

Effective passivation of quasi-2D perovskites enabled by π -conjugated planar molecules

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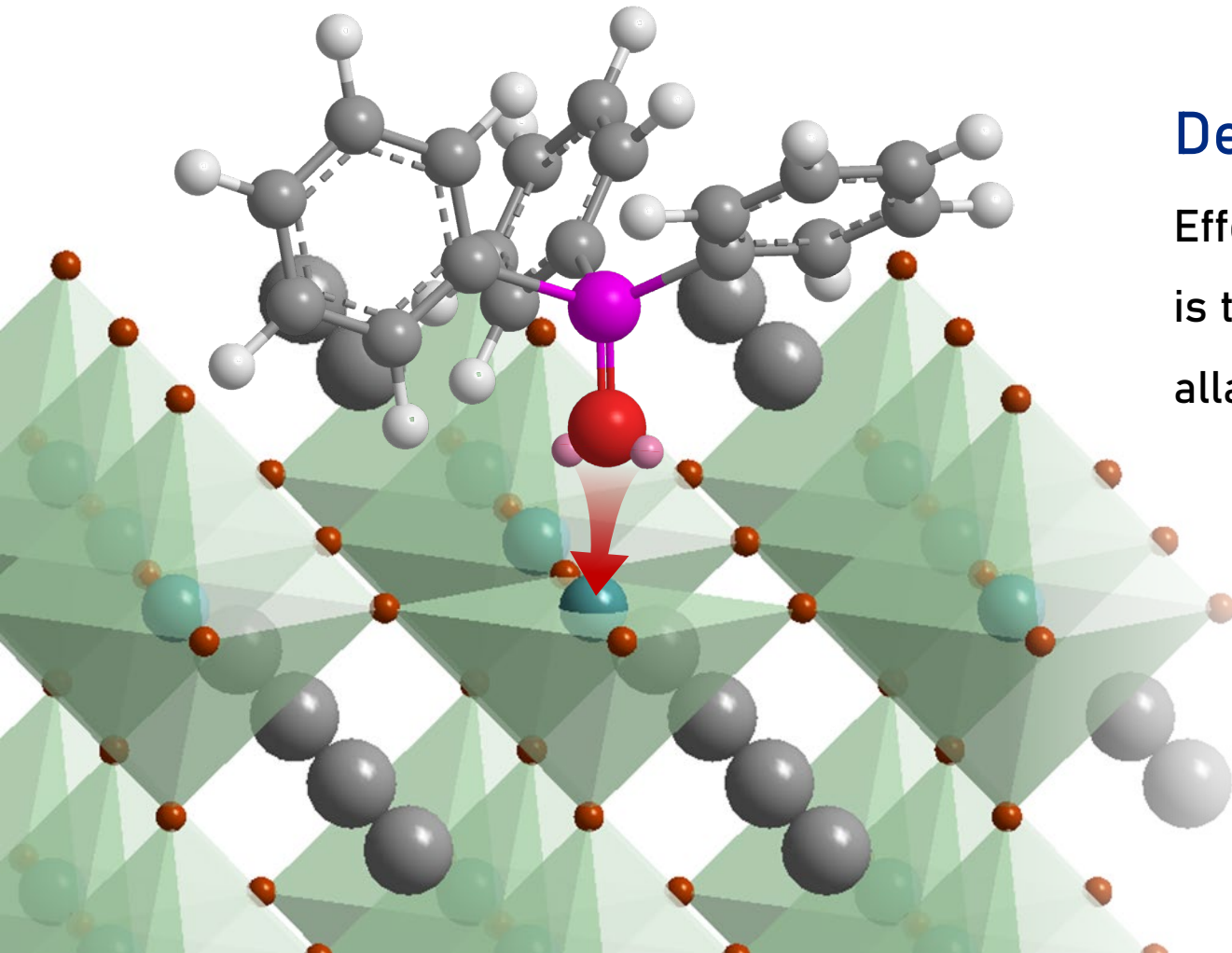
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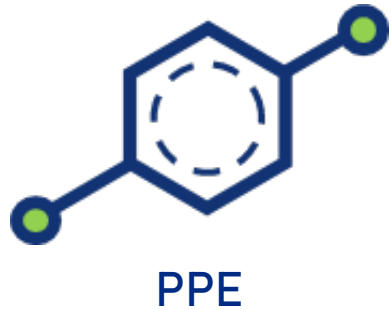
Introduction



Defect passivation

Effective passivation of the undercoordinated Pb^{2+} ions is the quintessential priority to boost stability and to allay non-radiative recombination of an exciton

Introduction



Problem

- Recently, owing to their excellent carrier mobility, passivating agents with π -conjugation have been highlighted as flawless alternatives.
- However, there have not been general rules for anticipating the passivation capability of a planar molecule

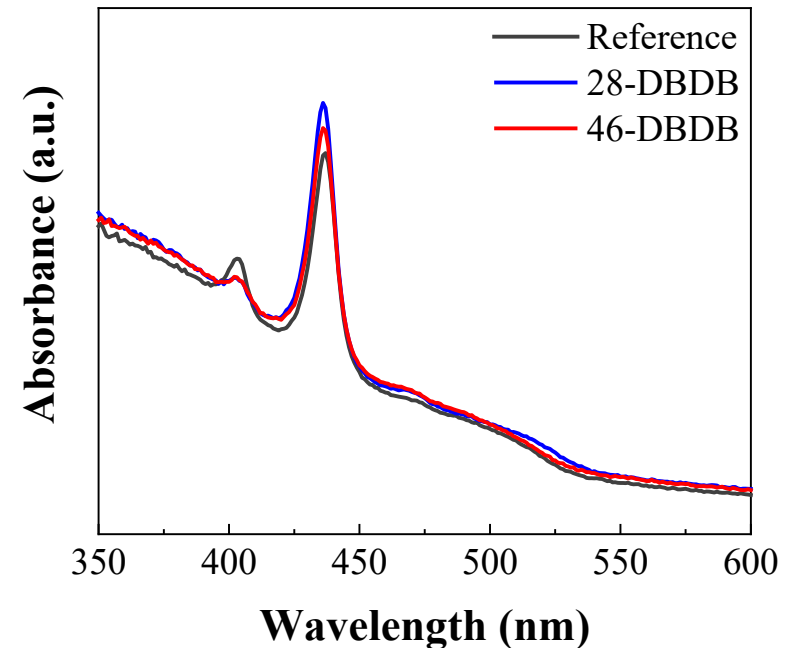
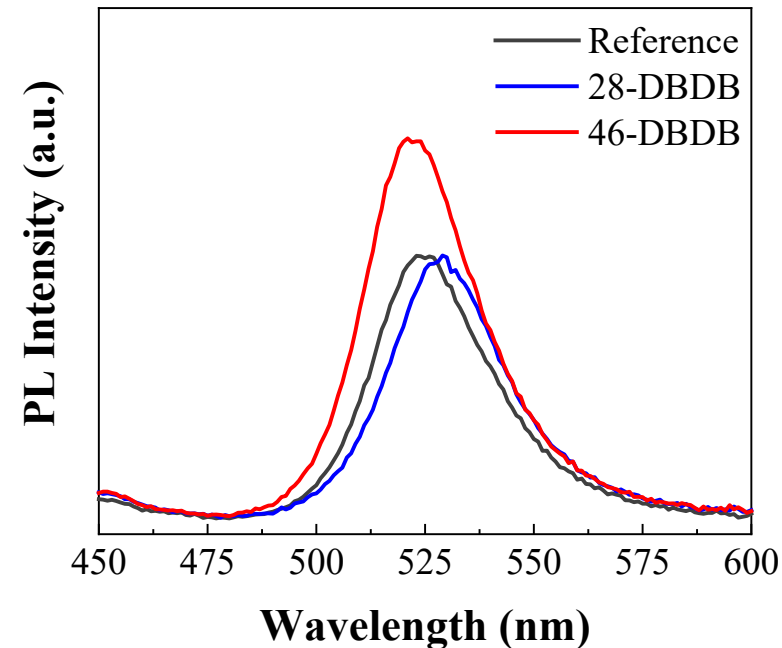
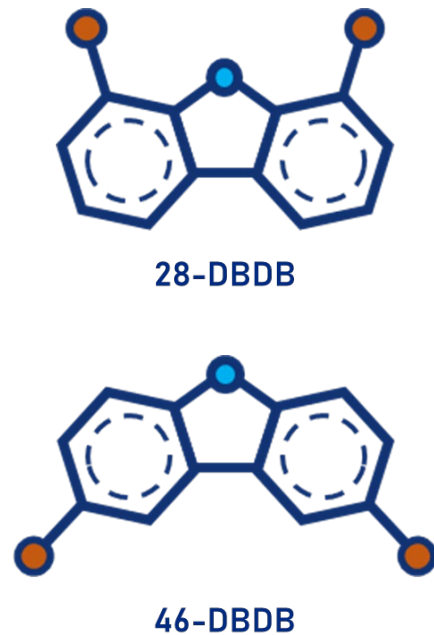
Goal

