Materiali Innovativi per il Fotovoltaico:

Perovskiti, Meccanica quantistica e Intelligenza artificiale

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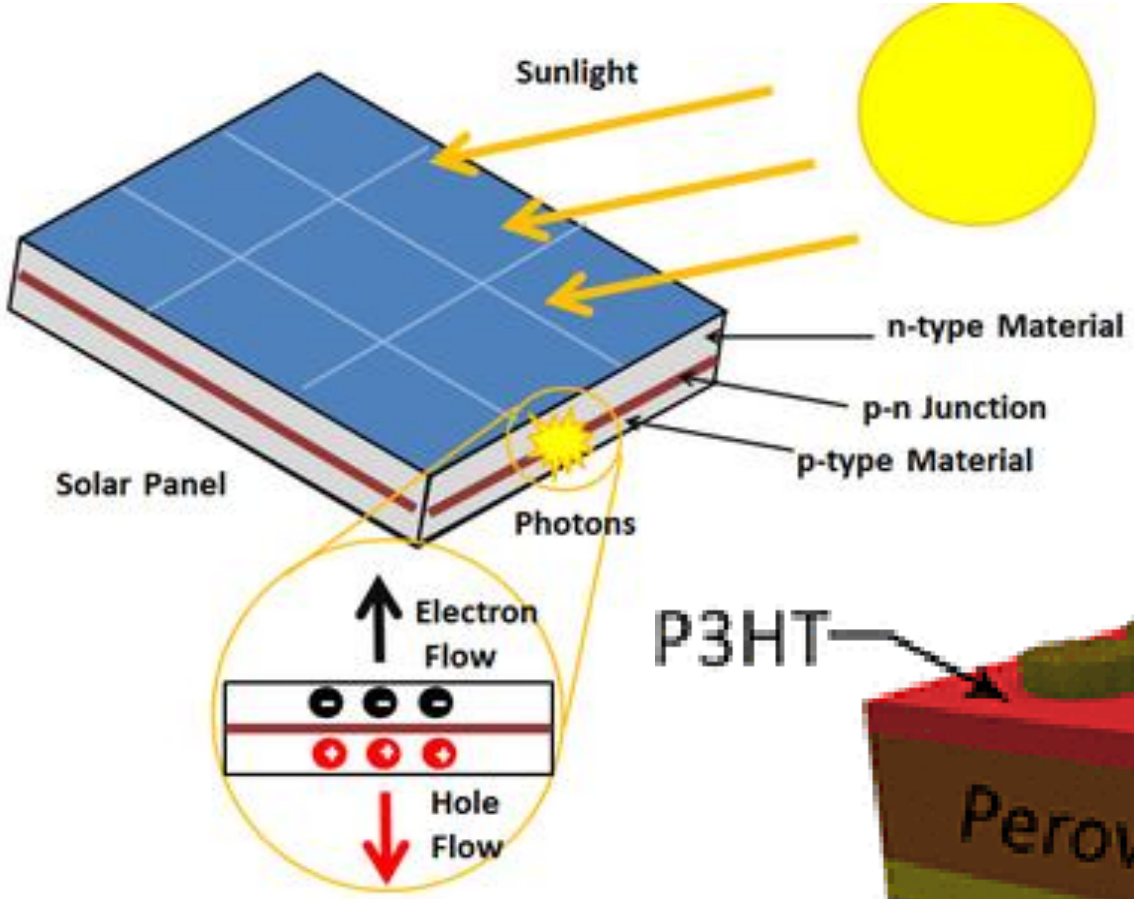
www.clhyo.org

Outline

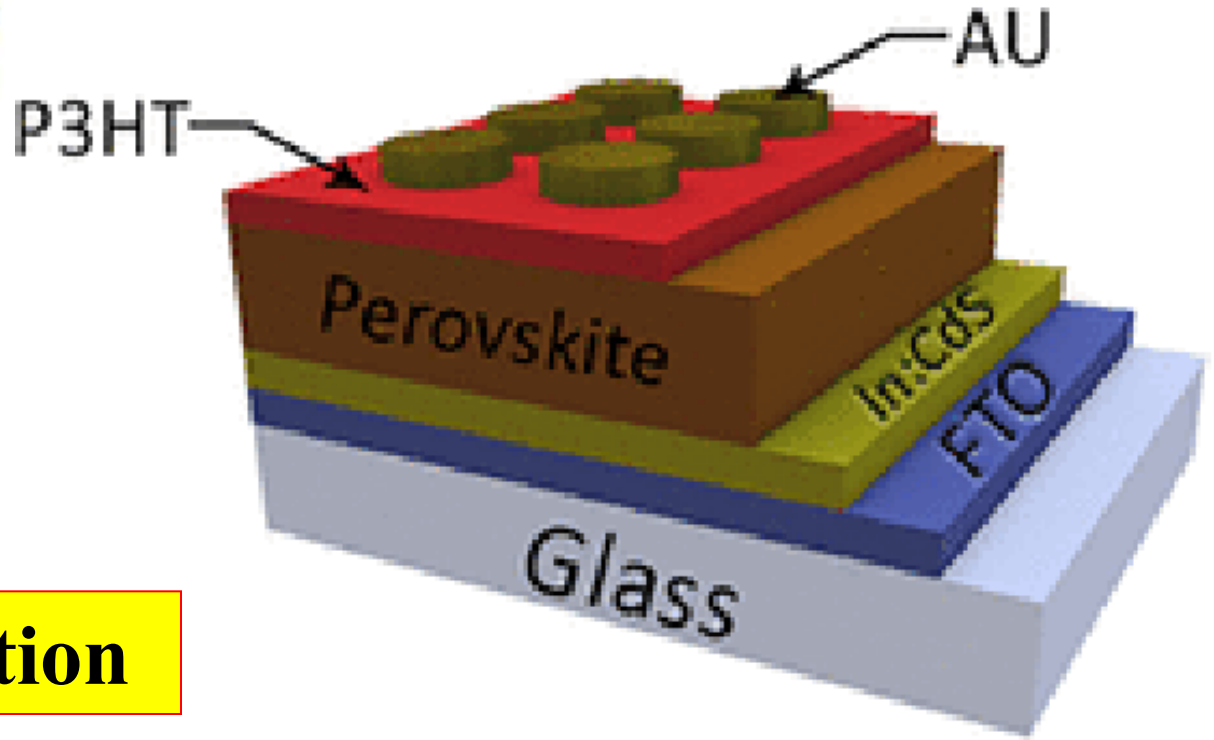
- **Context: Dye sensitized vs. perovskite solar cells**
- **Modelling strategies**
- **Artificial Intelligence**
- **Some results**
- **Conclusions**

