Enhancing charge transport in two-dimensional inorganic-organic perovskites through fluorine substitution

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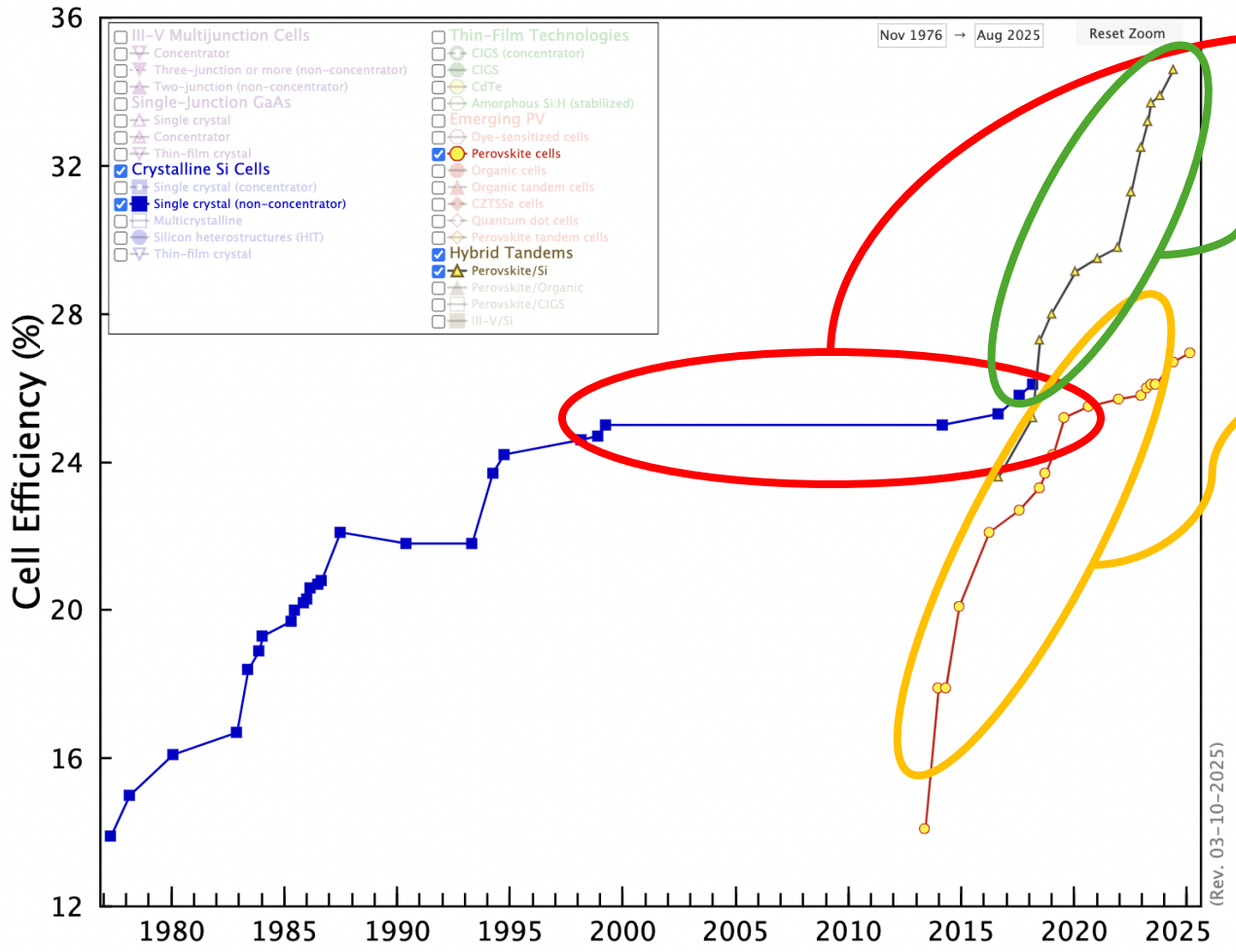
Introduction and Background: Perovskites



Large plateau in silicon-based solar cells

Significant rapid development when perovskite- and silicon-based solar cells are combined