This work aims to reveal the design strategy of planar molecules that may exhibit good passivating capability, thereby enabling efficacious discovery

Isomer-based investigations

Observation

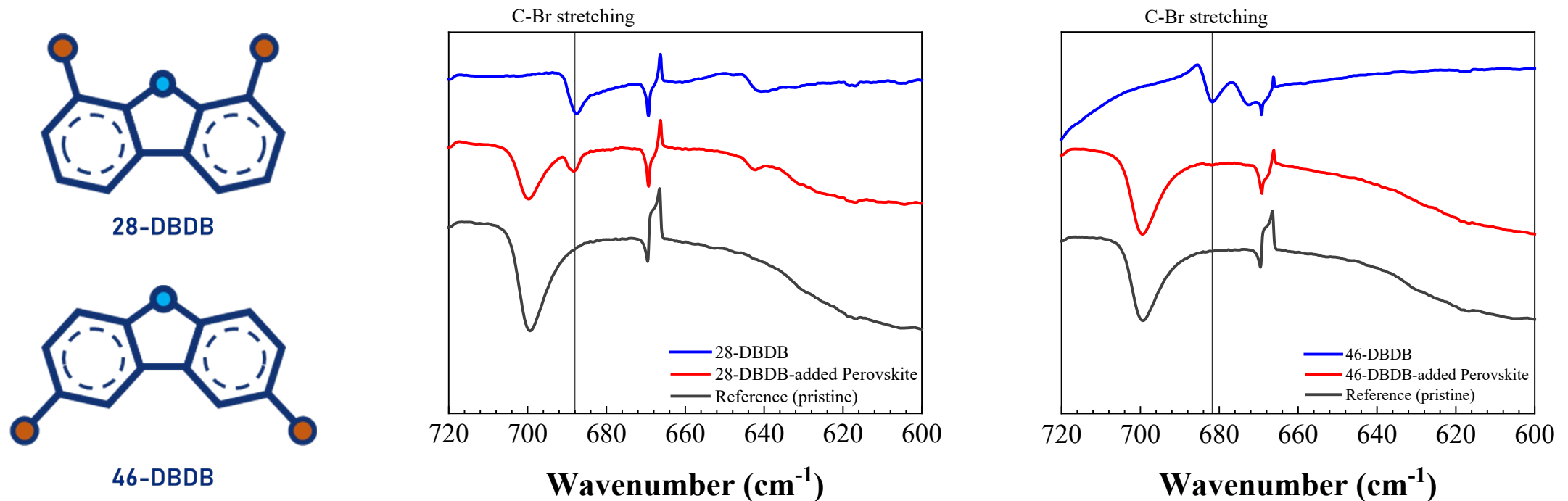
Photoluminescence intensity was increased upon 46-DBDB treatment and changed diminutively upon 28-DBDB addition while absorption spectra showed marginal change.



Isomer-based investigations

Observation

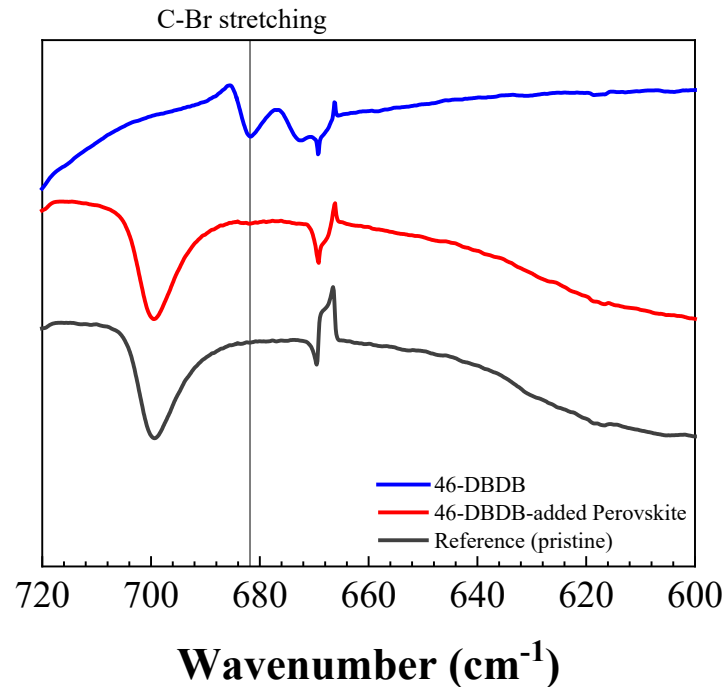
46-DBDB in perovskite film showed diminished C-Br stretching peak intensity compared to the pure molecule while 28-DBDB in perovskite film showed the same absorption profile as the molecule *per se*



Isomer-based investigations

Observation

The C-Br peak of the 46-DBDB molecule disappears when it comes into quasi-2D perovskite



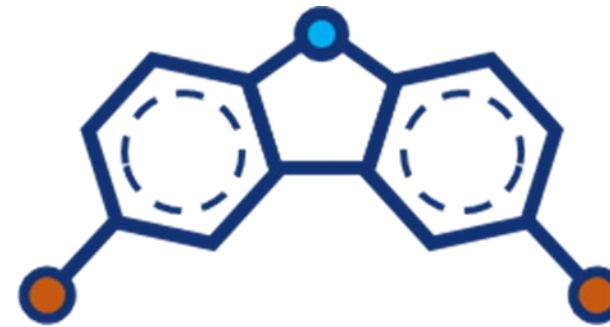
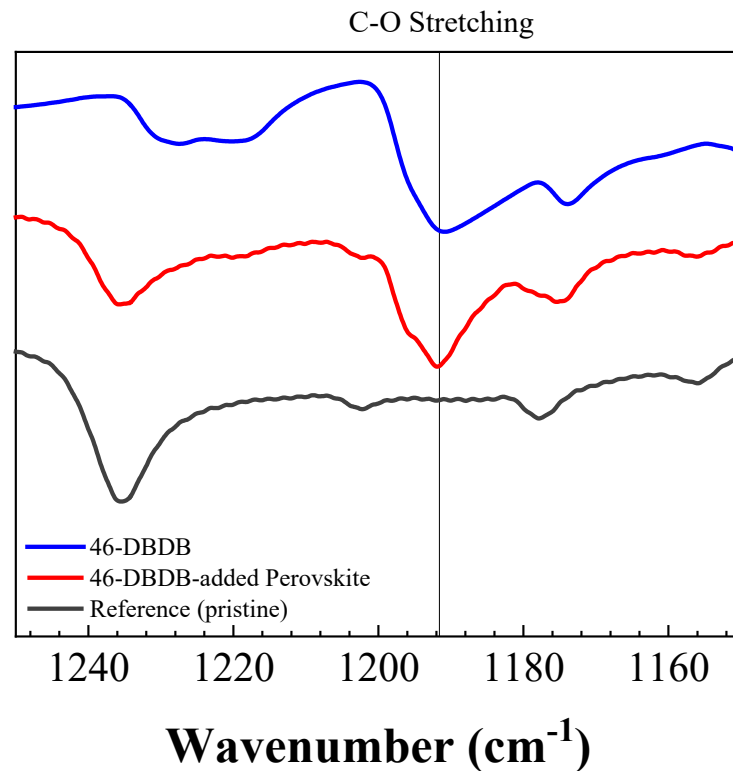
Hypotheses

