Enhancing Interlayer Charge Transport of Two-Dimensional Perovskites by Structural Stabilization via Fluorine Substitution

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Advisor: Prof. Oleg Prezhdo

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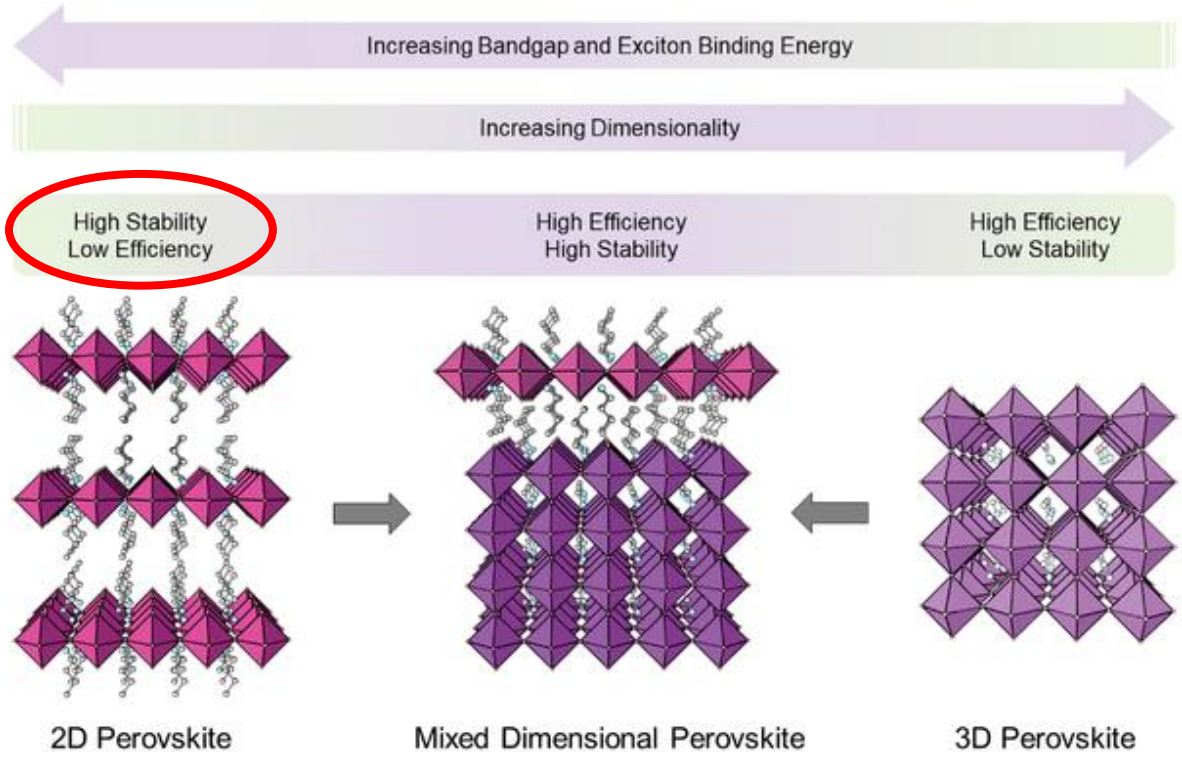
The Search for Better Energy Materials: Two-Dimensional Perovskites



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

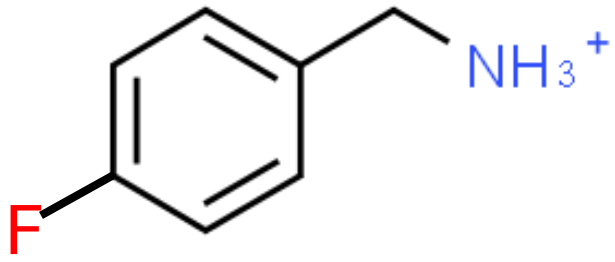
Answer:
Adjust the organic spacers to enhance charge transfer

