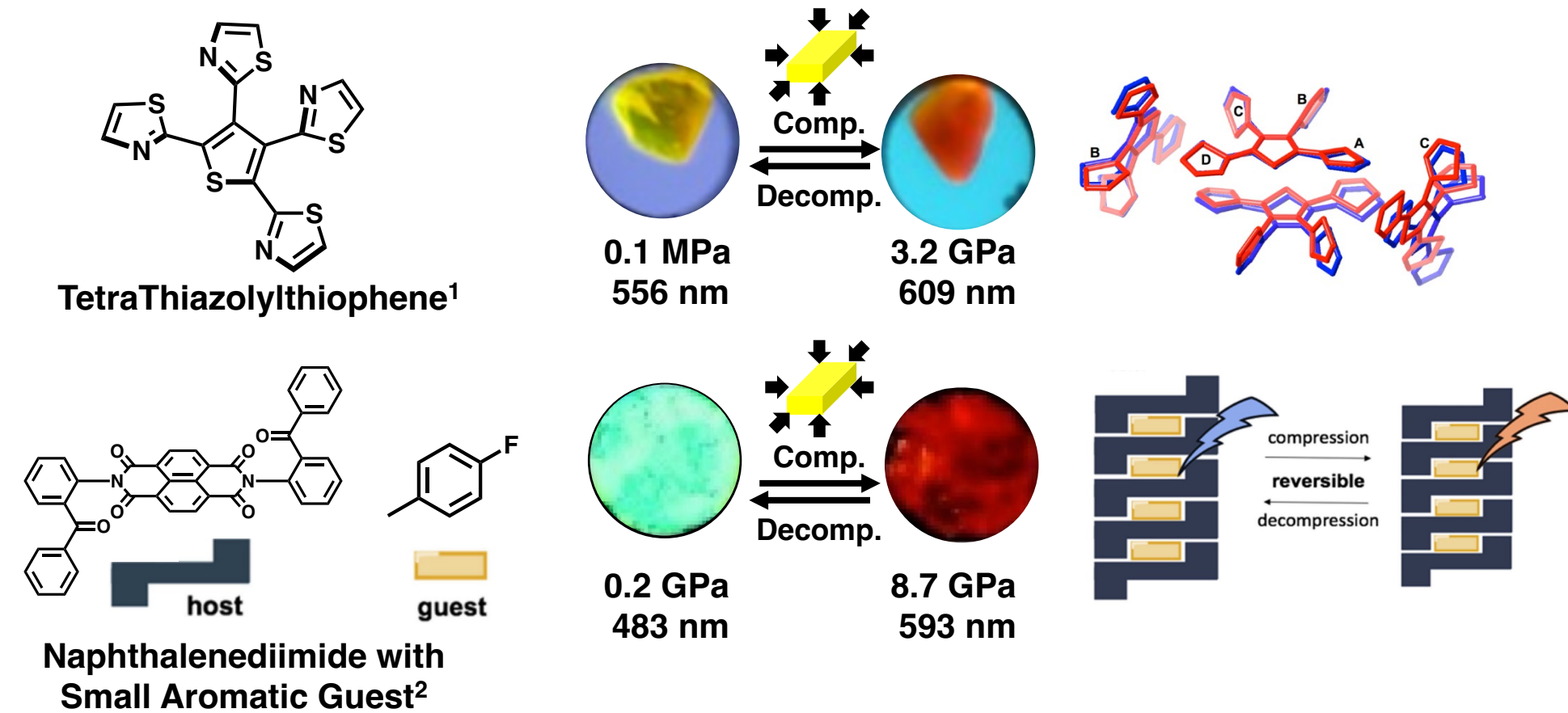


Crystal Structure and Piezofluorochromism of Organoboron Complexes with the [2.2]Paracyclophane Moiety

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Introduction

- Piezofluorochromism (PFC)
 - Reversible FL Color Changes in Response to **Isotropic Pressure**



The **Intermolecular** π - π Interaction is a Key Factor for Efficient PFC.