Silicon vs. peroskite solar cells

p-n junction



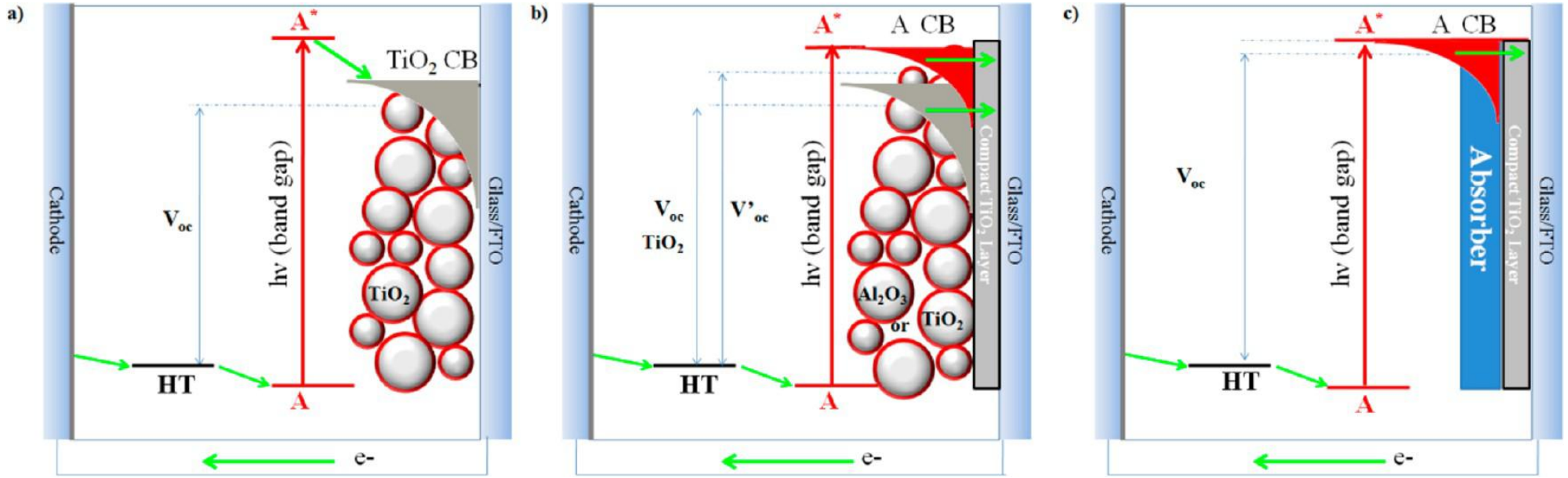
n-i-p heterojunction



Dye-Sensitized vs. Perovskite Solar Cells

Mesoporous-oxide based devices

Flat heterojunctions



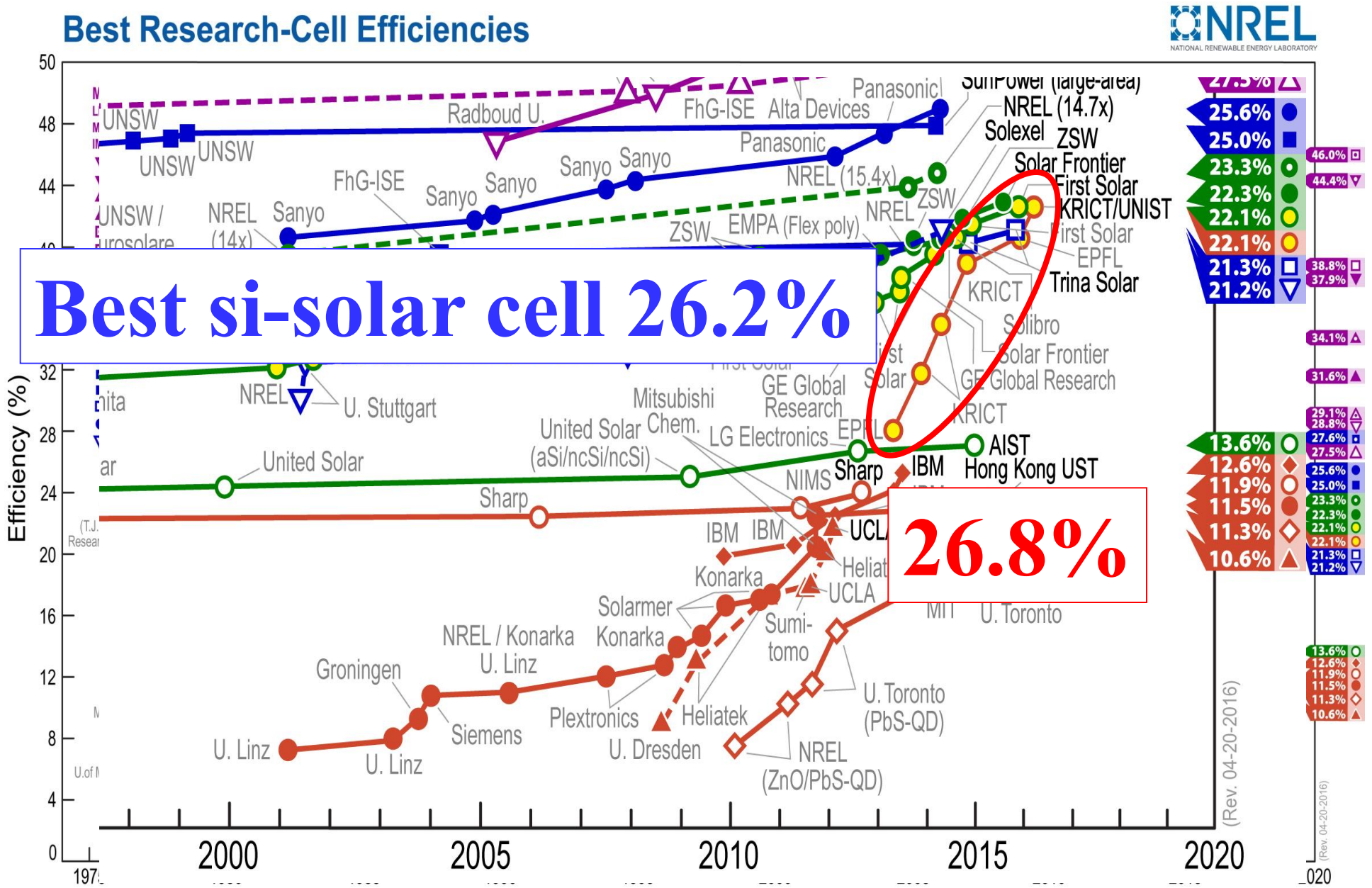
Dye-Sensitized Perovskite Solar Cell

- DSSC and PSC - TiO_2 : electon transport occurs in TiO_2
- PSC Al_2O_3 : electon transport occurs in the perovskite

H.S. Kim et al *Sci. Rep.* **2012,** *2*, 591.

M. Lee et al. *Science* **2012**, 338, 643.

Perovskite Solar Cells: Efficiency

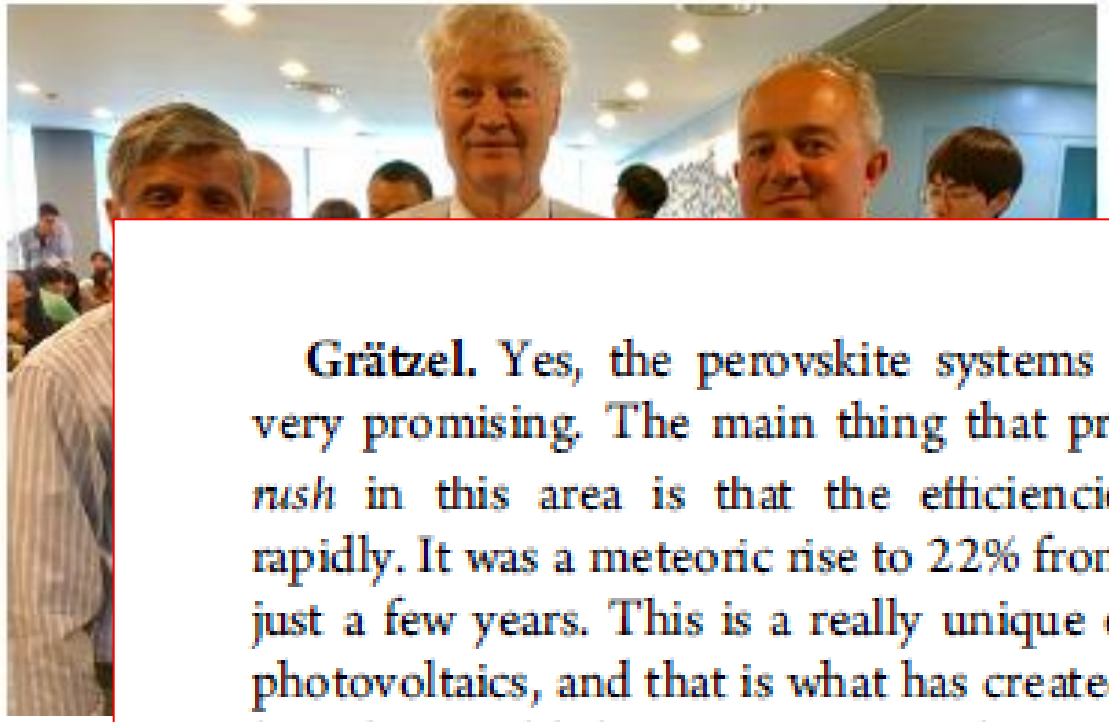


ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

ENERGY FOCUS

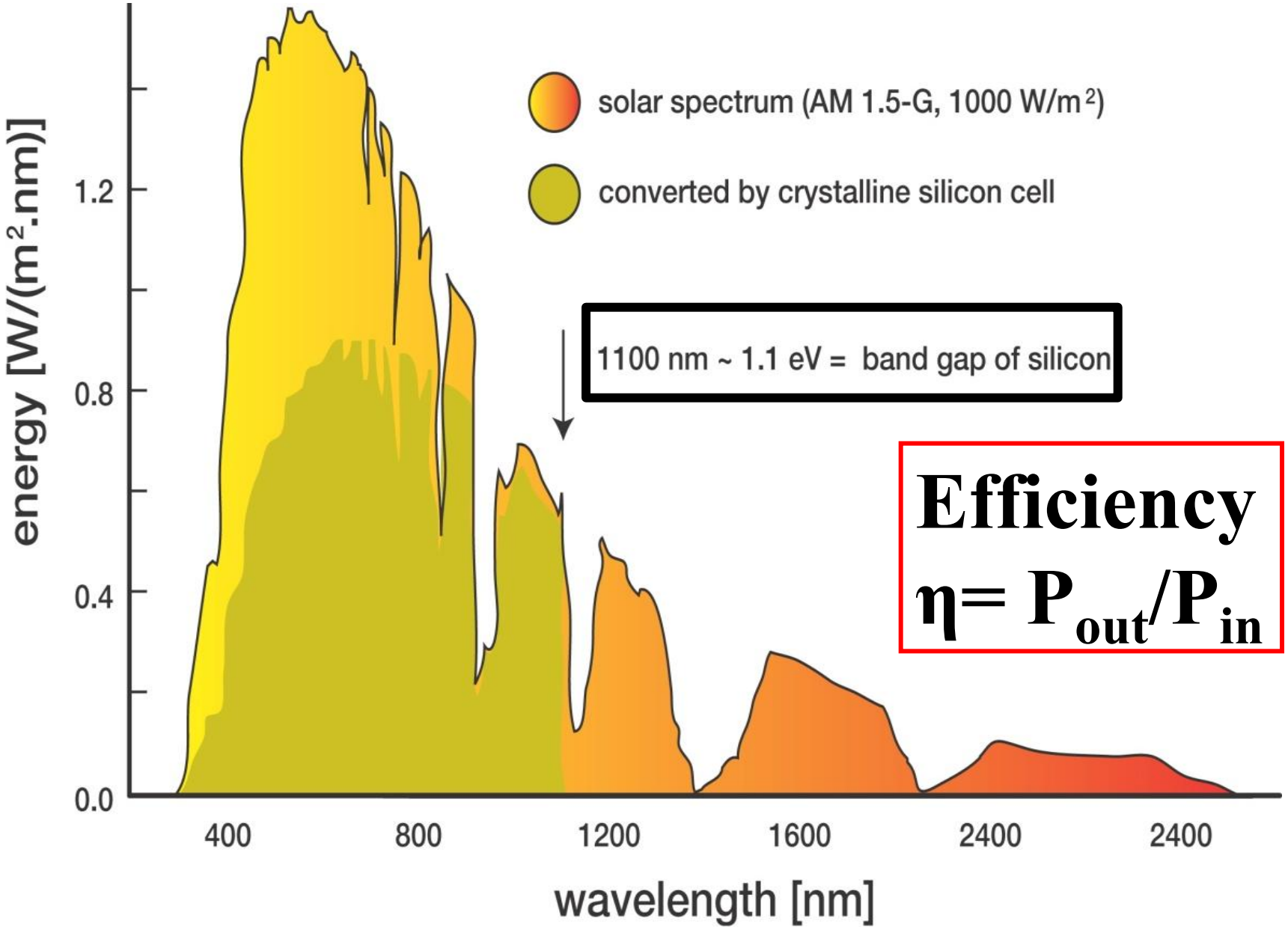
A Conversation with Michael Grätzel



Grätzel. Yes, the perovskite systems as light-harvesters are very promising. The main thing that produced a kind of *gold rush* in this area is that the efficiencies went up strikingly rapidly. It was a meteoric rise to 22% from a little bit over 3% in just a few years. This is a really unique event in the history of photovoltaics, and that is what has created a lot of excitement. I have been told that 10 000 researchers are now working in this field worldwide, from just a few in the beginning.