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

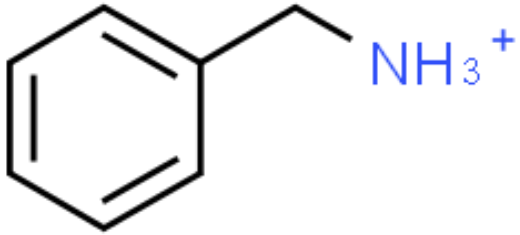
Using Fluorine to Enhance Charge Transfer

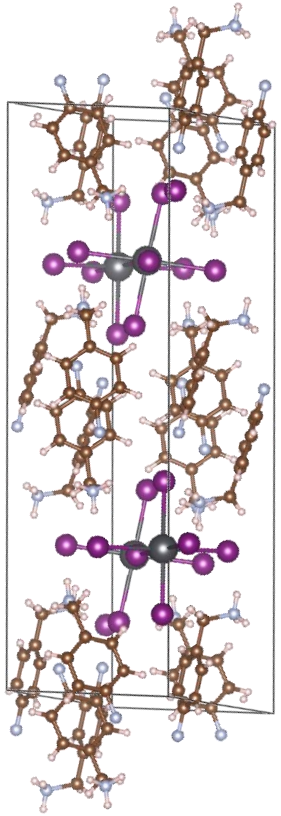
PCE

Fluorinated-Benzylammonium (F-BZA)

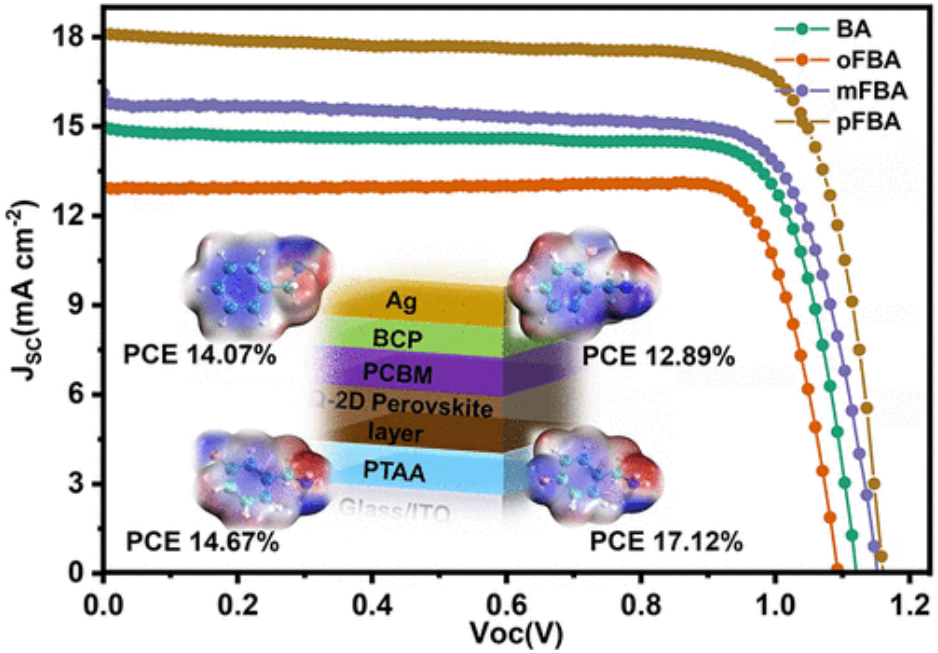


Benzylammonium (BZA)





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.

Understanding Charge Transfer: Marcus Theory

Marcus rate ∝ coupling (V_{kl})

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

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

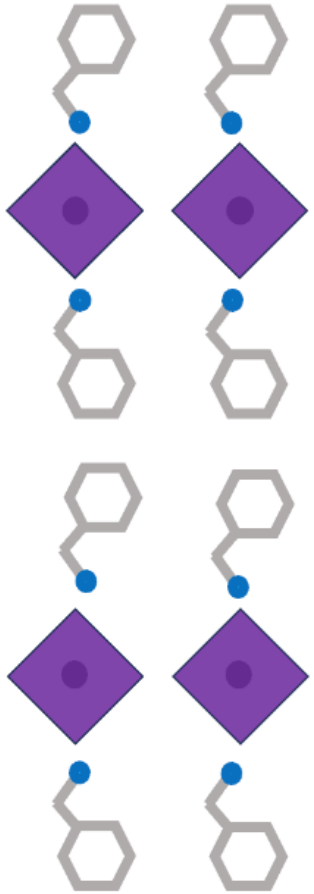
$$\lambda = \frac{\sigma^2}{2\mathrm{k_B T}} \qquad \sigma = \langle (dE - \langle dE \rangle)^2 \rangle$$