1. 46-DBDB somehow was not included in the perovskite film
2. 46-DBDB underwent hydrolysis and *in-situ* furnished HBr molecules.
3. 46-DBDB effectively passivated halide vacancies in the film

Isomer-based investigations

Hypothesis 1

46-DBDB somehow was not included in the final perovskite film

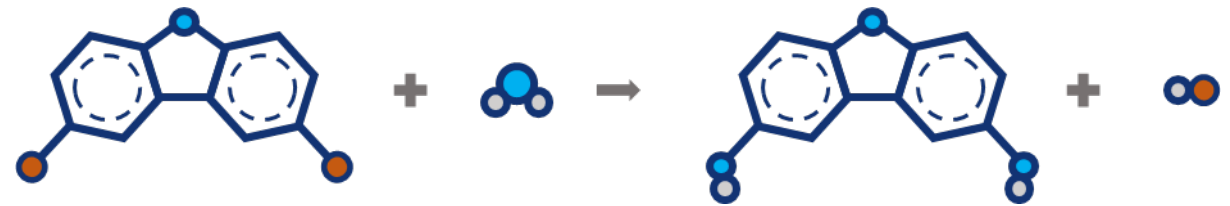
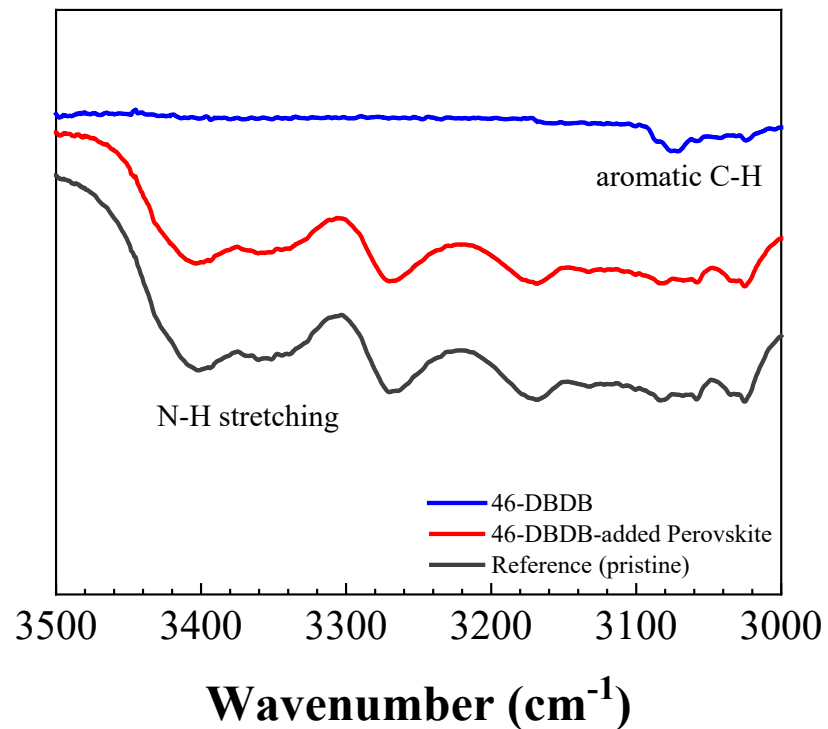


46-DBDB

Isomer-based investigations

Hypothesis 2

46-DBDB underwent hydrolysis and lose C-Br bonding



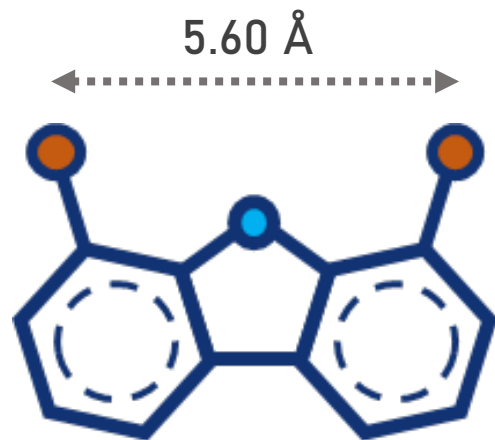
- In general, aromatic sp² C-Br hardly undergoes hydrolysis
- No O-H peak was observed

→ Structural change in the 46-DBDB would be negligible

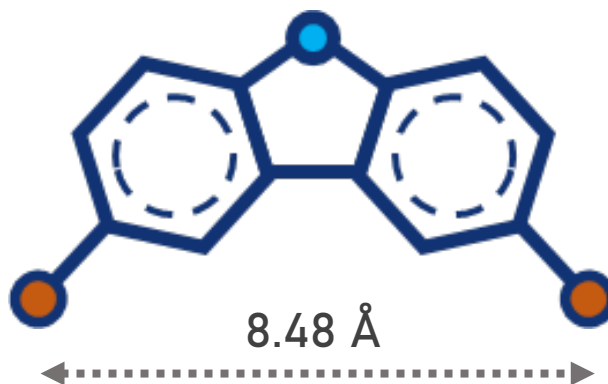
Mechanistic scrutinization

Proposition 1

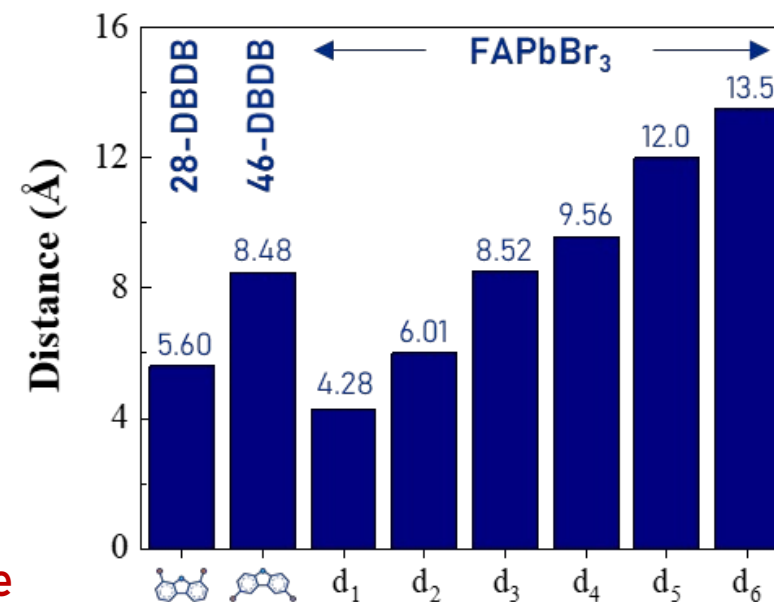
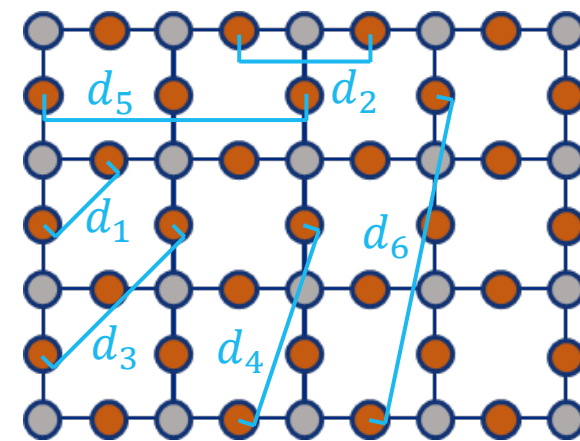
Ascended PL intensity is attributed to the geometrical effect.