Significant rapid development in perovskite-based solar cells

Maximum efficiency silicon

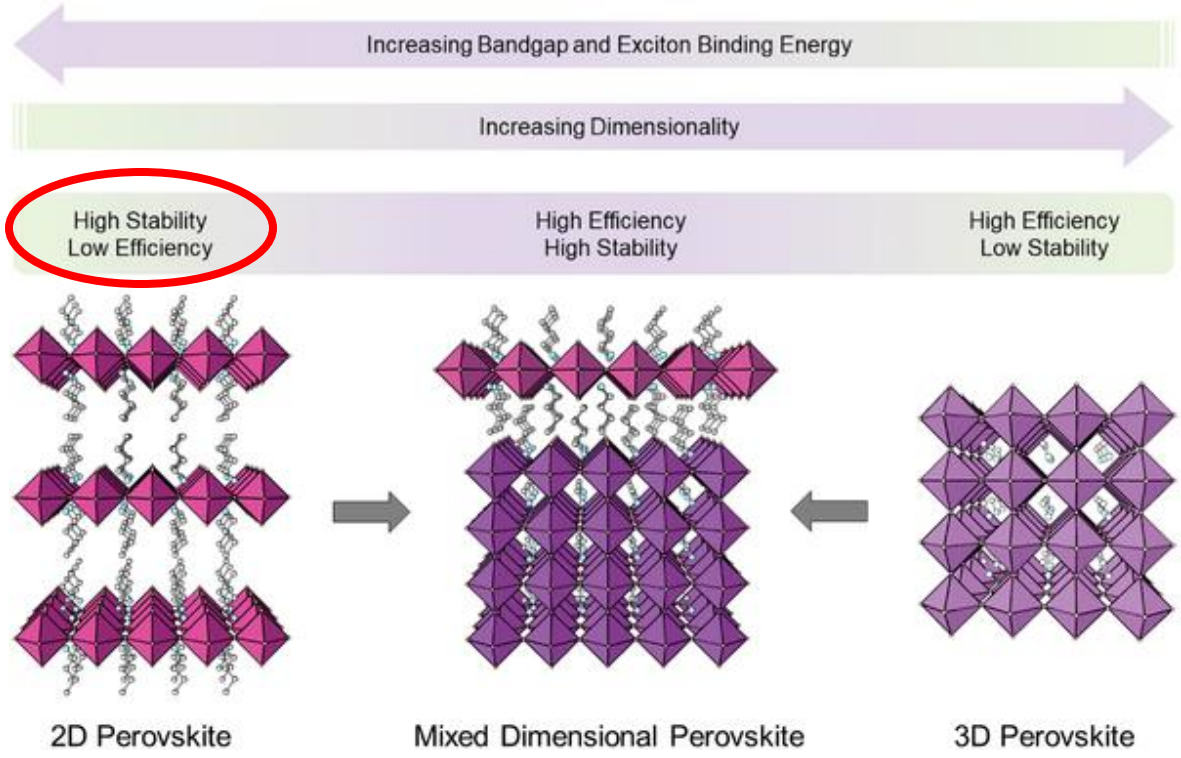
~25%

Maximum efficiency perovskites

~26%

National Renewable Energy Lab

The Search for Better Energy Materials: Two-Dimensional Perovskites



Question:
How can we improve the efficiency of 2D perovskites?

Answer:
Adjust the organic spacers to enhance charge transfer

Wu, G. et al. *Advanced Materials* **2022**, *34* (8), 2105635.

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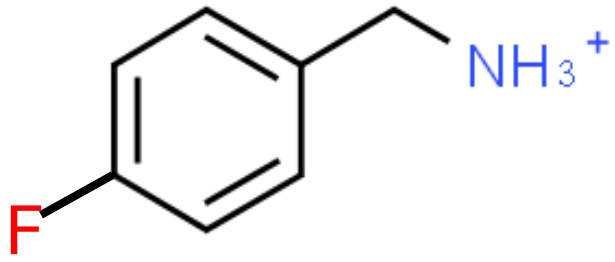
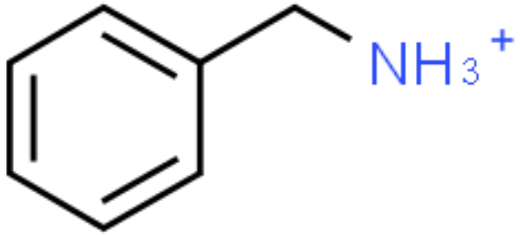
Using Fluorine to Enhance Charge Transfer

