectra of PTCs. **b)** Experimental (top) and calculated (bottom) Raman spectra of PTCs-THF.



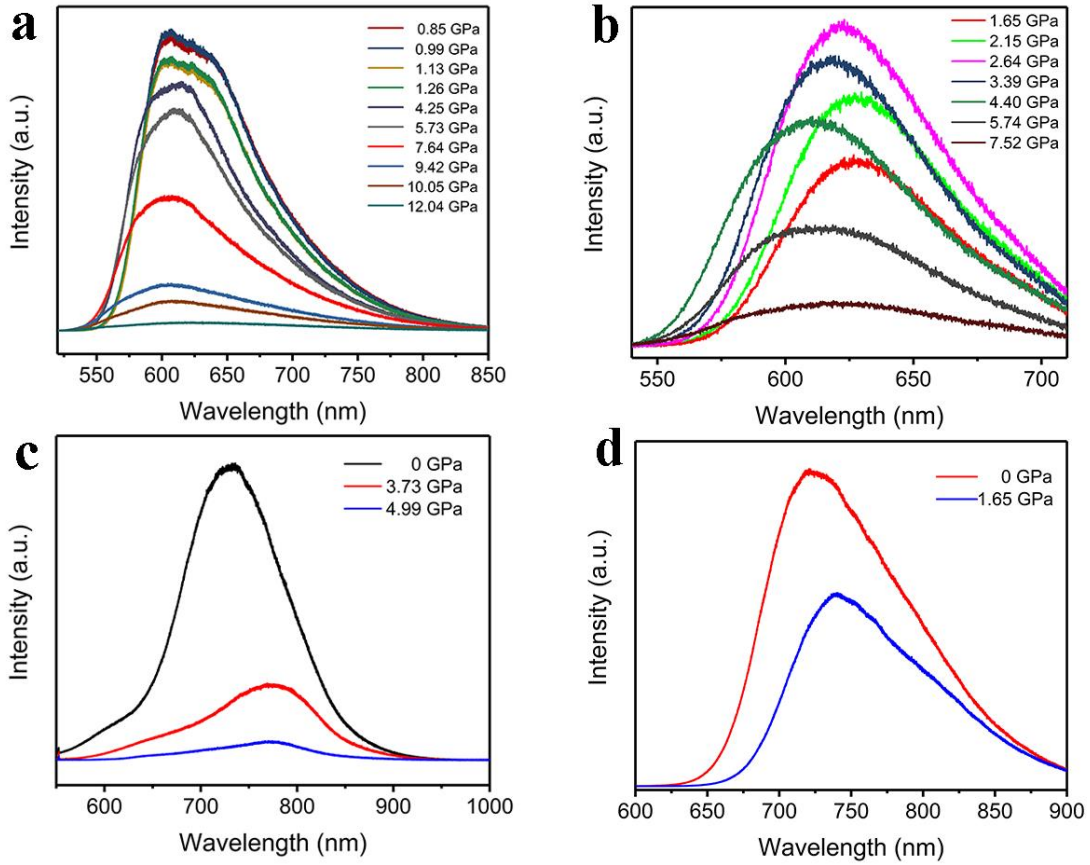
Supplementary Figure 8. The pressure dependence of the peak positions and intensities for some selected Raman modes of PTCs-THF. The dependence of **a)** peak intensity for the carbon ring stretching vibration ν(C-C_{ring}), and **b)** peak position for the C-C≡N in-plane bending vibration β(C-C≡N) from TCNB.



Supplementary Figure 9. The sketch maps for the Raman vibrations. **a)** the symmetrical deformation vibrations δs(C-C_{ring}) of perylene at 1367 cm^{-1}; **b)** the carbon ring stretching vibration ν(C-C_{ring}) of TCNB at 1541 cm^{-1}; **c)** out-of-plane bending vibration β(C-C≡N) of TCNB at 549 cm^{-1}. The size of the arrow represents the amplitude of the vibration.



Supplementary Figure 10. Frontier orbital diagrams of the **a)** PTC and **b)** PTC-THF calculated by the density functional theory (DFT) method at B3LYP/6-31G (d, p).



Supplementary Figure 11. PL spectra of perylene-TCNB cocrystals soaked in **a)** 1,4-dioxane, **b)** pyridine, **c)** CCl_4 and **d)** m-xylene.