De Angelis, F.; Kamat, P. *ACS Energy Lett.*, **2017**, 2, 1674–1676

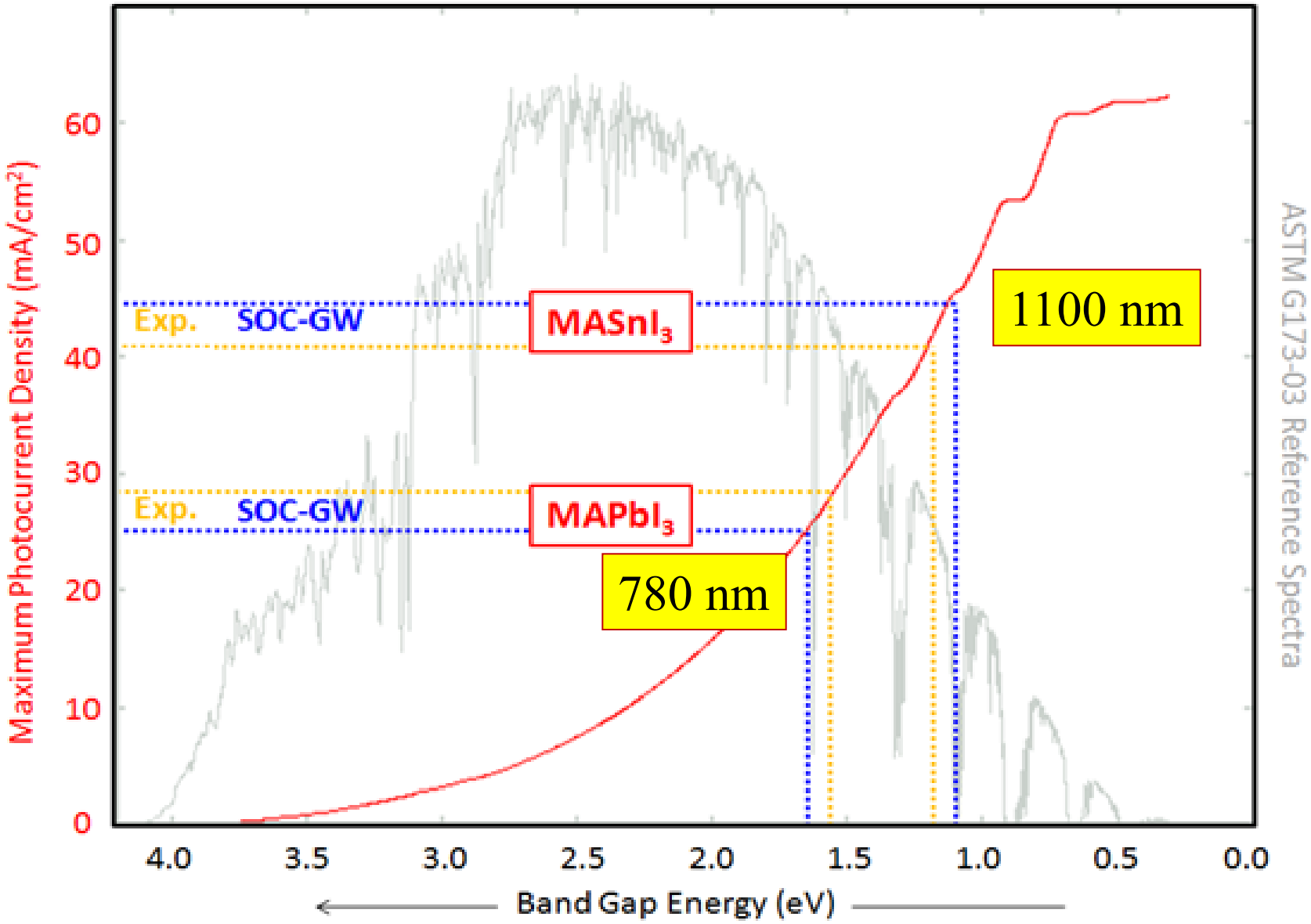
The solar power spectrum



Efficiency

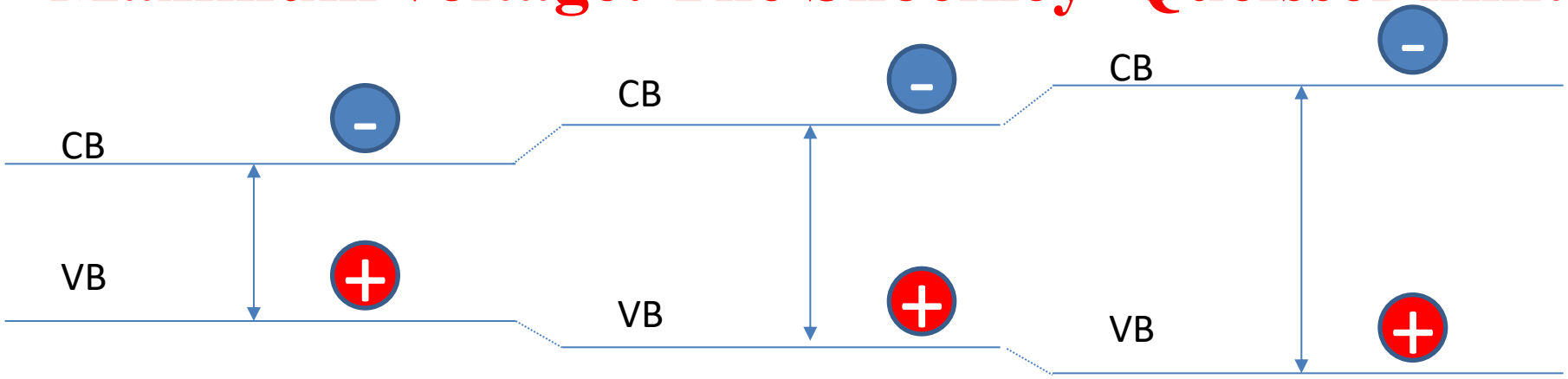
$\eta = P_{out}/P_{in}$

Maximum Jsc: Solar absorption



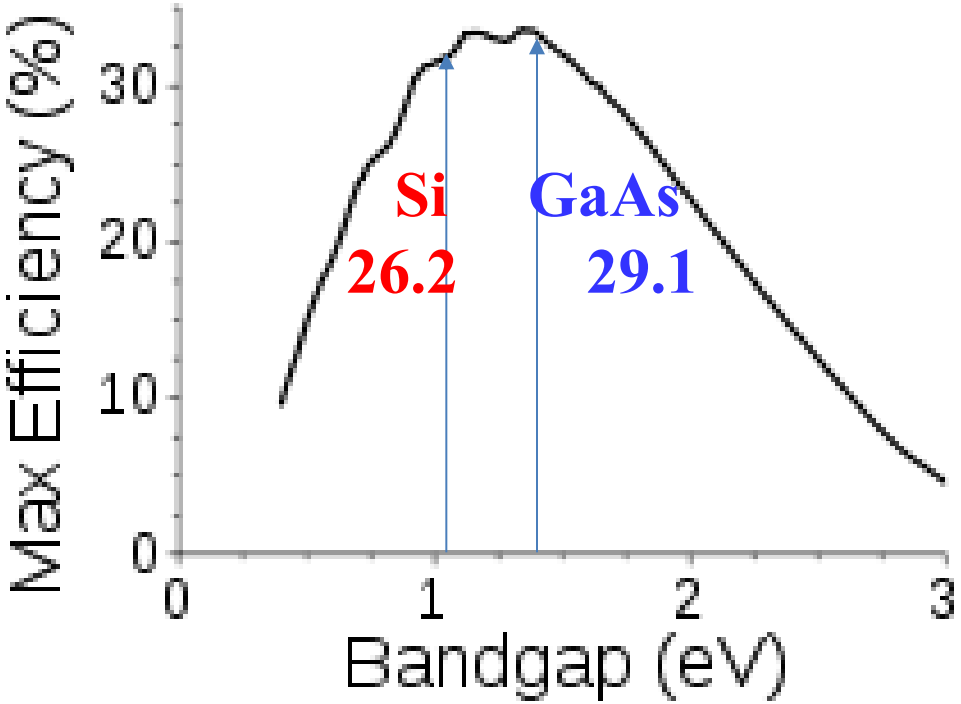
P. Umari, E. Mosconi, F. De Angelis *Sci. Rep.* **2014**, *4*, 4467.

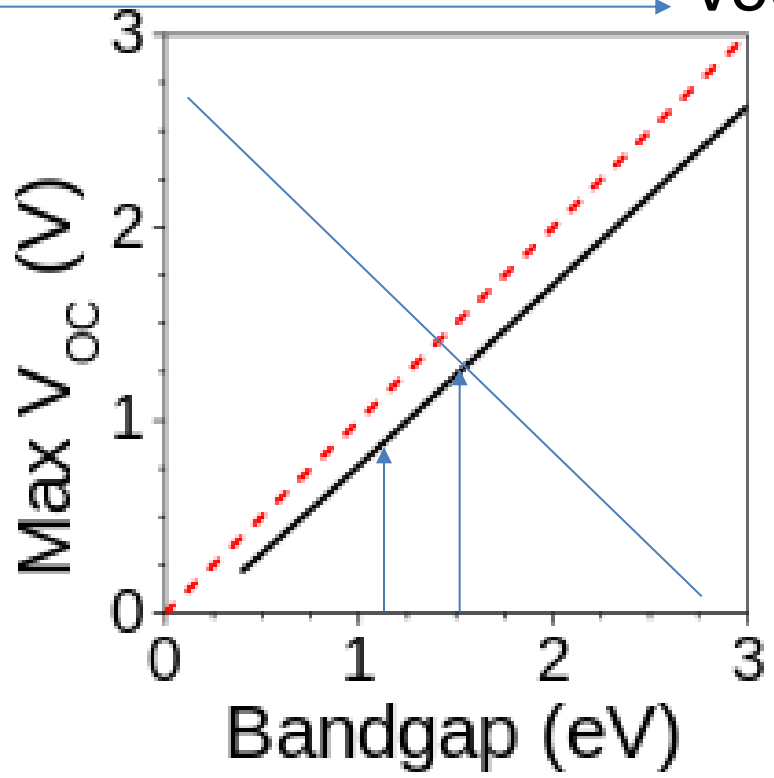
Maximum voltage: The Shockley–Queisser limit