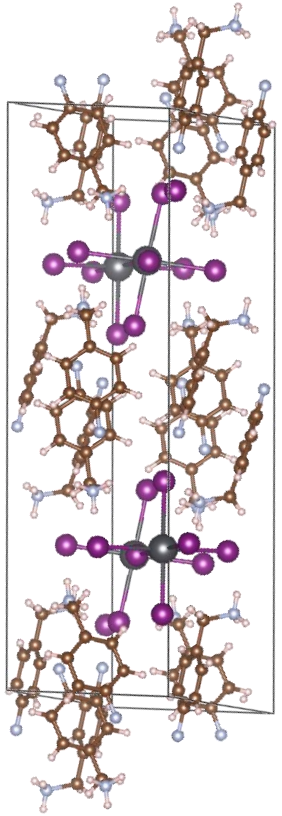
PCE

Fluorinated-Benzylammonium (F-BZA)

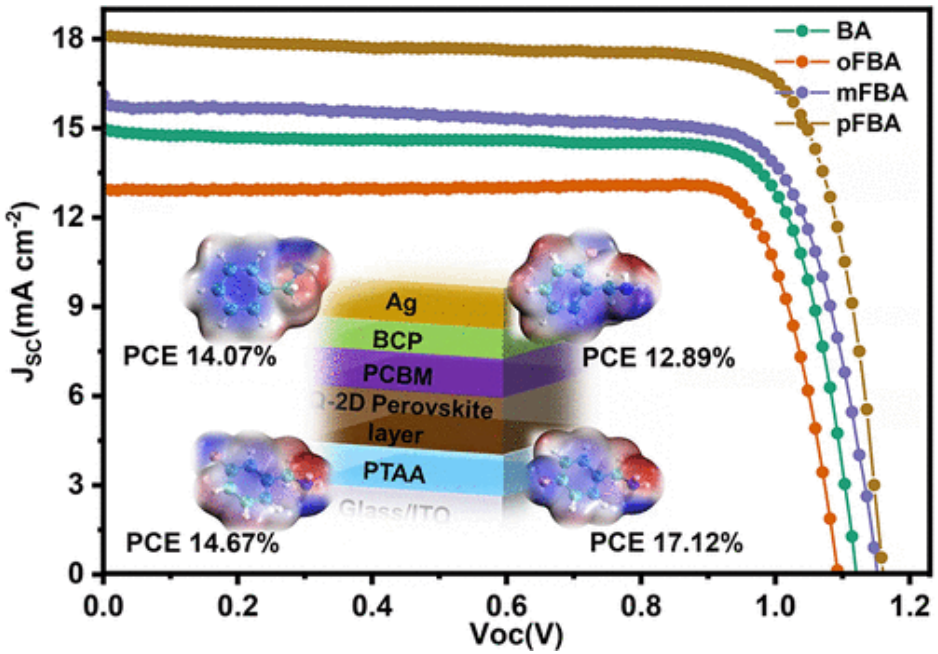


Benzylammonium (BZA)





Why the para- position?



Question:
HOW does fluorine improve charge transfer and efficiencies?

Yan, G. Chemistry of Materials 2022, 34 (7), 3346-3356.
Wang, Z. ACS Applied Materials & Interfaces 2022, 14 (6), 7917-7925.

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Understanding Charge Transfer: Marcus Theory

Marcus rate ∝ coupling (V_{kl})

Marcus rate ∝ site energies^{-1} $\left(\frac{1}{\lambda}\right)$

$$k_{Marcus} = \left(\frac{V_{kl}{}^2}{\hbar}\right)\sqrt{\frac{\pi}{\lambda k_B T}}\, exp\left(-\frac{(\Delta A + \lambda)^2}{4\lambda k_B T}\right)$$

$$\lambda = \frac{\sigma^2}{2k_B T} \qquad \sigma = \langle (dE - \langle dE \rangle)^2 \rangle$$

$$\mu_{hopping} = \frac{eD}{k_B T} = \frac{e k_{Marcus} L^2}{k_B T}$$

Charge Carrier Hopping Mobility

Marcus, R. A. The Journal of Chemical Physics 1965, 43 (8), 2654-2657.