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

Charge Carrier Hopping Mobility

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

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

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

Donor Energies

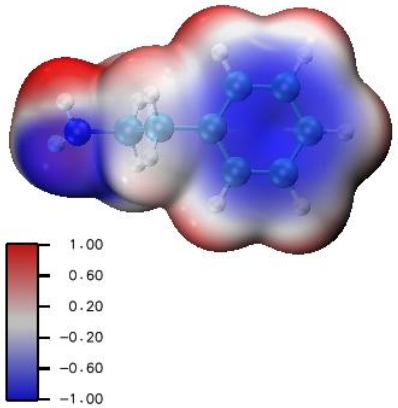
Acceptor Energies

Donor-Acceptor Couplings

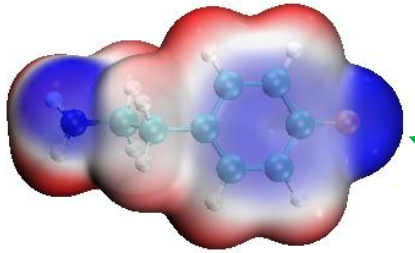
Kondov, I. The Journal of Physical Chemistry C 2007, 111 (32), 11970-11981.

Fluorine's Effects on Electronic Structure

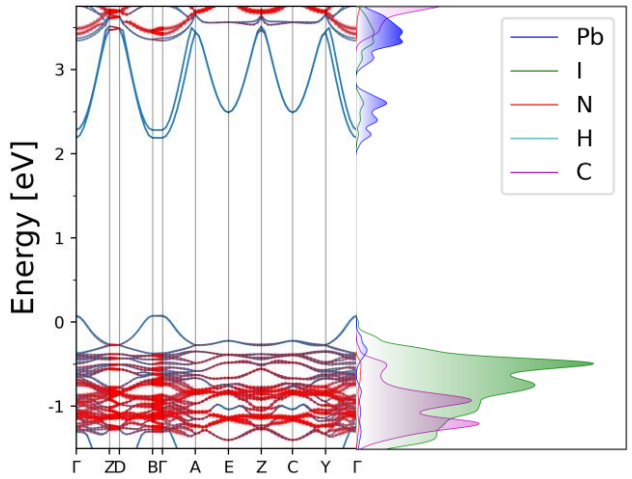
Non-Fluorinated

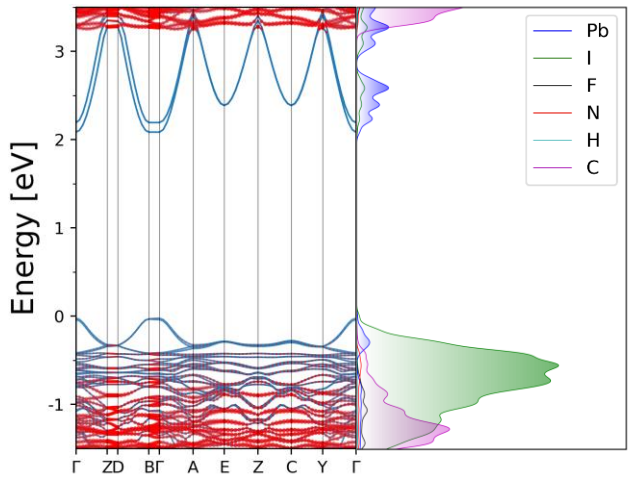


Fluorinated

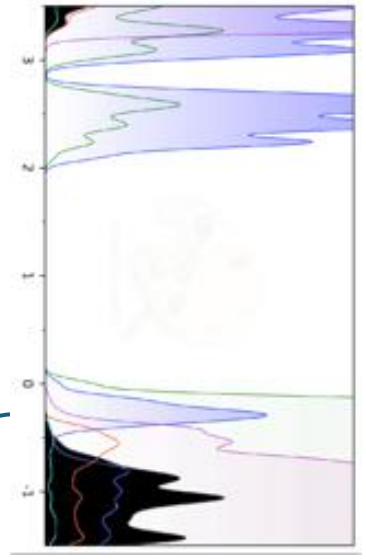


Charge density migrates to fluorine
Potential to enhance charge transfer





Fluorine does NOT contribute to band edge states



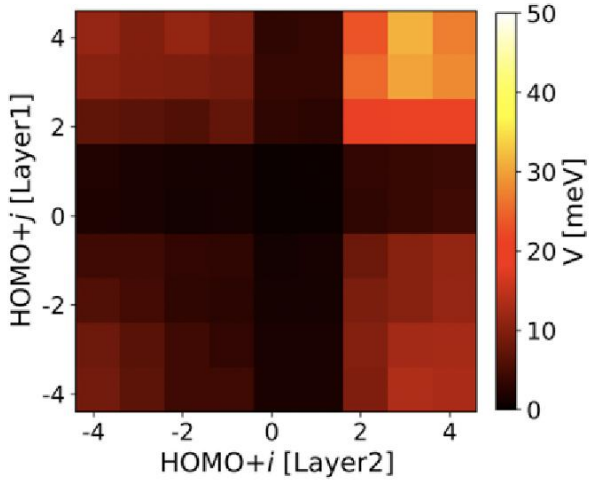
LUMO

HOMO

Fluorine has minimal influence in coupling

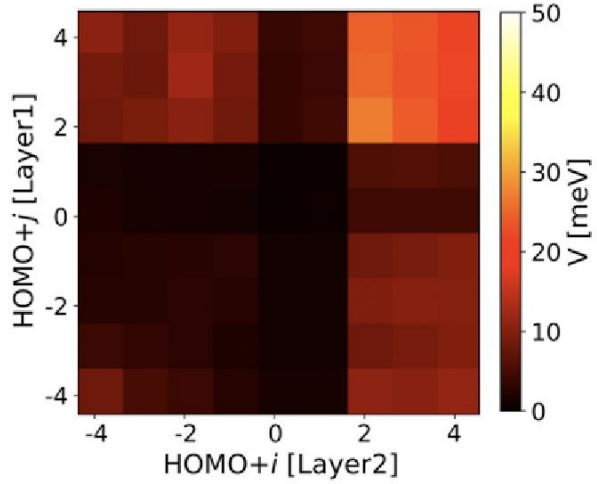
Fluorine's Effects on Marcus Rate: Nonadiabatic Coupling & Reorganization Energy