28-DBDB



46-DBDB



→ The geometrical effect is insufficient to fully explain the difference

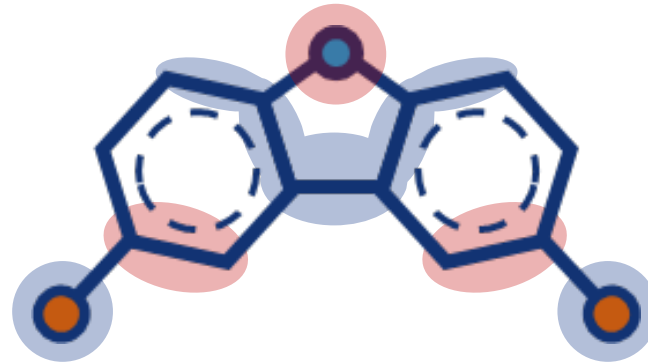
Mechanistic scrutinization

Proposition 2

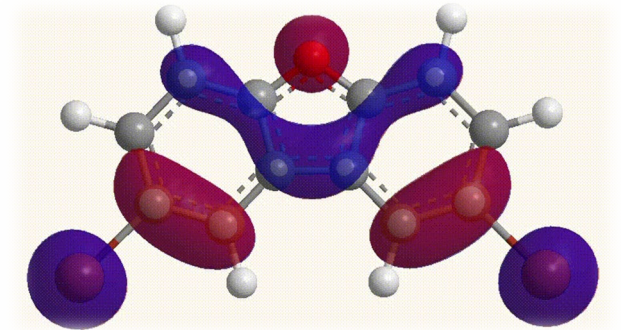
Potential passivating moieties should contribute to the HOMO of the molecule.



28-DBDB



46-DBDB



Mechanistic scrutinization

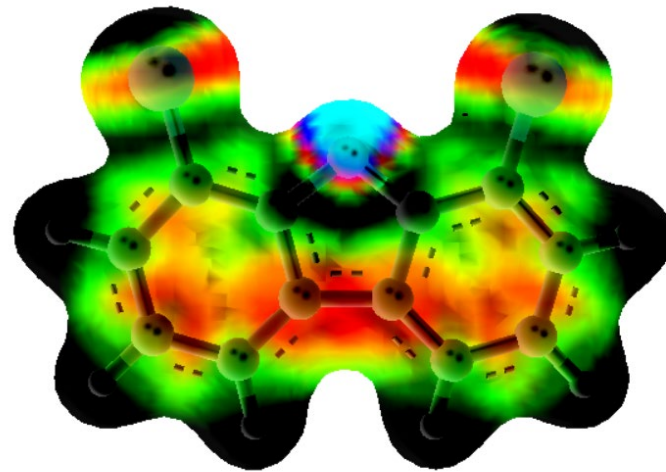
Alternative explanation

Electrostatic potential (ESP) would play a crucial role in passivation capability