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Projection Diabatization Method (POD): Computing Nonadiabatic Couplings

Acceptor

Donor

Fragment-based diabatization method

Create donor and acceptor blocks

$$\tilde{H} = \begin{bmatrix} \tilde{H}_{DD} & \tilde{H}_{DA} \\ \tilde{H}_{AD} & \tilde{H}_{AA} \end{bmatrix}$$

Diagonalize each block separately

$$H' = \begin{bmatrix} \varepsilon_{1,D} & 0 & & V_{DA} \\ 0 & \varepsilon_{2,D} & & \\ \vdots & & \ddots & \\ & V_{AD} & & \varepsilon_{1,A} & 0 \\ & & & 0 & \varepsilon_{2,A} \\ & & & \vdots & & \ddots \end{bmatrix}$$

Donor Energies

Acceptor Energies

Donor-Acceptor Couplings

Kondov, I. The Journal of Physical Chemistry C 2007, 111 (32), 11970-11981.

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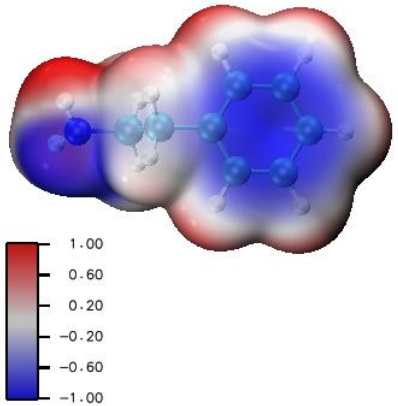
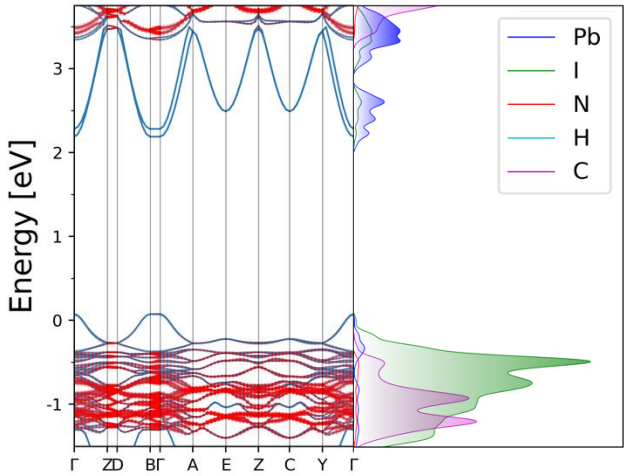
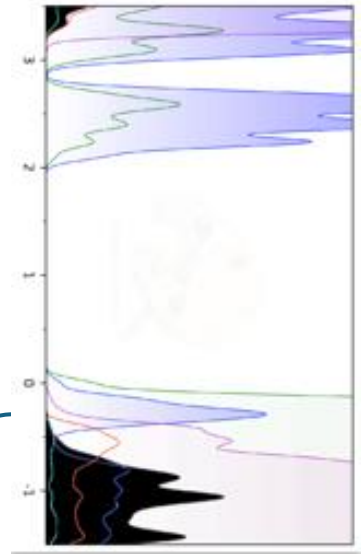
Fluorine's Effects on Electronic Structure

Non-Fluorinated





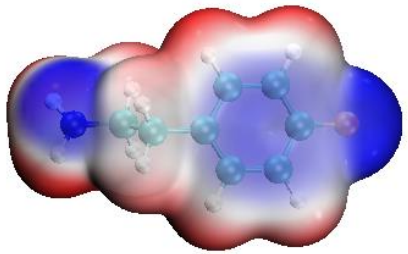
Fluorine does NOT contribute to band edge states