Non-Fluorinated

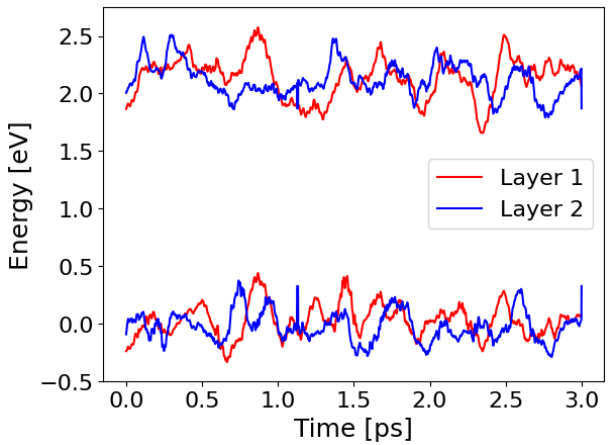


POD Method

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

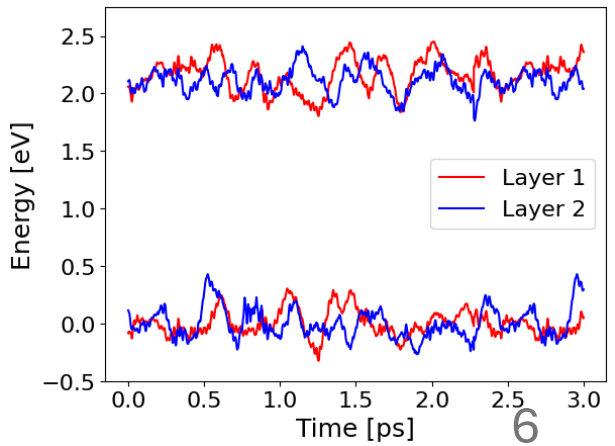


Fluorinated



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

HOMO ~ -2.5 eV



HOMO ~ -2.75

Putting the pieces together: charge transfer rates

Non-Fluorinated	LUMO
	HOMO
Fluorinated	LUMO
	HOMO

RMS Electronic Coupling

Reorganization Energy

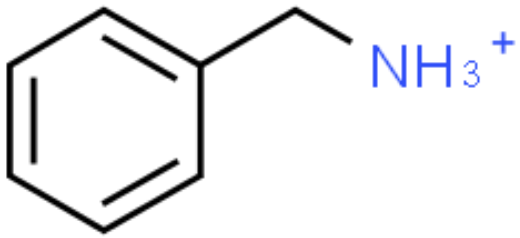
Marcus Rate

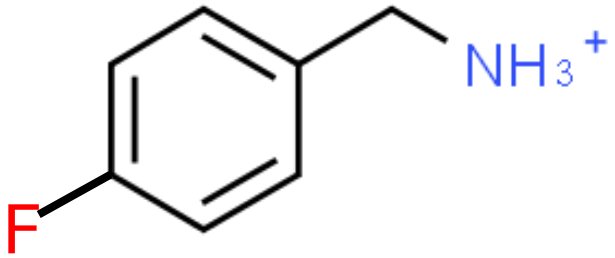
Distance Between Layers

Charge Carrier Hopping Mobility

Fluorine as a Structural Stabilizer

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

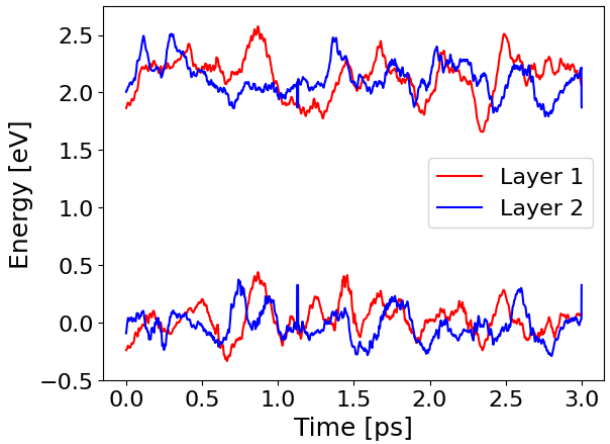




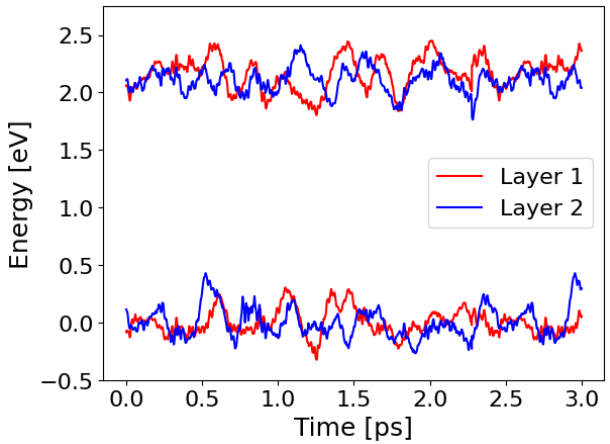
Displacement decreases with addition of fluorine atoms

Conclusions

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



HOMO ~ -2.5 eV



HOMO ~ -2.75

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

Thank you!

Collaborators

Wei Li

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David Beljonne

Advisor

Oleg Prezhdo

Extra Slides