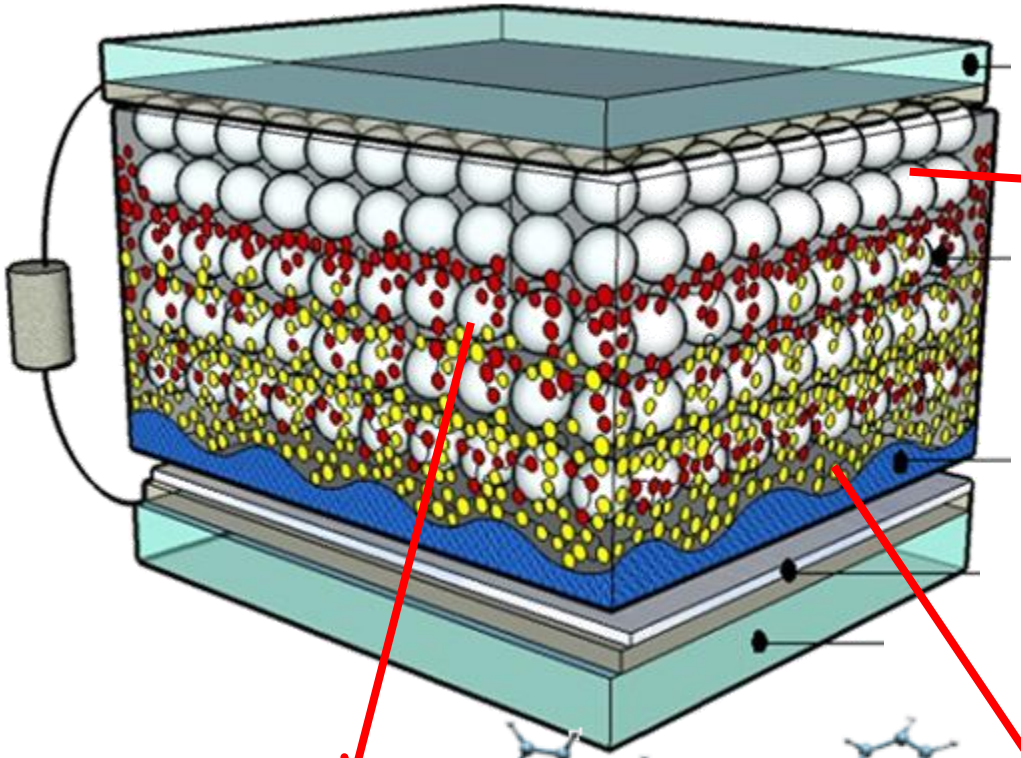
Jsc

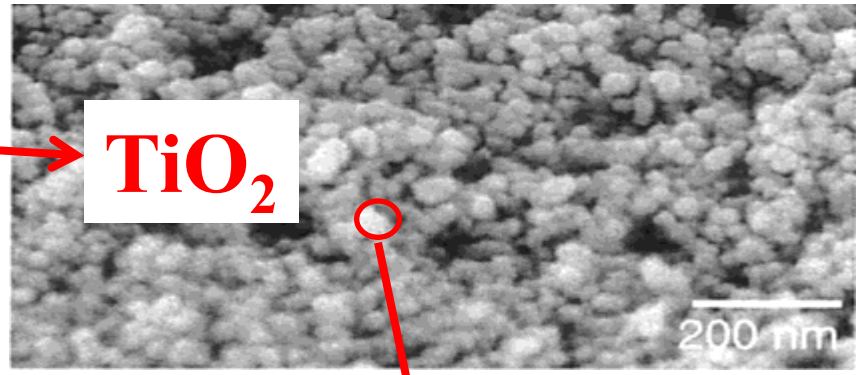
Voc



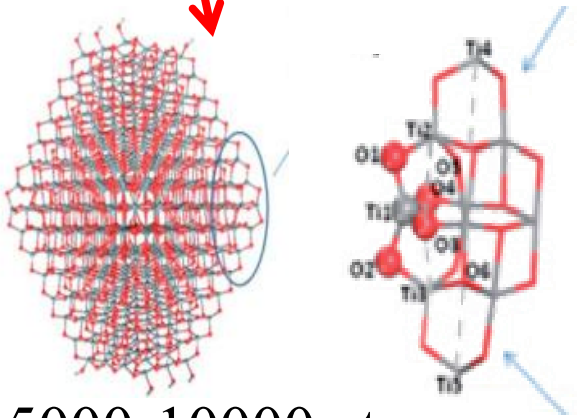


Modeling Dye-sensitized solar cells

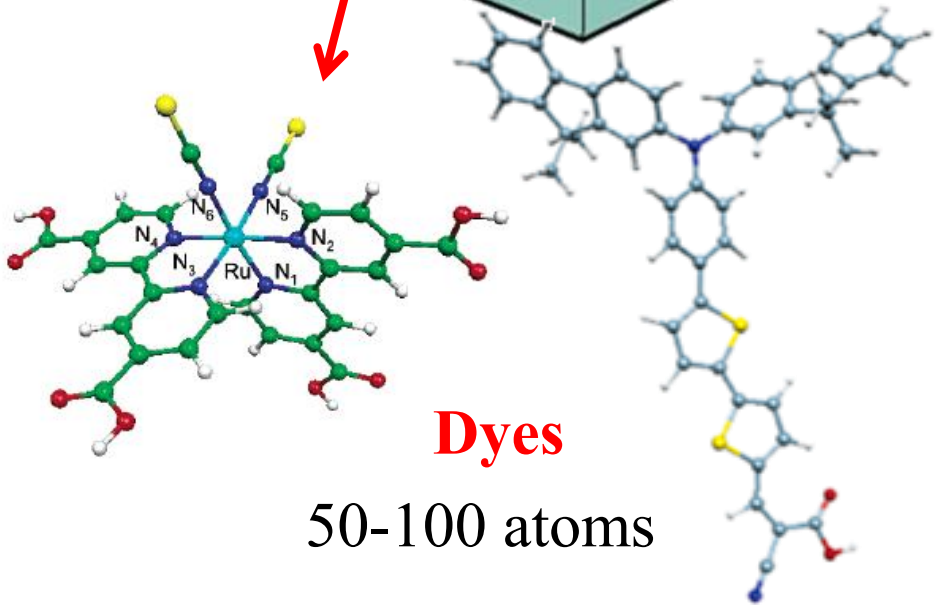




~20 nm

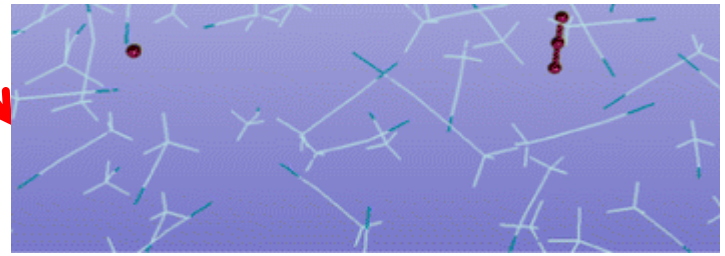


5000-10000 atoms



Dyes

50-100 atoms



redox mediator

500-1000 atoms

100 years trying to solve the electronic Schrödinger equation:

$$\hat{H}_e \varphi_n(\mathbf{r};\mathbf{R}) = \varepsilon_n(\mathbf{R})\varphi_n(\mathbf{r};\mathbf{R})$$

The Hamiltonian for the electronic motion:

$$\hat{H}_e = -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_{a,i}\frac{Z_a}{r_{ai}} + \sum_{i>j}\frac{1}{r_{ij}} + \sum_{a>b}\frac{Z_a Z_b}{R_{ab}}$$

The electron-electron repulsion term makes it unsolvable for n>1

(SOB!!)

Machine Learning Force Fields

Cite This: *Chem. Rev.* 2021, 121, 10142–10186

Oliver T. Unke,[△] Stefan Chmiela,[△] Huziel E. Sauceda, Michael Gastegger, Igor Poltavsky, Kristof T. Schütt, Alexandre Tkatchenko,* and Klaus-Robert Müller*

Physically Motivated Force Fields

$$U(R) = \sum_{bonds} k_r \left(r - r_{eq}\right)^2 \qquad \textit{bond}$$

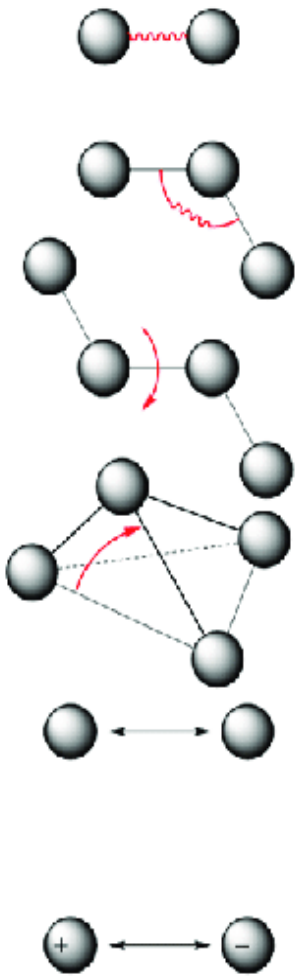
$$+ \sum_{angles} k_\theta \left(\theta - \theta_{eq}\right)^2 \qquad \textit{angle}$$

$$+ \sum_{dihedrals} k_\phi \left(1 + \cos\left[n\phi - \gamma\right]\right) \qquad \textit{dihedral}$$

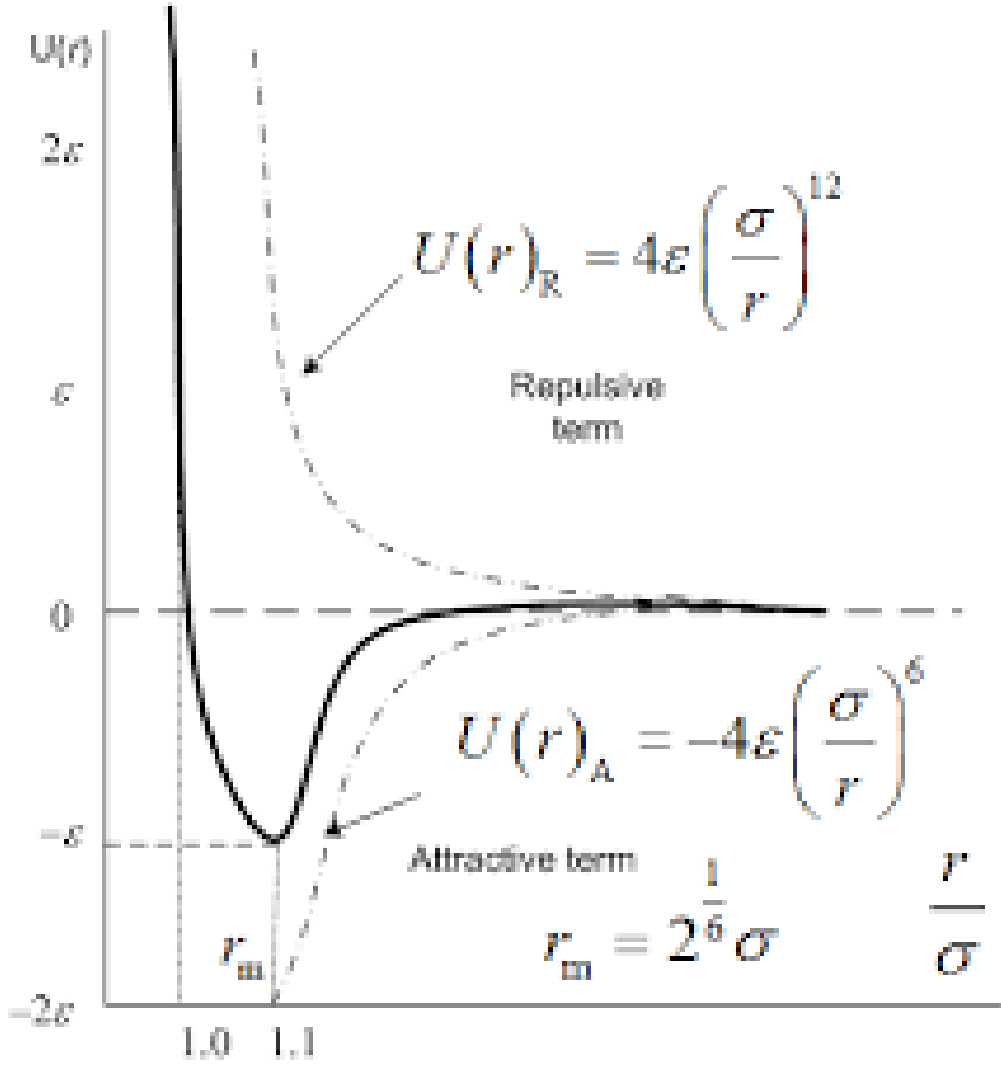
$$+ \sum_{impropers} k_\omega \left(\omega - \omega_{eq}\right)^2 \qquad \textit{improper}$$

$$+ \sum_{i<j}^{atoms} \varepsilon_{ij} \left[\left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^{6} \right] \qquad \textit{van der Waals}$$

$$+ \sum_{i<j}^{atoms} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \qquad \textit{electrostatic}$$



Lennard-Jones potential



Machine Learning Force Fields

$$f(\mathbf{x}) \approx \hat{f}(\mathbf{x}) = \sum_{i=1}^{M} \alpha_i K(\mathbf{x}, \mathbf{x}_i)$$