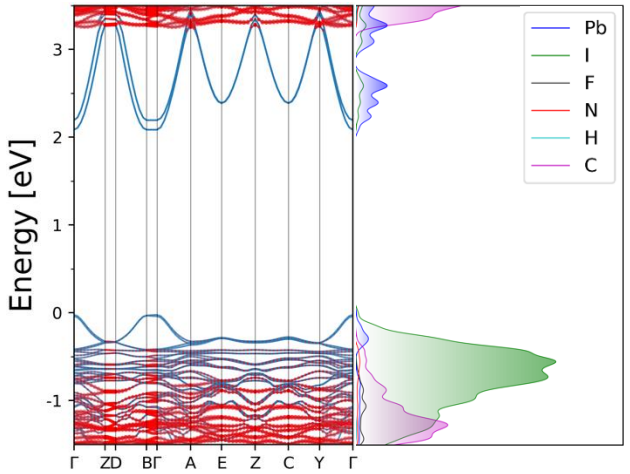


LUMO

HOMO

Fluorinated





Charge density migrates to fluorine
Potential to enhance charge transfer

Fluorine has minimal influence in coupling

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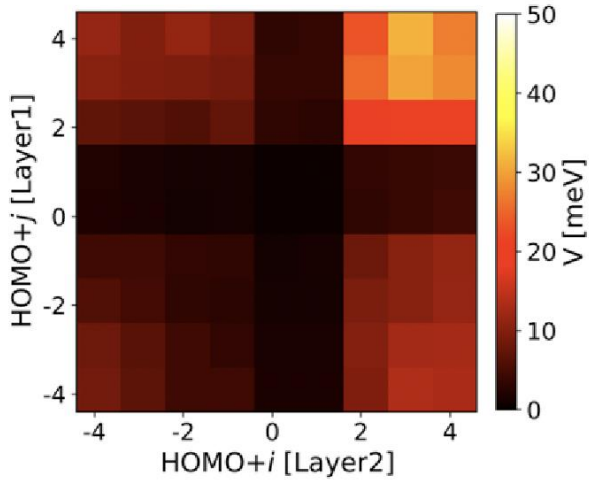
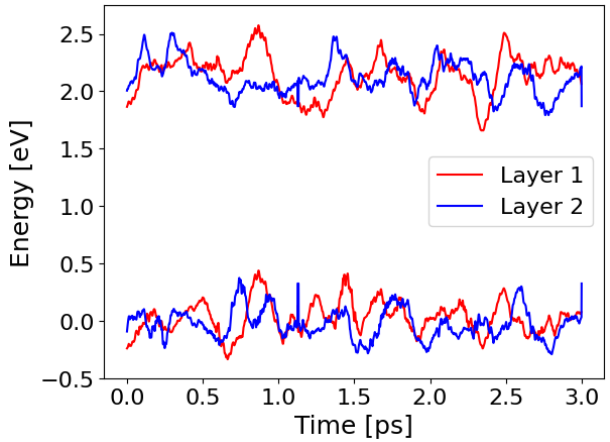
Fluorine's Effects on Marcus Rate: Nonadiabatic Coupling & Reorganization Energy

Non-Fluorinated



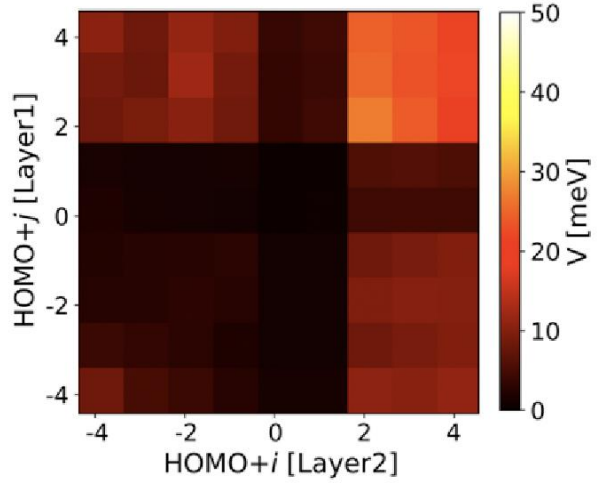
POD Method

$$H' = \begin{bmatrix} \varepsilon_{1,D} & 0 & & & \\ 0 & \varepsilon_{2,D} & & & V_{DA} \\ \vdots & & \ddots & & \\ & & & \varepsilon_{1,A} & 0 \\ & V_{AD} & & 0 & \varepsilon_{2,A} \\ & & & \vdots & \ddots \end{bmatrix}$$