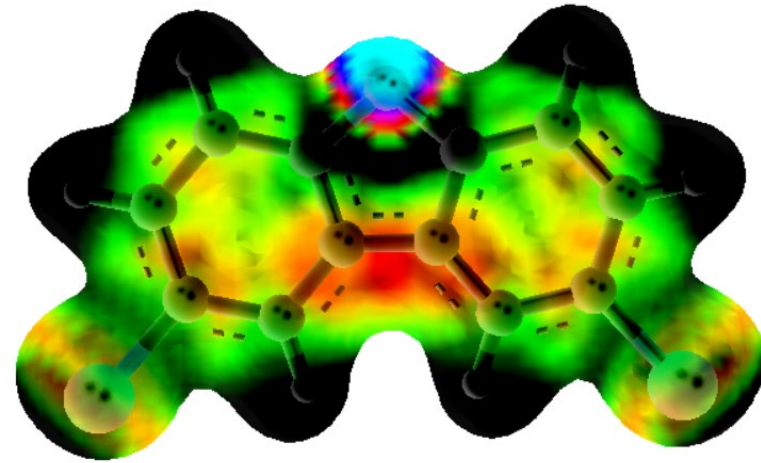
Positive



Negative



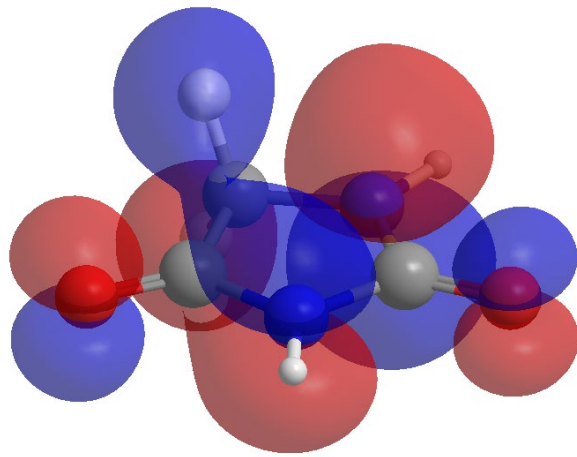
28-DBDB



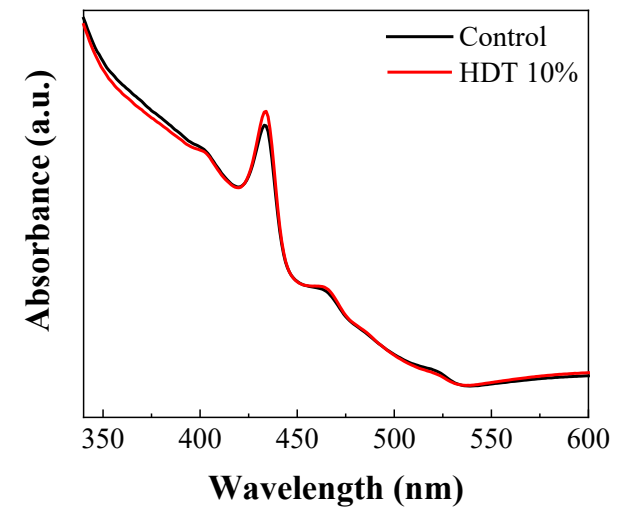
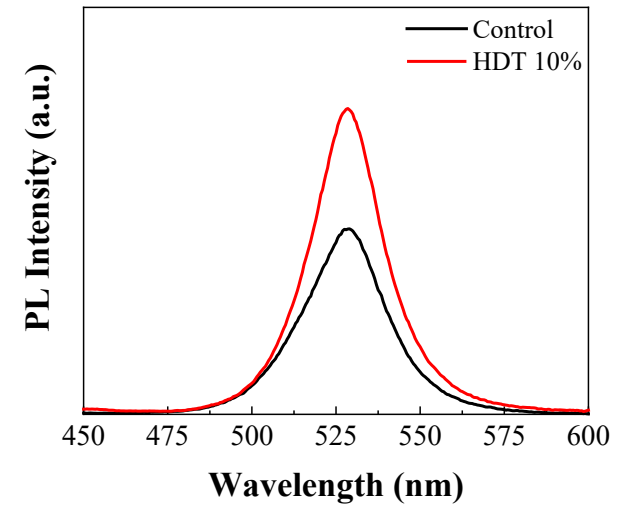
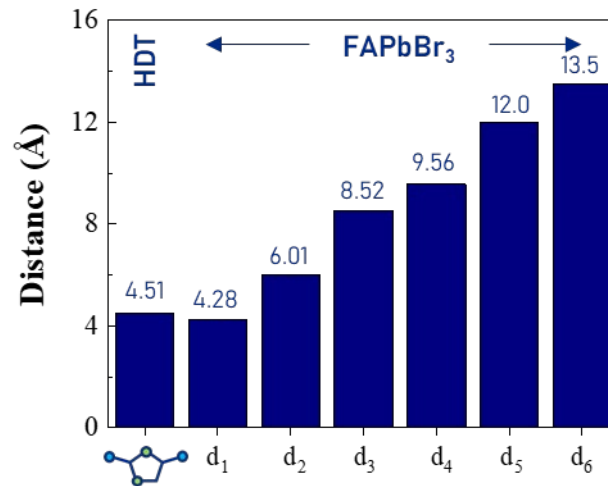
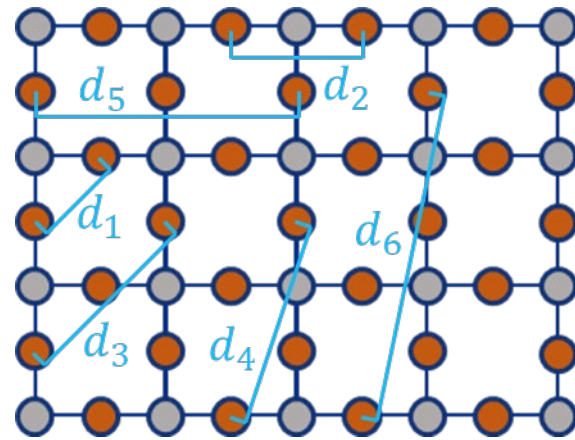
46-DBDB

→ The ESP-based narrative cannot duly explain the superiority of the 46-DBDB over the 28-DBDB

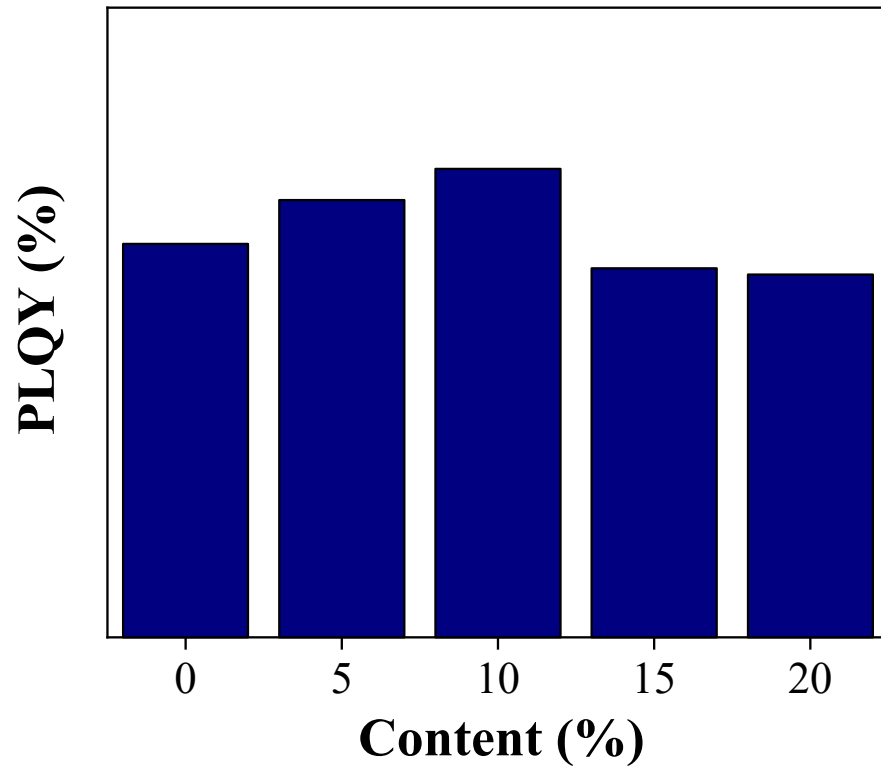
HDT demonstration



4.51 Å



One more thing: Additive amount



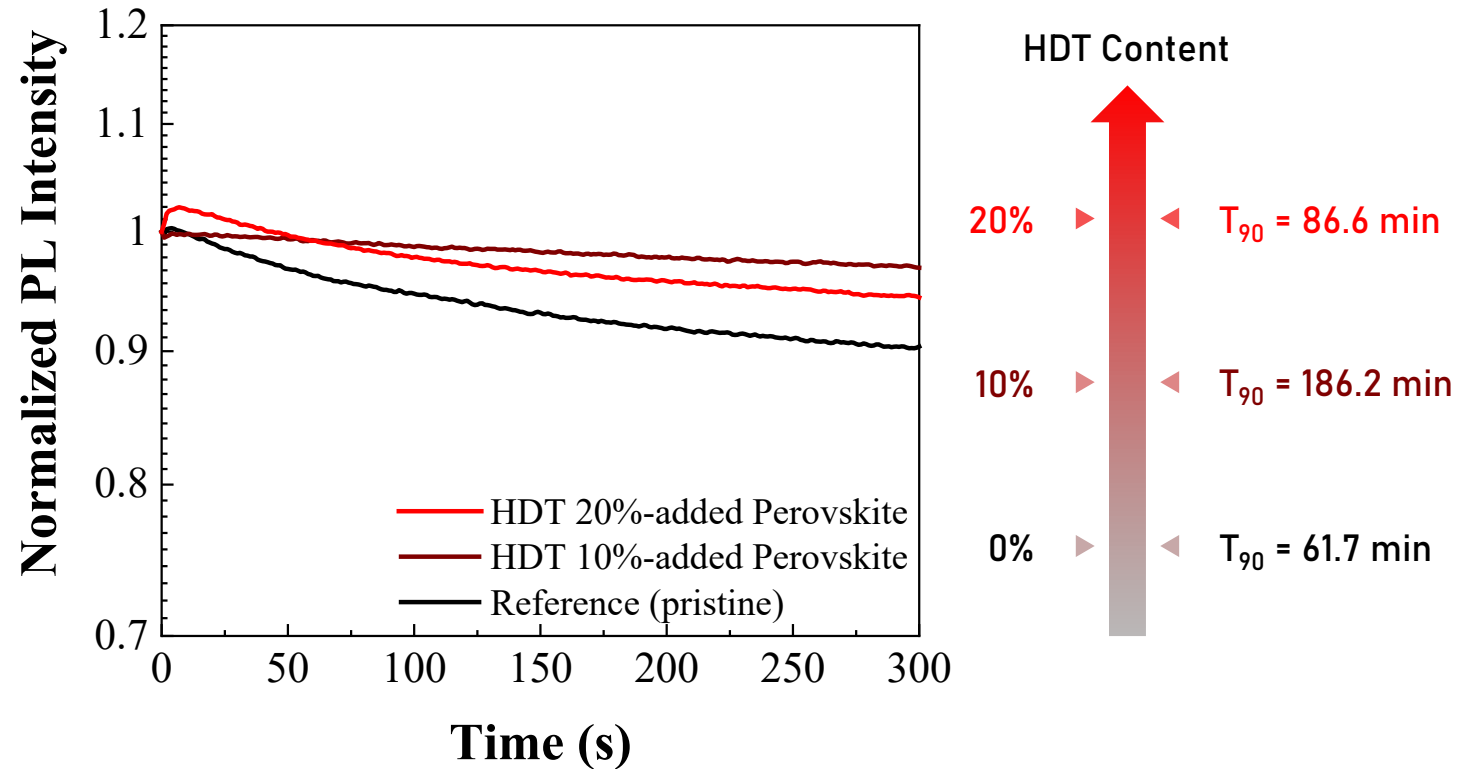
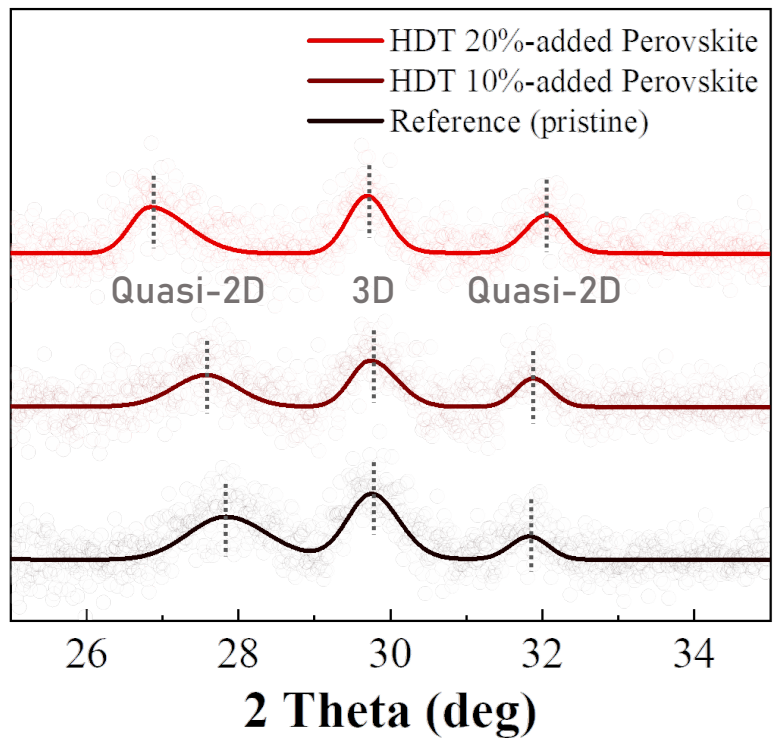
Observation