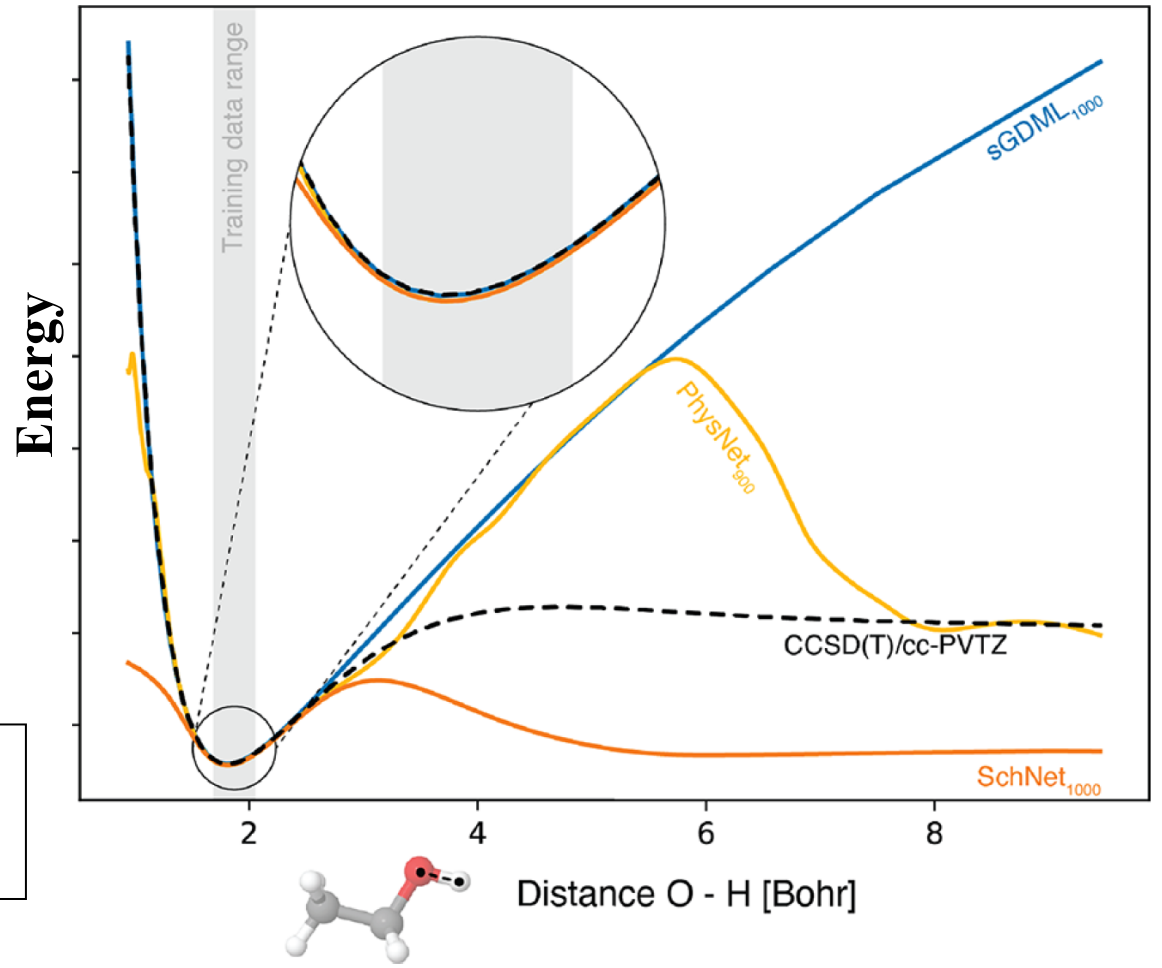
Coefficients

Similarity function

Training set: define f(x) through some algorithm (learning by comparing x x')

Production run: use f(x) for values of x not in the training set

ML Force Fields – trustful region



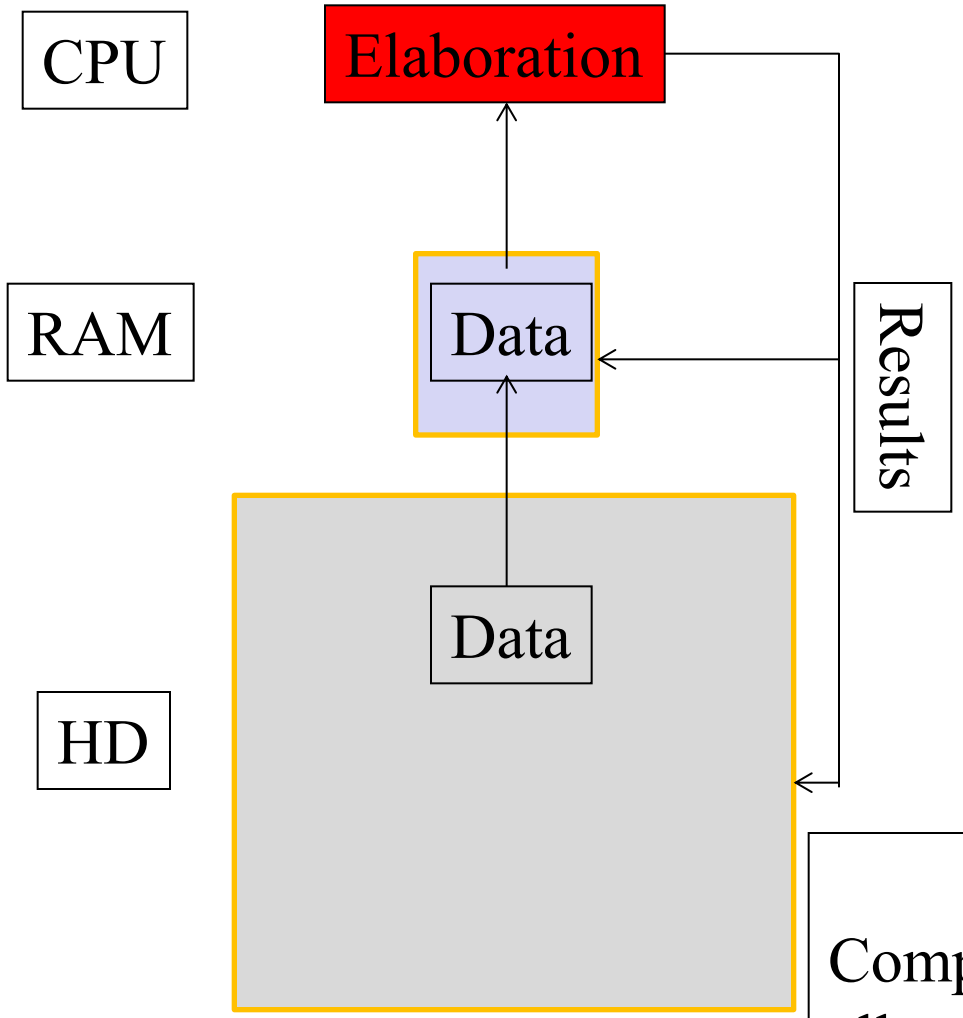
Computational resources





Computational resources: Feasibility

Execution schema



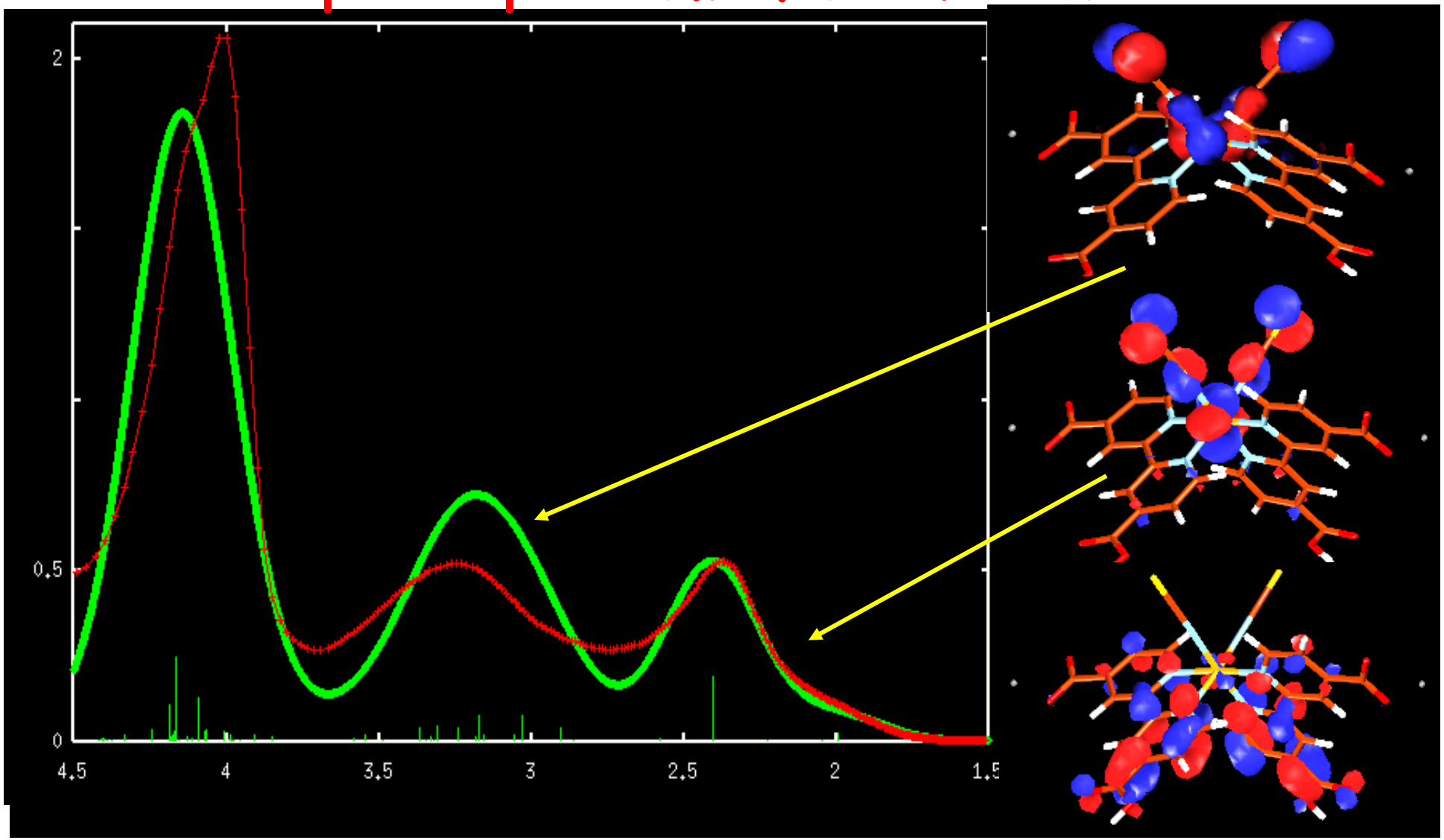
Feasibility problems

Elaboration time per data
Complex algorithms, requiring several operations

Number of data/Results
Systems dimensions and algortihm complexity

Unfeasible	Slow
Computer cannot allocate the data	Execution time too long

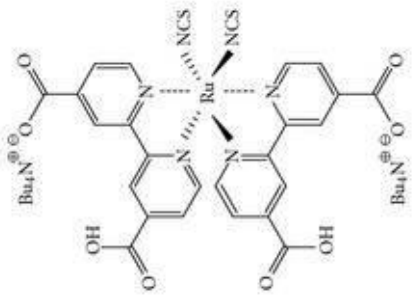
Absorption spectrum of N719 in water:



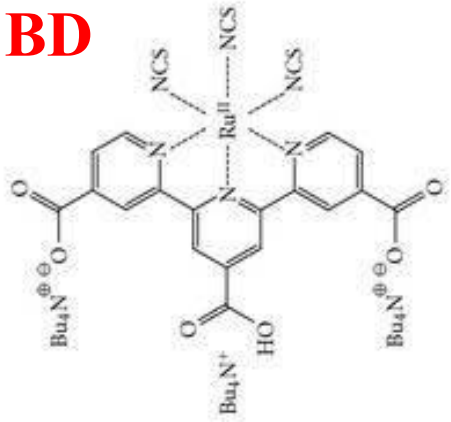
S. Fantacci, F. De Angelis, A. Selloni — ***J. Am. Chem. Soc.*** **2003, *125*, 4381.**
F. De Angelis, S. Fantacci, A. Selloni — ***Chem. Phys. Lett.*** **2004, *389*, 204.**
F. De Angelis, S. Fantacci, M.K. Nazeeruddin — ***Chem. Phys. Lett.*** **2005, *415*, 115.**
F. De Angelis,. S. Fantacci, M. Grätzel et al. — ***J. Am. Chem. Soc.*** **2005, *127*, 16835.**

Ruthenium dyes: The hunt for red photons!