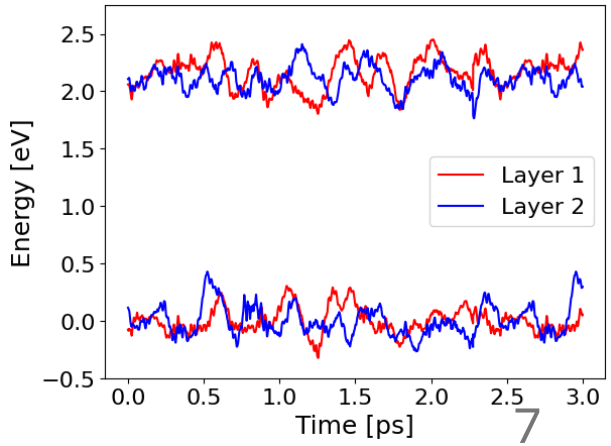


$$\lambda = \frac{\sigma^2}{2k_B T} \qquad \sigma = \langle (dE - \langle dE \rangle)^2 \rangle$$

HOMO ~ -2.5 eV



HOMO ~ -2.75



Fluorinated

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Putting the pieces together: charge transfer rates

Non-Fluorinated	LUMO
	HOMO
Fluorinated	LUMO
	HOMO

RMS Electronic Coupling

Reorganization Energy

Marcus Rate

Distance Between Layers

Charge Carrier Hopping Mobility

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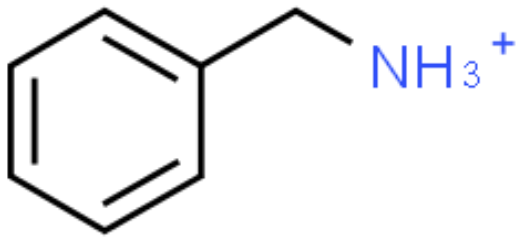
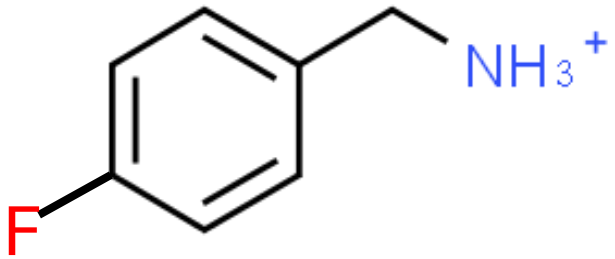
Fluorine as a Structural Stabilizer

	Average Displacement (Å)							
	Pb	I	N	H	C	F	Organic Spacers	Inorganic Crystals
Non-Fluorinated								
Fluorinated								