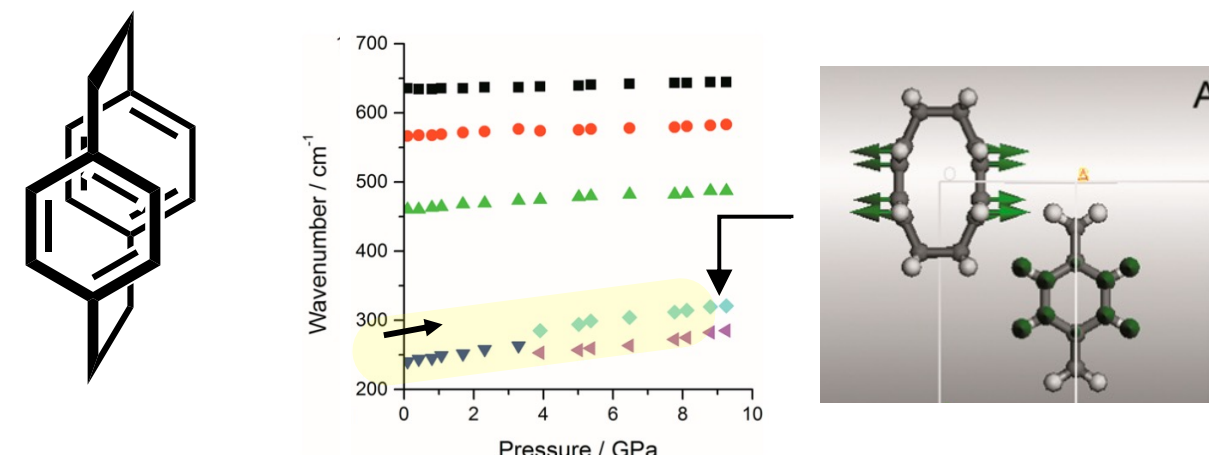
➔ What about the Case of PFC by **Intramolecular** π - π Interaction?

[1] Nagura, K.; Saito, S.; Yamaguchi, S. *et al.* *J. Am. Chem. Soc.* 2013, 135, 10322–10325.

[2] Ono, T.; Hiseada, Y. *et al.* *ChemPhotoChem* 2018, 2, 416–420.