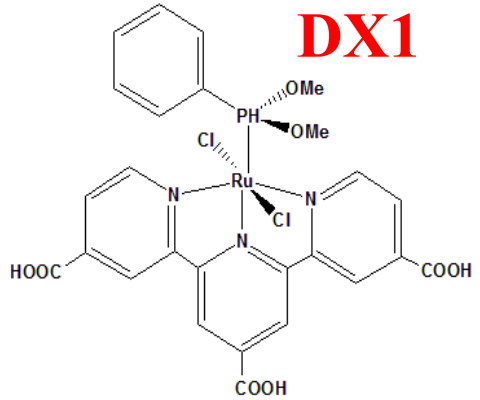
N3/N719



BD



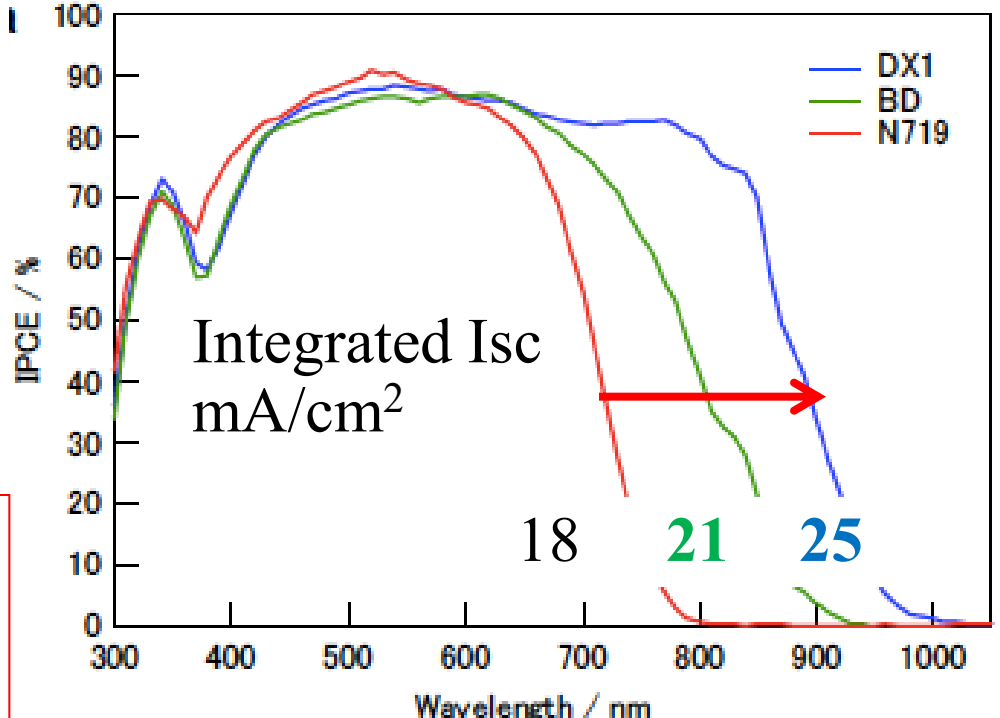
DX1



$$J_{SC}(\mathrm{mA/cm^2}) = \int P_{in}(\mathrm{mW/cm^2}) \times \frac{\lambda}{1240} \times \frac{\mathrm{IPCE}(\lambda)}{100}\, d\lambda$$

$$\mathrm{IPCE} = \mathrm{LHE} \times \phi_{INJ} \times \phi_{COLL}$$

$$\mathrm{LHE}(\lambda) = 1 - 10^{-\alpha(\lambda)d}$$



Red-shift of the absorption spectrum corresponds to higher current

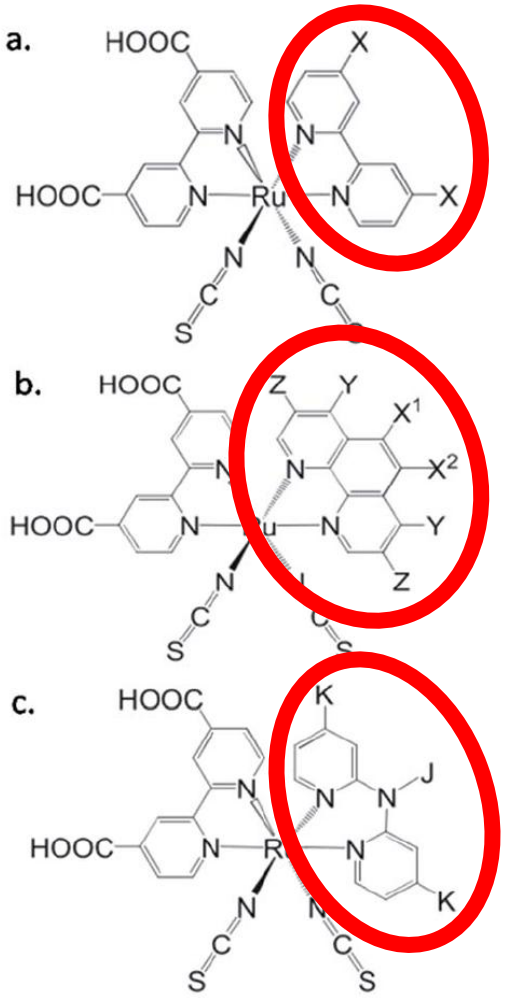
CrossMark click for updates

Cite this: *RSC Adv.*, 2015, **5**, 23865

RSC Advances

Quantitative structure–property relationship modeling of ruthenium sensitizers for solar cells applications: novel tools for designing promising candidates†

Sara Tortorella,[a] Gabriele Marotta,[b] Gabriele Cruciani*[a] and Filippo De Angelis*[b]



Ligand descriptors

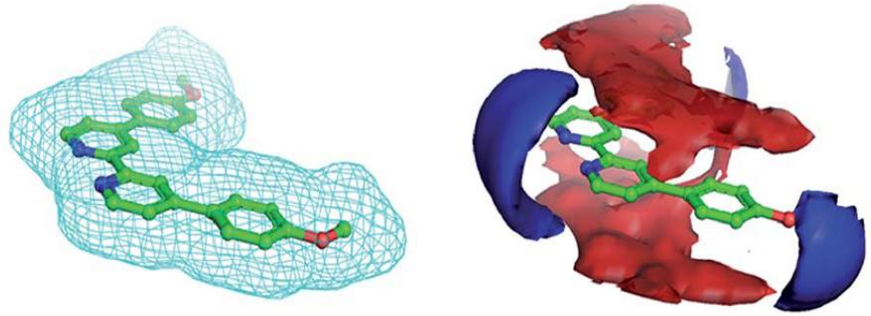
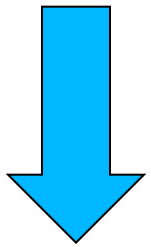


Fig. 1 Example of (a) shape and (b) hydrophobic (red) and hydrophilic (blue) molecular interaction fields (MIFs) for ligand 11.



Ligand library / Efficiency data

1 •–H

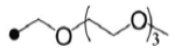
2 •–CH_3

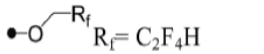
3 •–C_6H_{13}

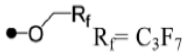
4 •–C_9H_{19}

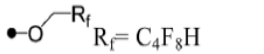
5 •–$C_{13}H_{27}$

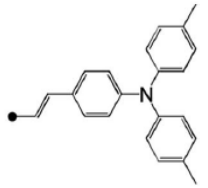
6 •–$C_{18}H_{37}$

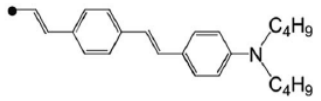
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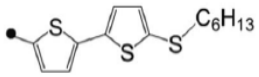
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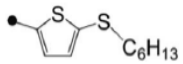
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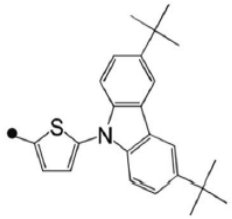
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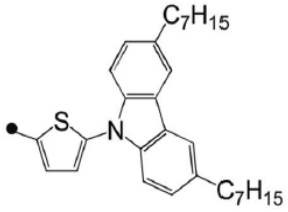
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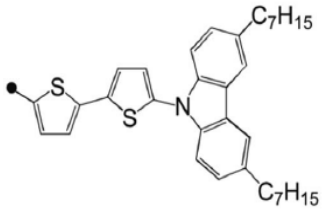
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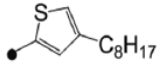
B: 1,10-phenantroline scaffold

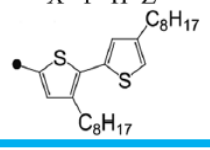
60 $X^1 = H, X^2 = NH_2, Y = Z = H$

61 $X^1 = X^2 = NH_2, Y = Z = H$

62 $X^1 = H, X^2 = NO_2, Y = Z = H$

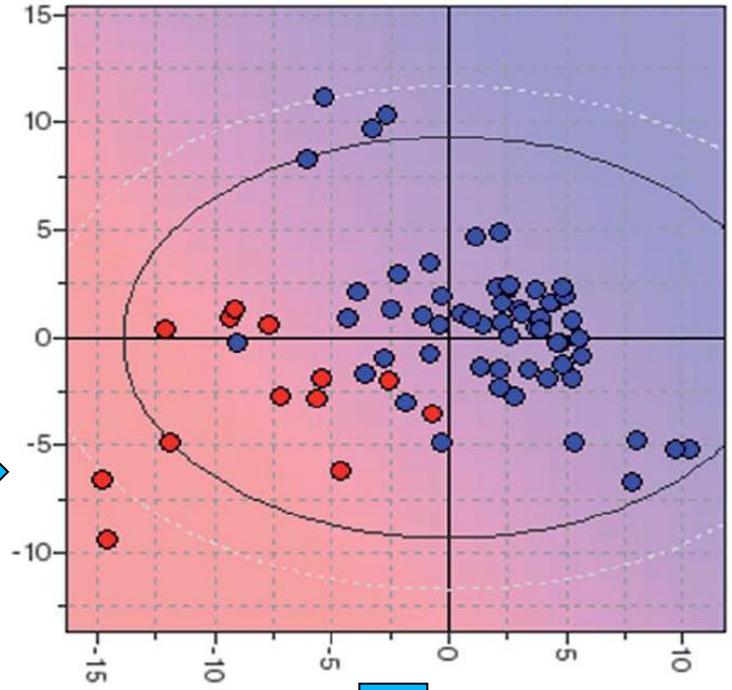
63 $X^1 = X^2 = NO_2, Y = Z = H$

64 X=Y=H Z= 

65 X=Y=H Z= 

J.-F. Yin et al. *Coord. Chem. Rev.*, **2012**, 256, 3008–3035.