Displacement decreases with addition of fluorine atoms

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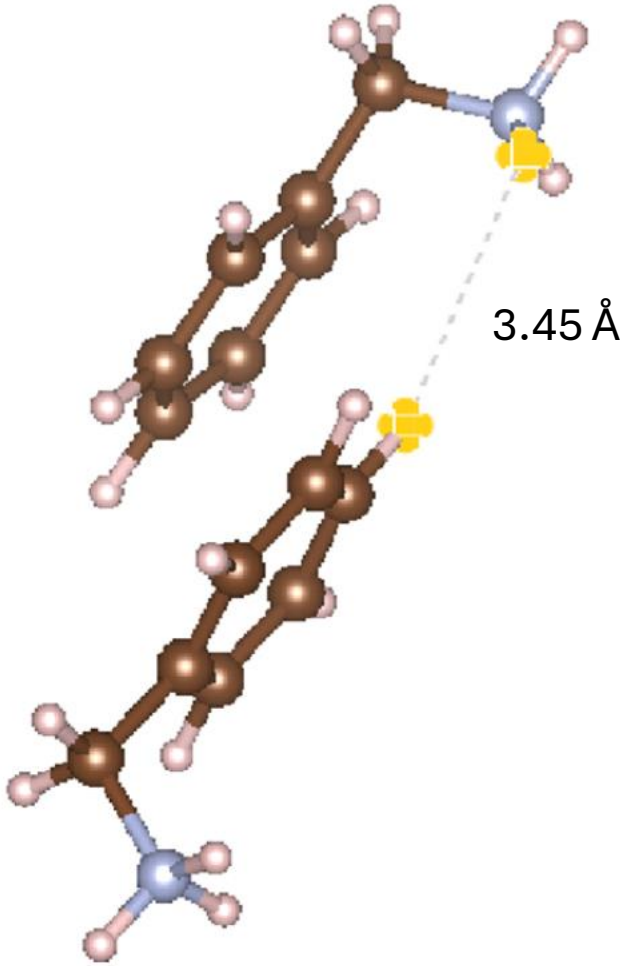
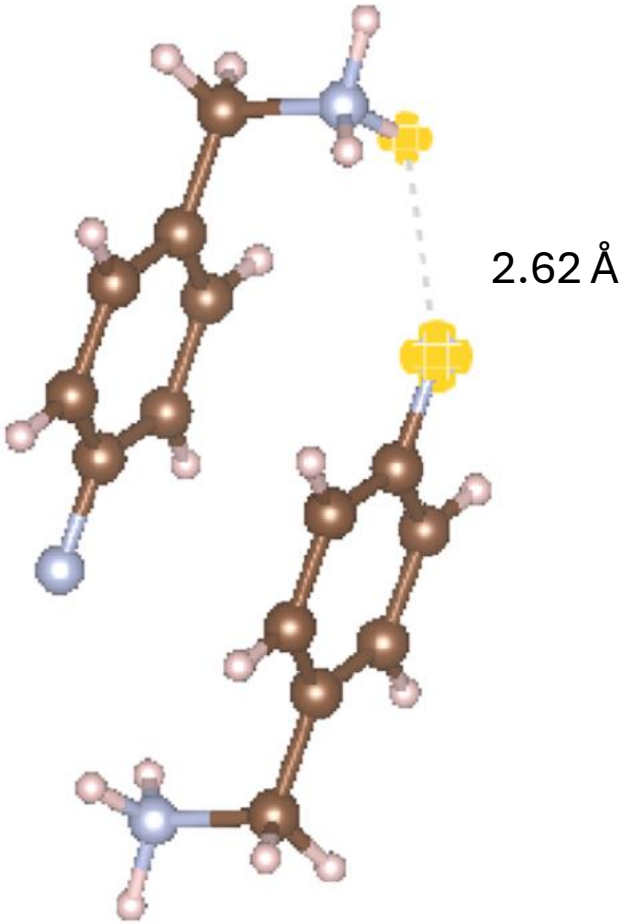
Results: Evidence of Hydrogen Bonding

Non-Fluorinated



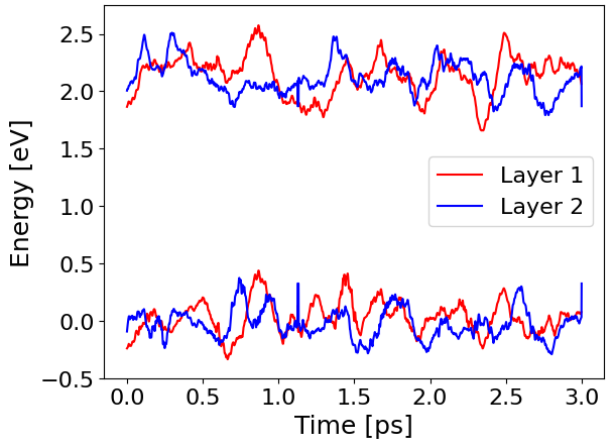
Fluorinated

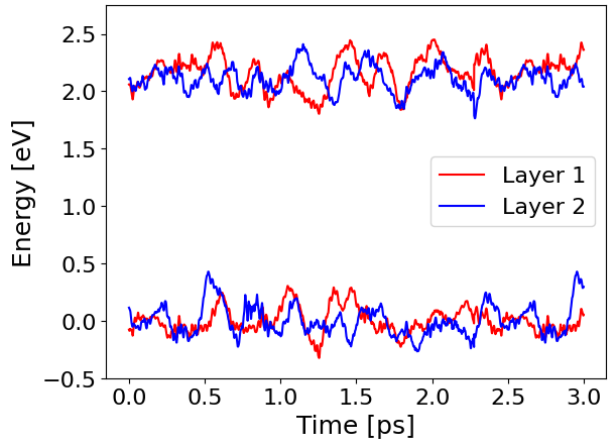


H-F hydrogen bonding between 2-3Å

Conclusions

Fluorine substitution enhances the PCE of the 2D perovskite **not** through coupling effects but through **reorganization energy and structural stabilization**.





	Organic Spacers	Inorganic Crystals
BZA	1.25	0.81
F-BZA	1.02	0.72

Acknowledgements

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Claudio Quarti
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Oleg Prezhdo

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