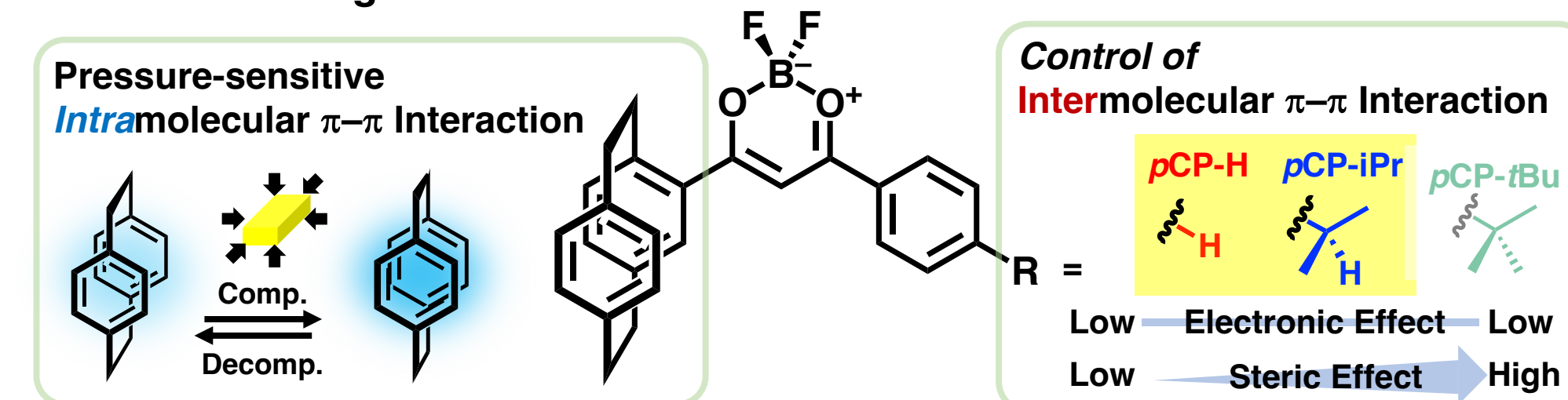
This Work

- [2.2]Paracyclophane
 - Ring-shaped Compound Bridged by Methylene Chains at *p*-Positions
 - Intramolecular** π - π Interaction Which is Sensitive to Pressure³



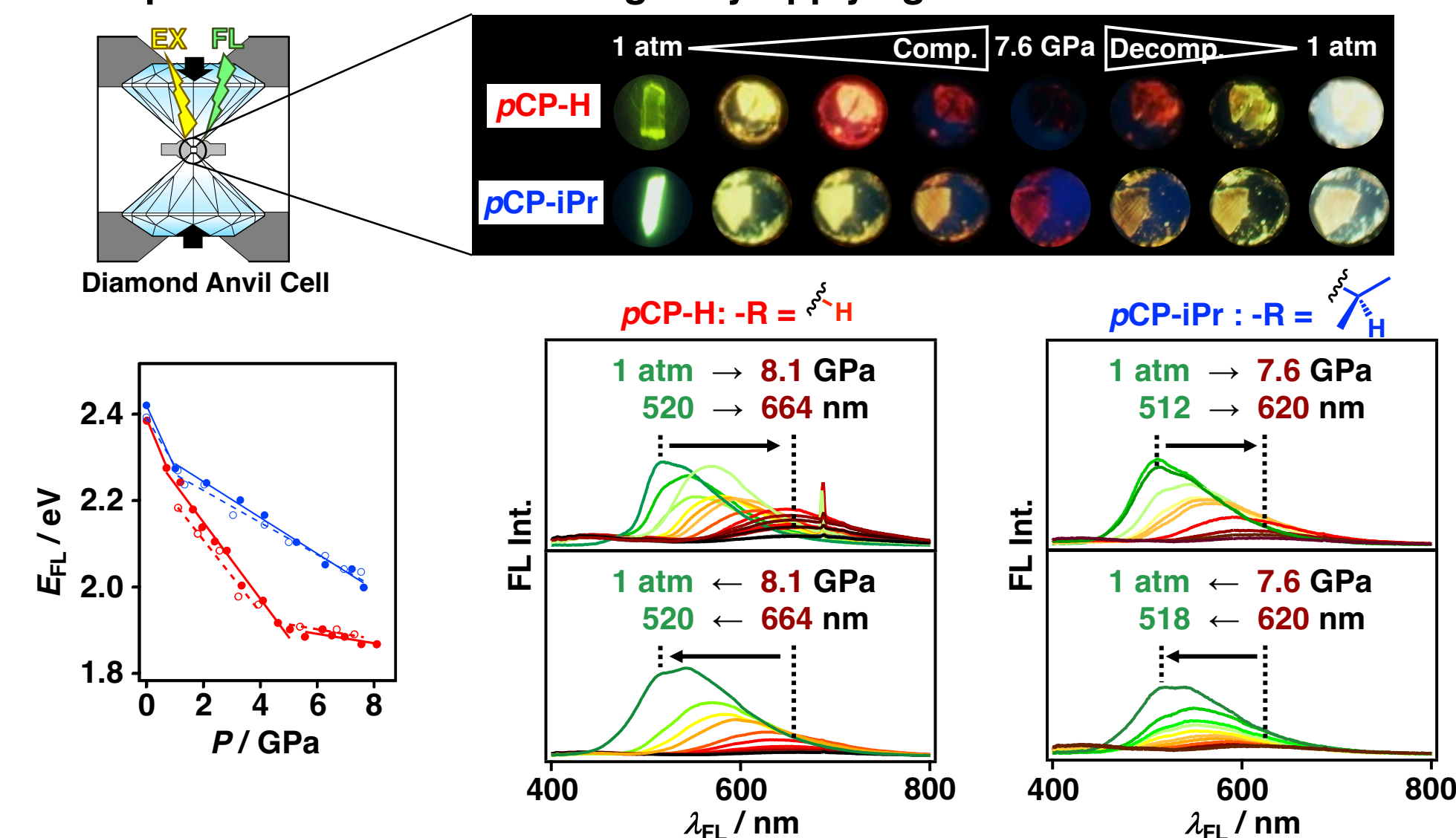
➔ Can It Work as the Pressure-sensitive Moiety?