- There exists a 'HDT content window'
- Under excess HDT content, the passivation effect was compensated by other factor(s)

One more thing: Additive amount

Observation

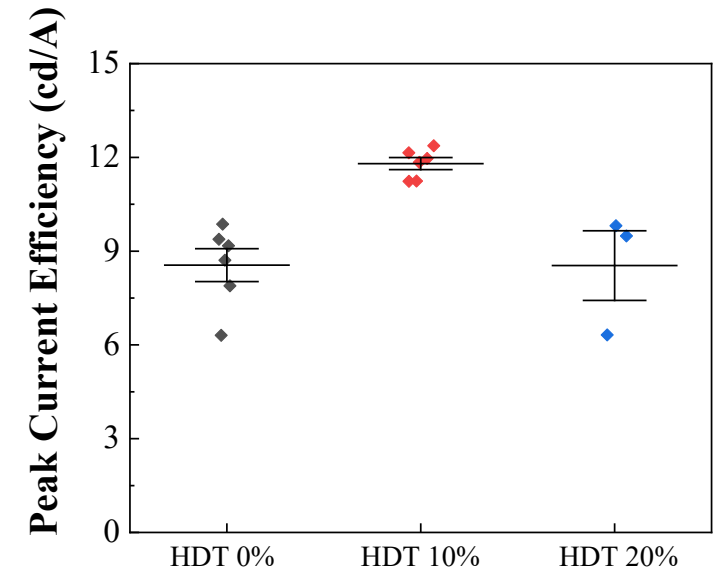
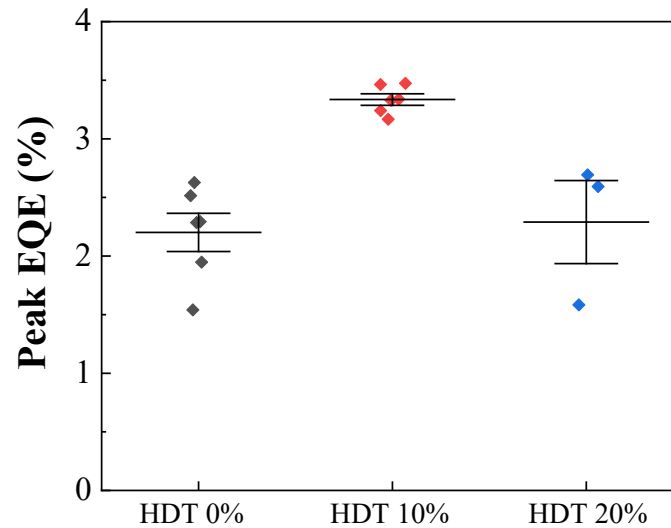
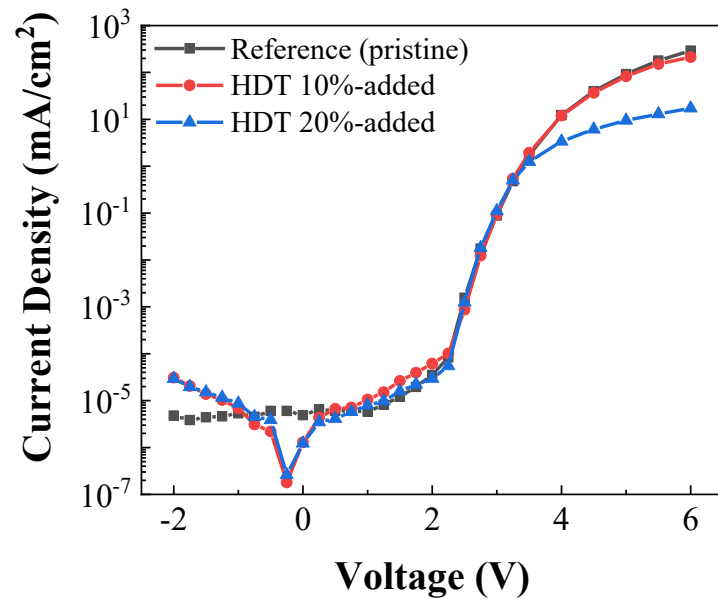
Excess HDT aggravated structural homogeneity and ultimately resulted in stability mitigation



Device demonstration

Observation

Excess HDT aggravated the performance of light-emitting diodes



Conclusion

Effective passivation with planar molecules would require the following:

- HOMO located at the atoms that may interact with the perovskite surface
- Those atoms spaced by the proper distance dictated by the crystal structure
- An appropriate amount that would not damage the structural integrity