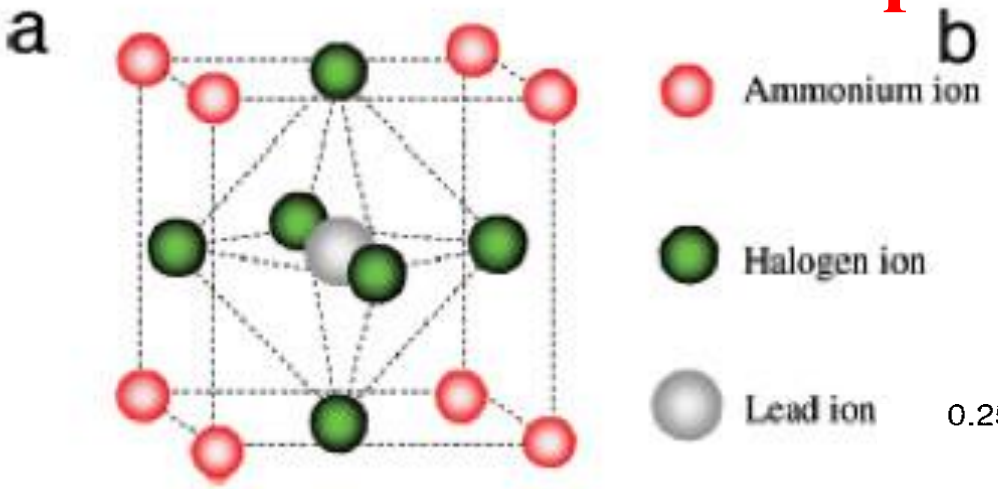
Structure/property correlation



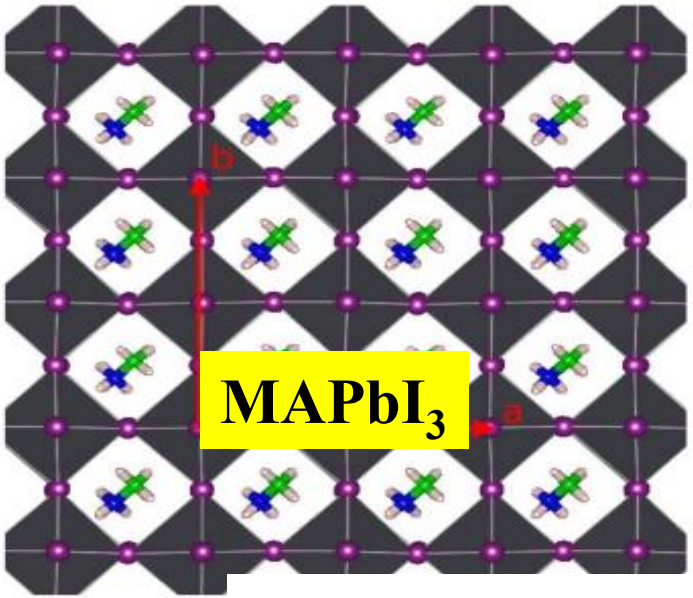
New ligand / New dye

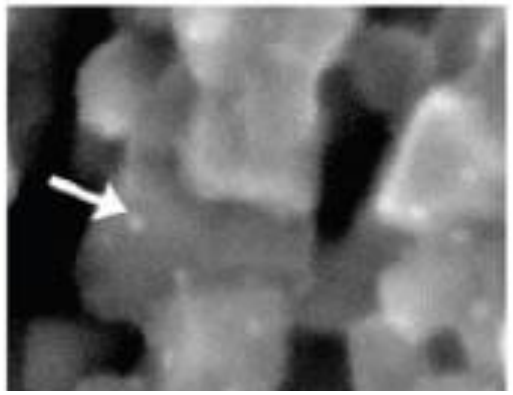
Same efficiency!

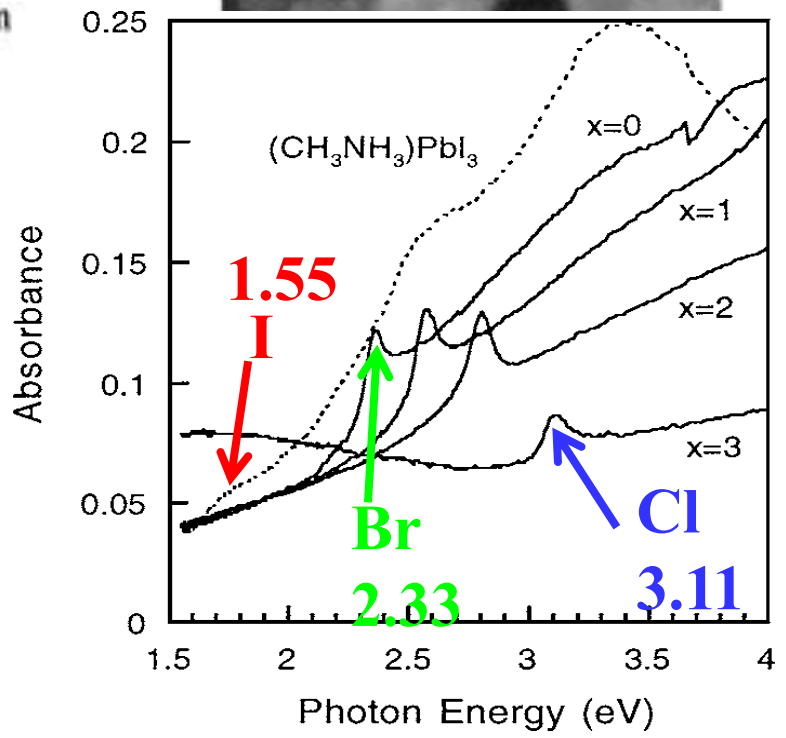
Perovskite solar cells:
Metal-halide perovskites