- Molecular Design



FL Properties of Crystals under High Pressure

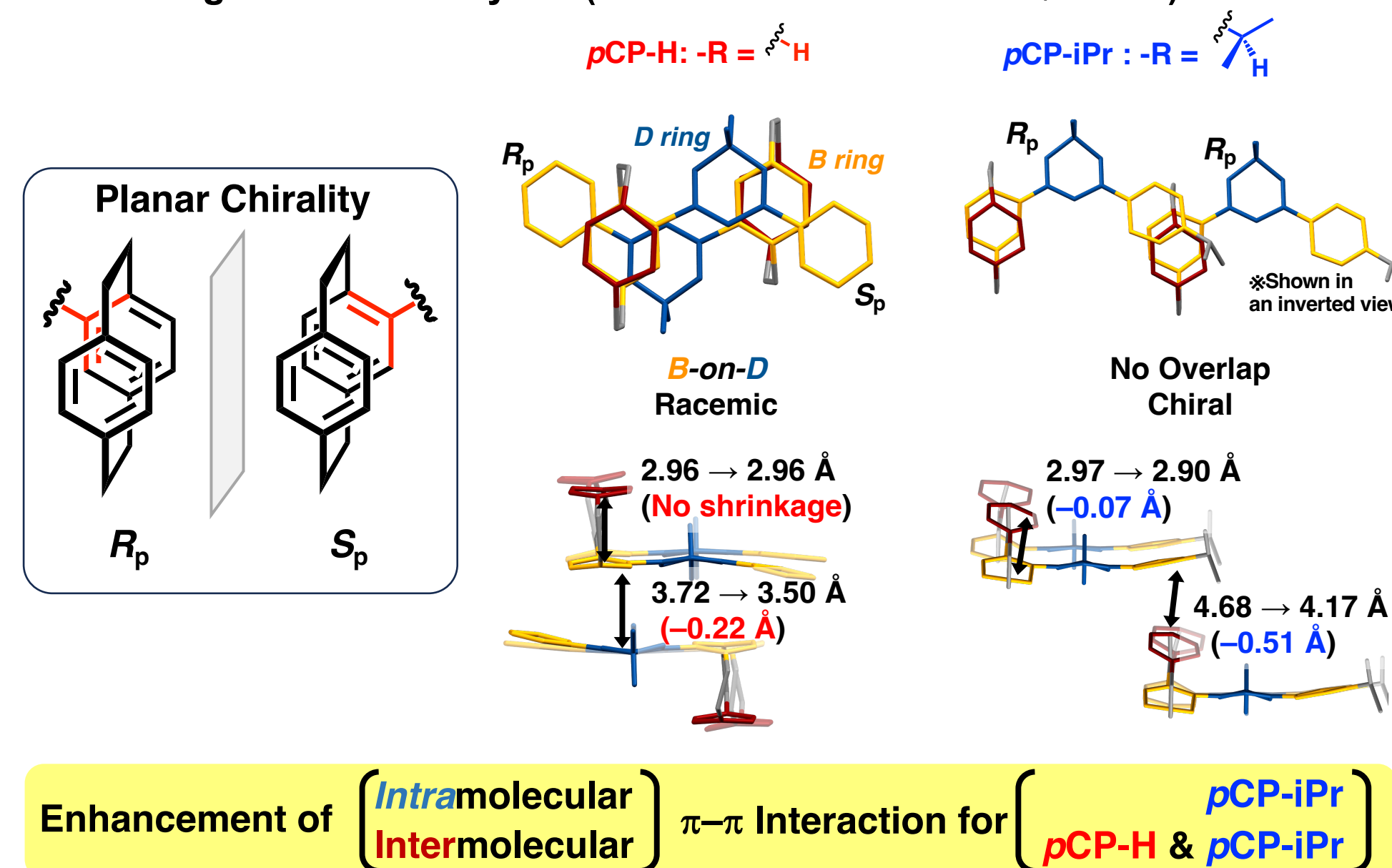
- FL Spectra and FL Color Changes by Applying Pressure