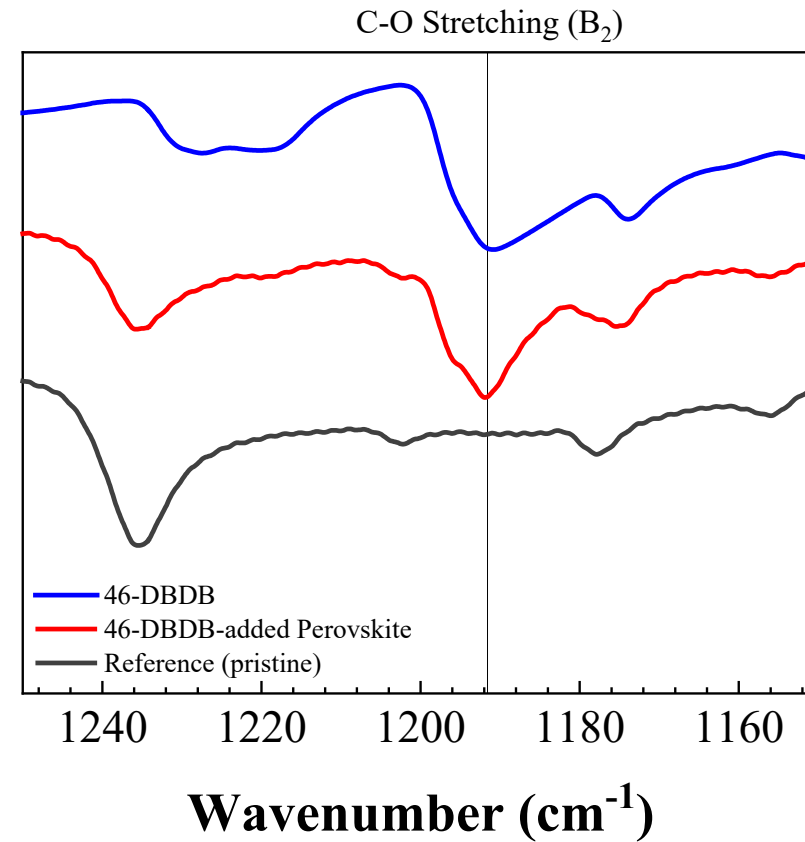
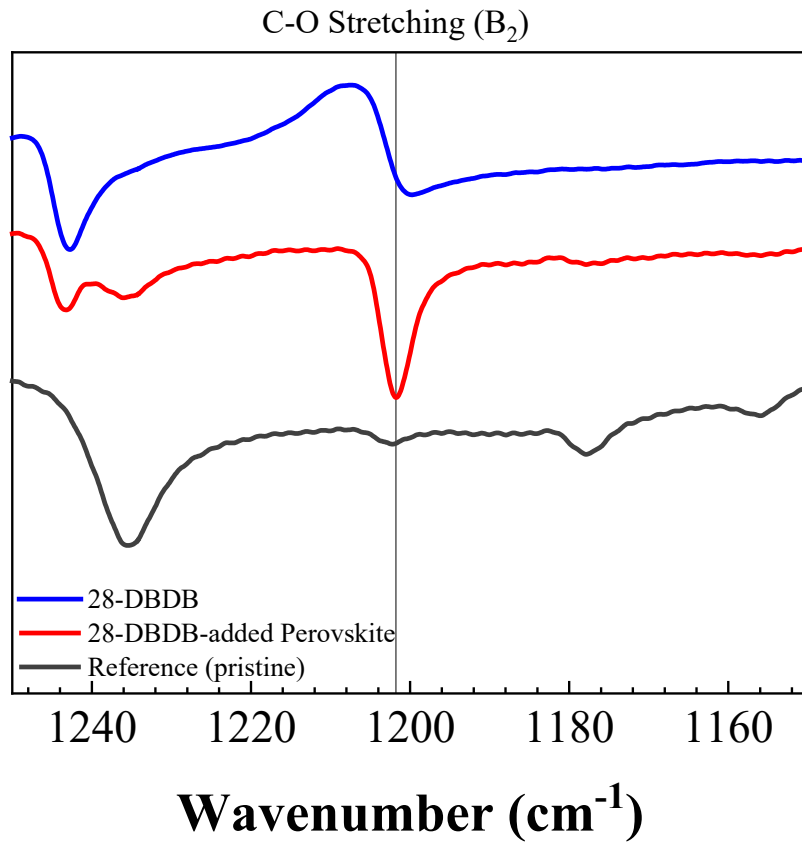
Thank you for your attention

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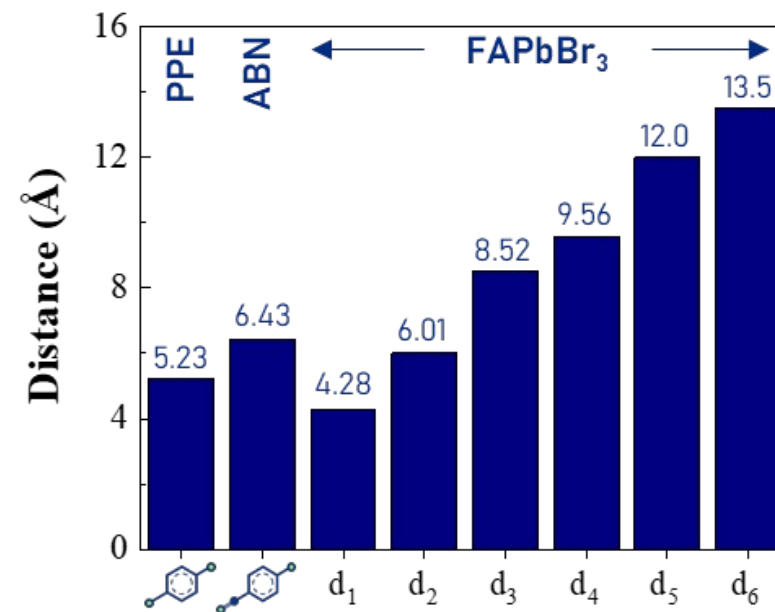
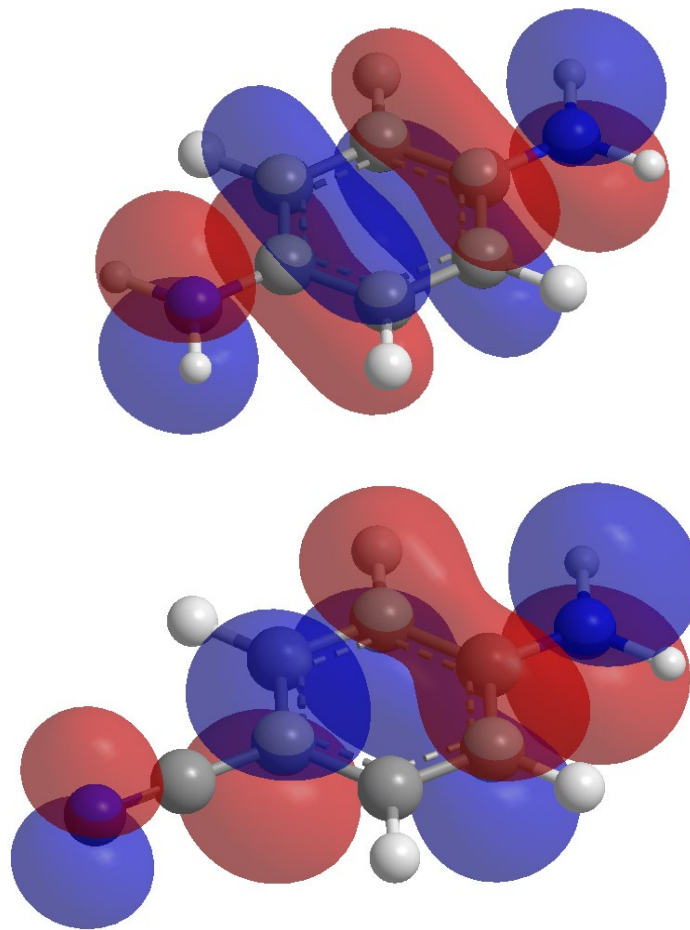
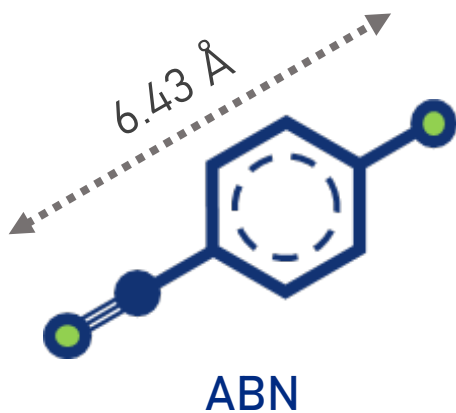
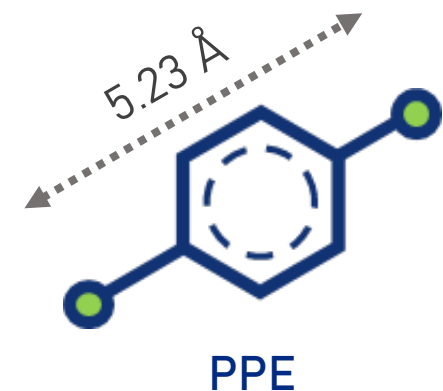
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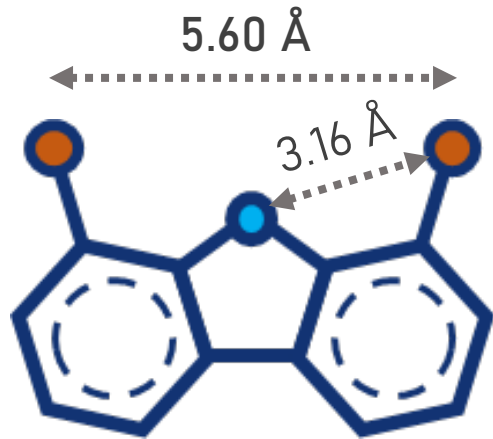
Appendix I: Oxygen atom effect