Remarkable PFC with Different Pressure-sensitivity Each Other

Crystal Structures under Atm. and High Pressure

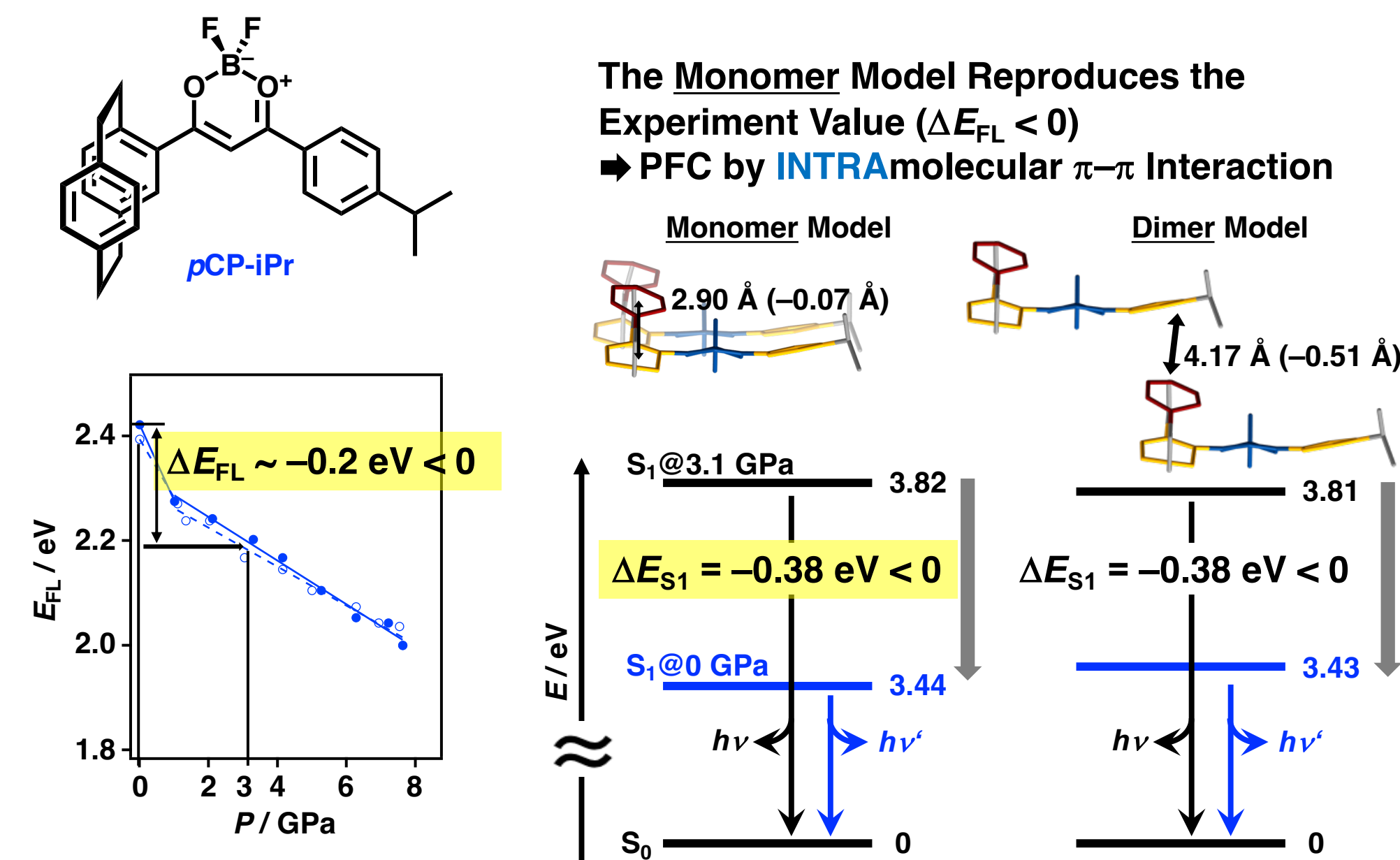
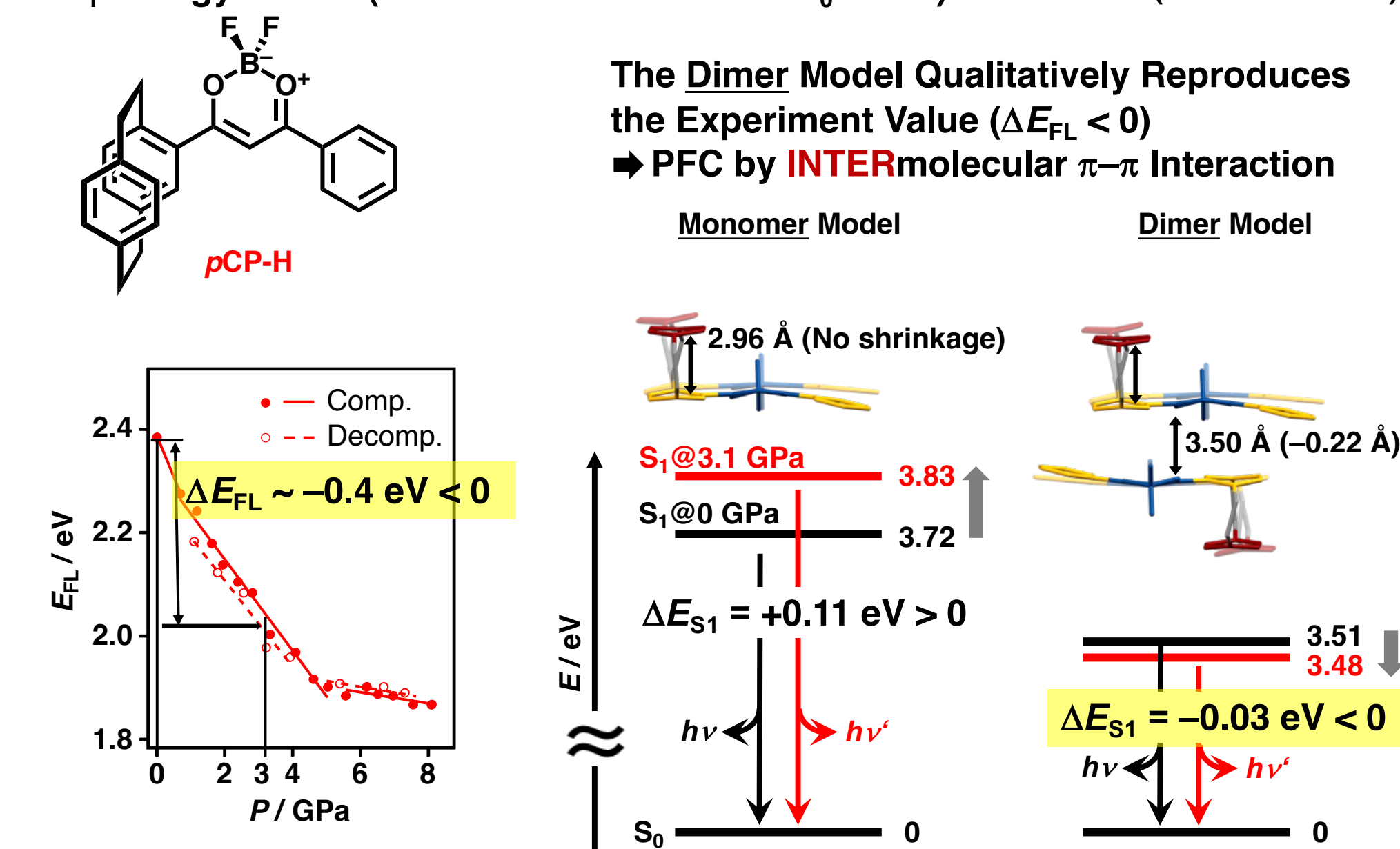
- π -Stacking Manners in Crystal (at Atm. Press. and 3 GPa, 293 K)