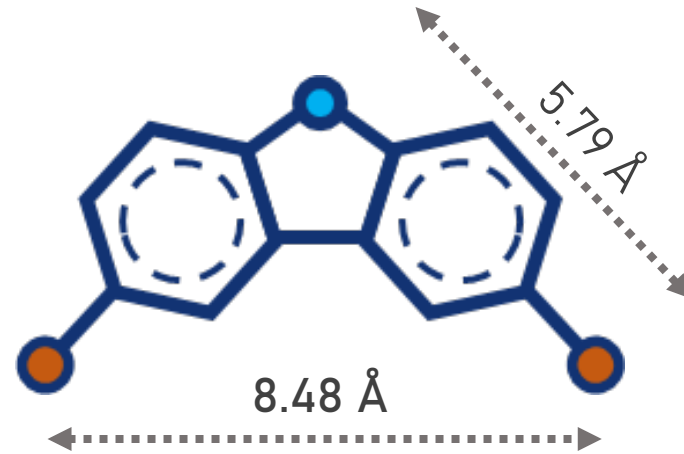
Appendix II. PPE and ABN: Geometrical effect



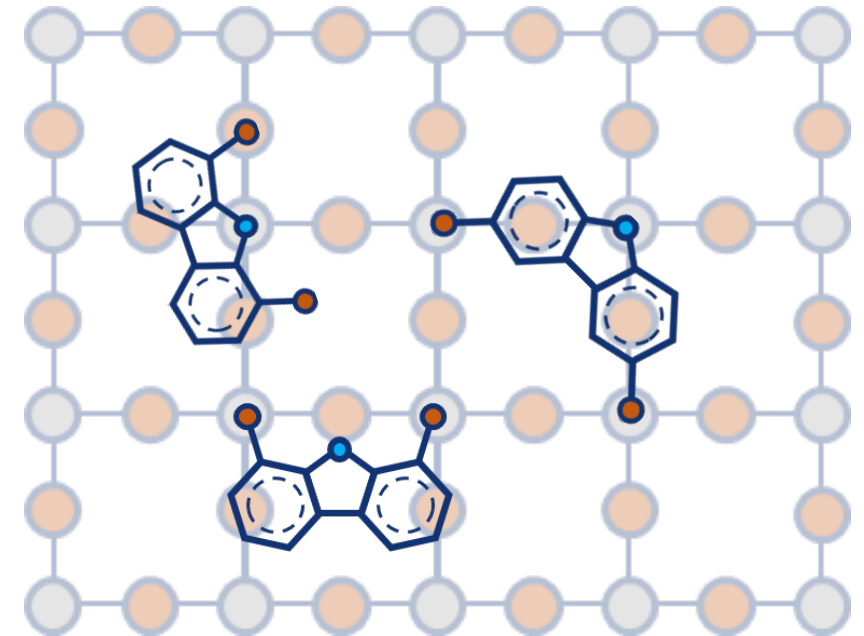
Appendix III: More on the geometrical effect



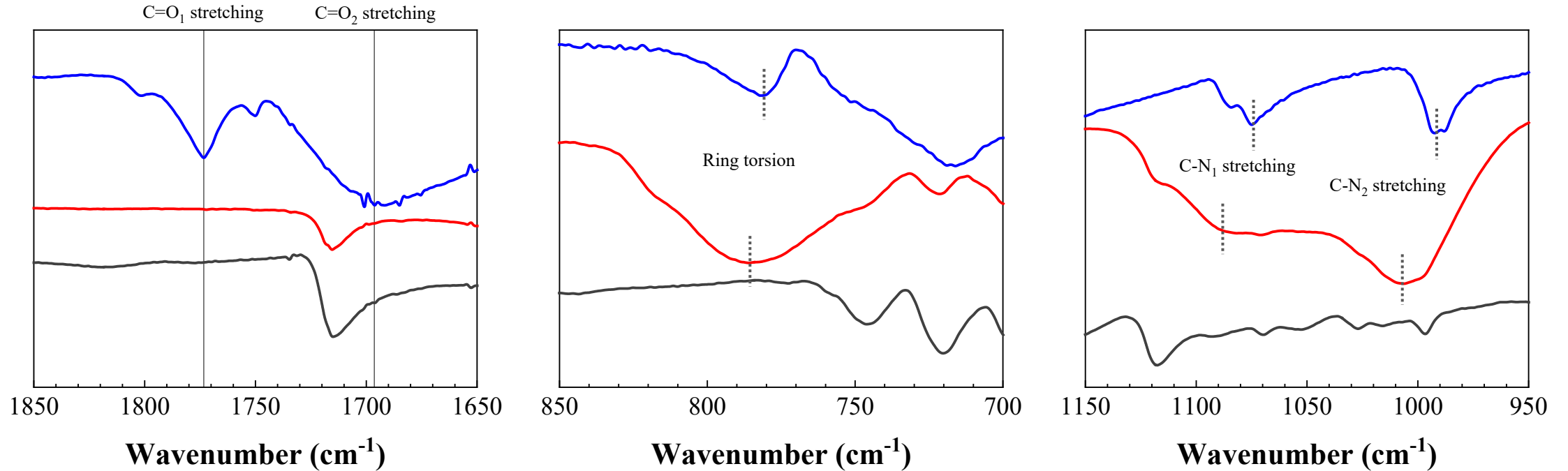
28-DBDB



46-DBDB



Appendix IV. Hydantoin demonstration



- HDT
- HDT-added Perovskite
- Reference (pristine)