TD-DFT Calculation Using Crystal Structures

- S_1 Energy Levels (Relative Values to Each S_0 Level)

(ω B97XD/6-31G**)

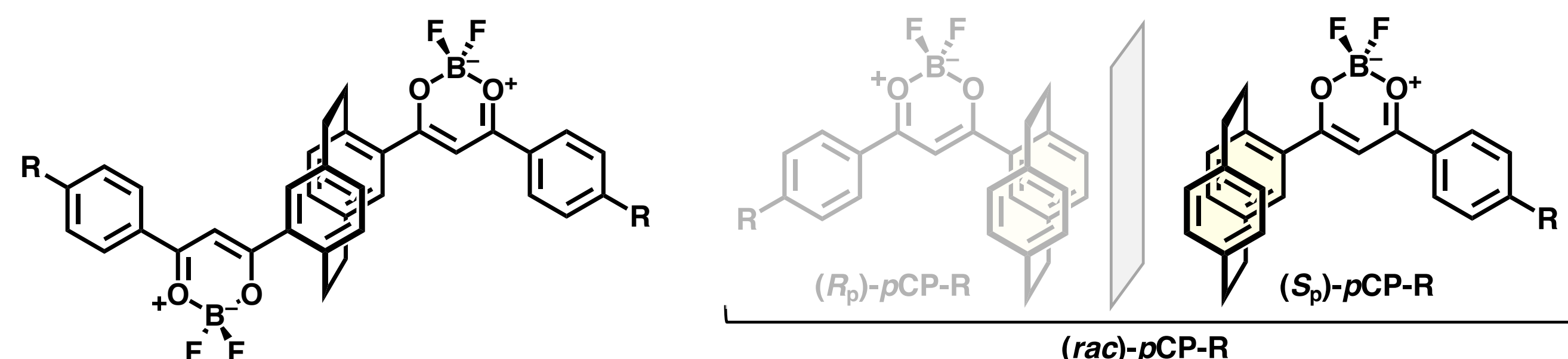


Conclusion

- pCP-H (racemic):** PFC by **Intermolecular** π - π Interaction Changes
- pCP-iPr (chiral):** ➔ **Higher/Lower** Pressure-sensitivity of FL

[2.2]Paracyclophane Can Work as the Pressure-sensitive Moiety!

Future Work (in Progress)



- Acknowledgements
 - FL Measurements under High Pressure: Prof. Masaaki Abe and Group Members (Grad. Sch. of Sci., Univ. of Hyogo)
 - X-ray Crystallographic Analyses under High Pressure: Dr. Hiroyasu Sato (Rigaku)

- Publications
 - Irii, S.; Ikeda, H. *et al.* *Tetrahedron Lett.* 2022, 101, 153913.
 - Irii, S.; Ikeda, H. *et al.* *J. Mater. Chem. C* 2025, in Press., DOI:10.1039/D5TC03195H.