AMX_3

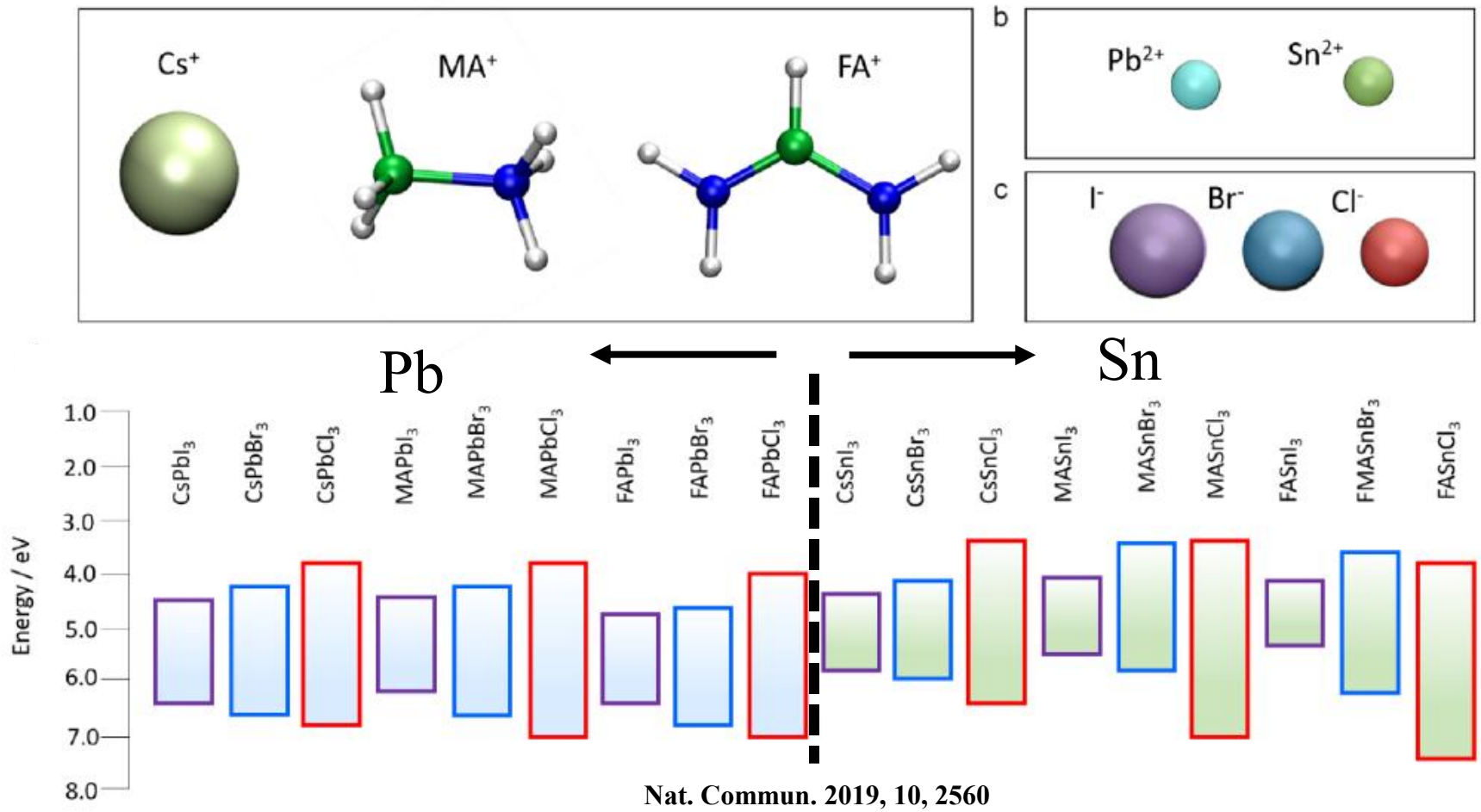






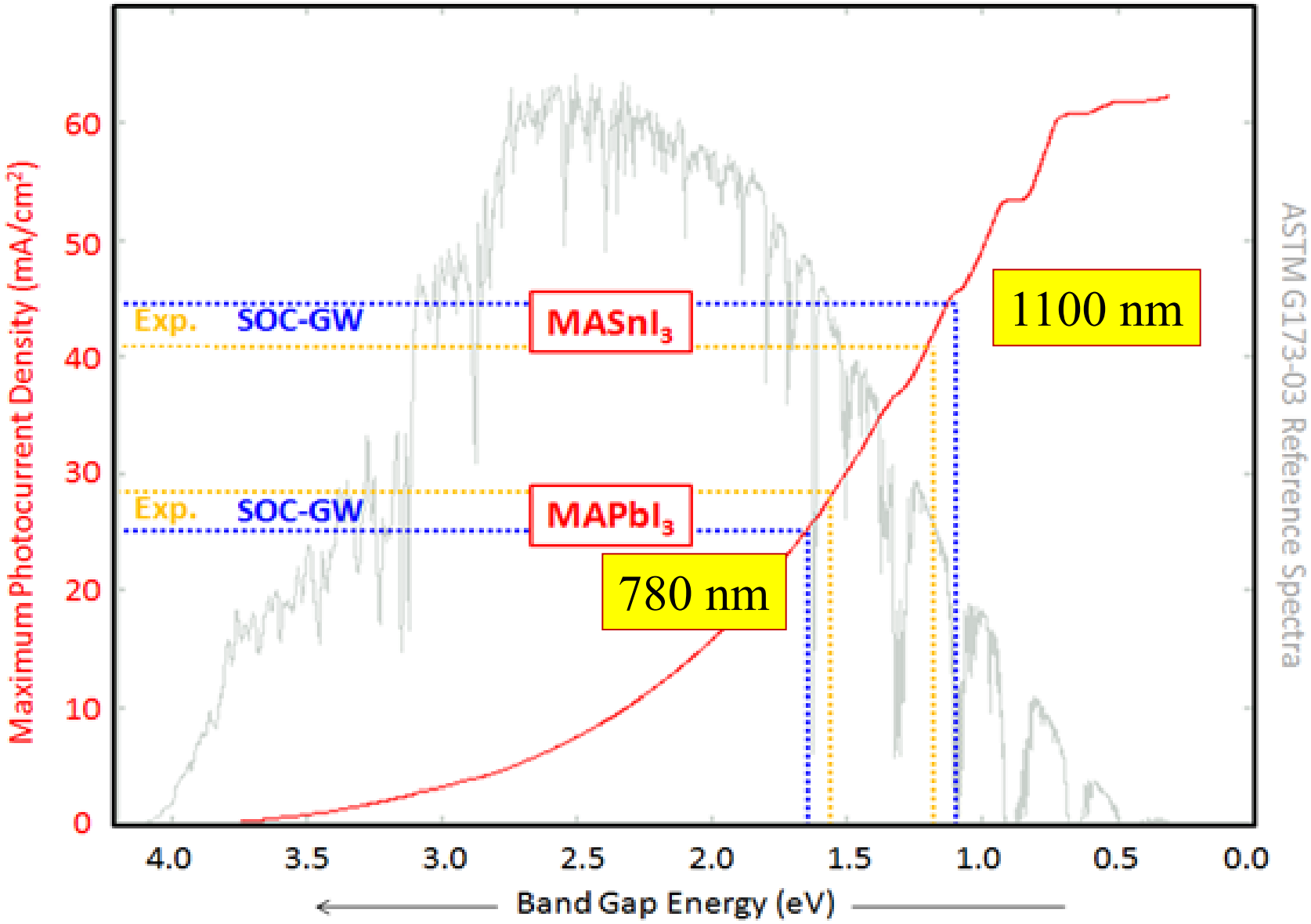
A. Kojima et al. *J. Am. Chem. Soc.* **2009,** *131*, 6050

3D perovskites hyperspace:
Compositional tuning of energy levels



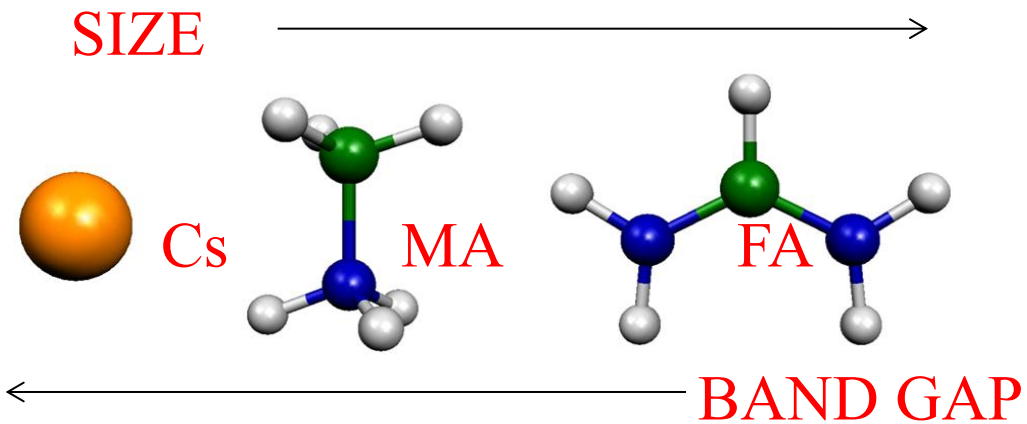
Nat. Commun. 2019, 10, 2560

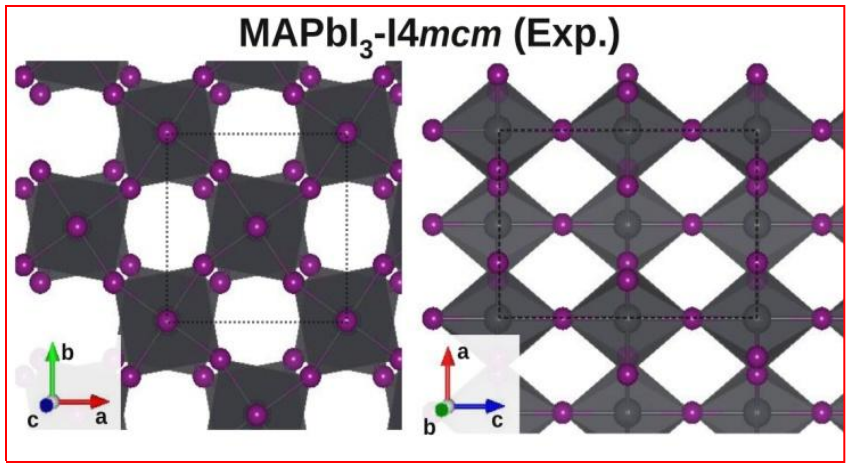
Maximum Isc: Sn vs. Pb

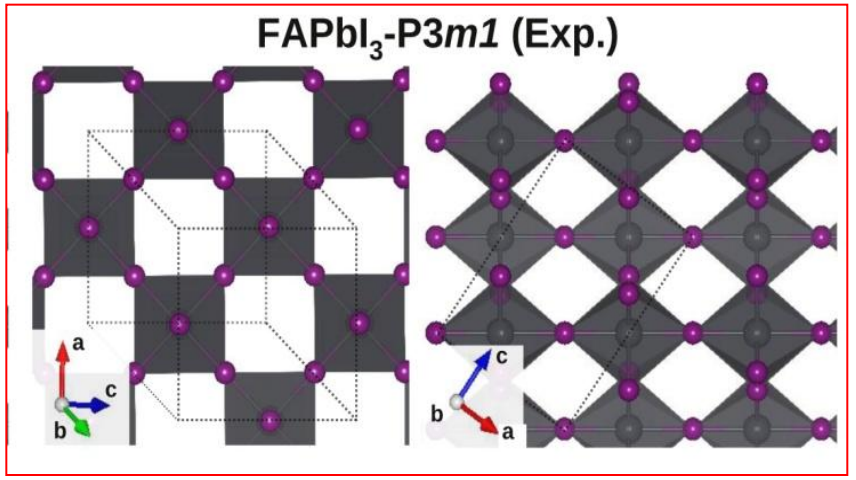


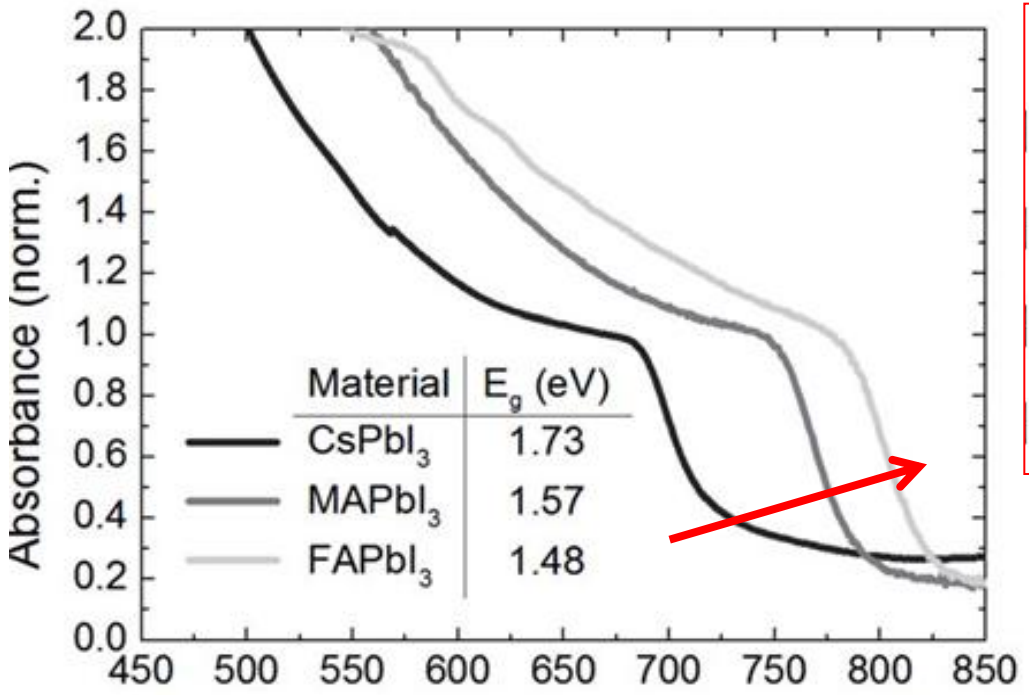
P. Umari, E. Mosconi, F. De Angelis *Sci. Rep.* **2014**, *4*, 4467.

Role of cations: MA vs. FA









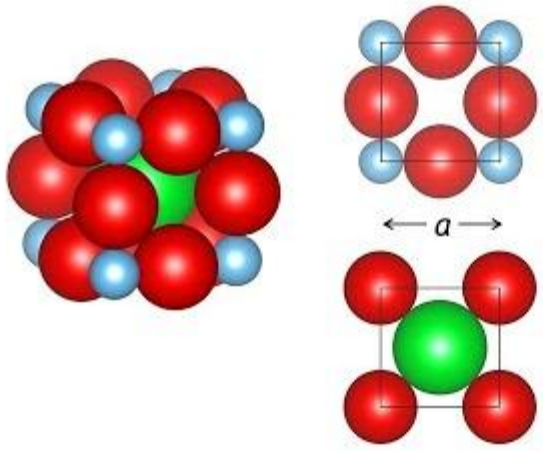
A. Amat et al. *Nano Lett.* **2014,** *14*, 3608

	MA	FA
SR-DFT	1.66	1.63
SOC-DFT	0.60	0.45
SOC-GW	**1.67**	**1.48**

The Impact of Machine Learning in Energy Materials Research: The Case of Halide Perovskites

Cite This: *ACS Energy Lett.* 2023, 8, 1270−1272

Tolerance Factor



$$a = 2(r_B + r_X)$$

$$a = \frac{2(r_A + r_X)}{\sqrt{2}}$$

$$a = \sqrt{2}(r_A + r_X)$$

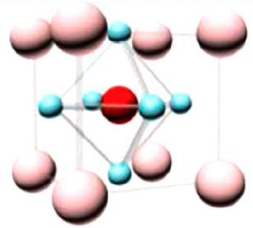
$$t = \frac{r_A + r_X}{\sqrt{2}\left(r_B + r_X\right)}$$

$$t = \frac{R_A/R_B + 1}{[2(\bar{\mu}+1)^2 + (\Delta\mu)^2]^{1/2}}$$

DFT

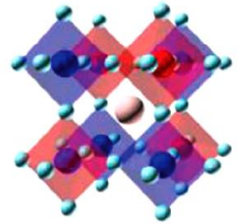
354 Perovskites

Single Perovskite



A = K, Rb, Cs
B = Sn, Pb
X = Cl, Br, I

Double Perovskite

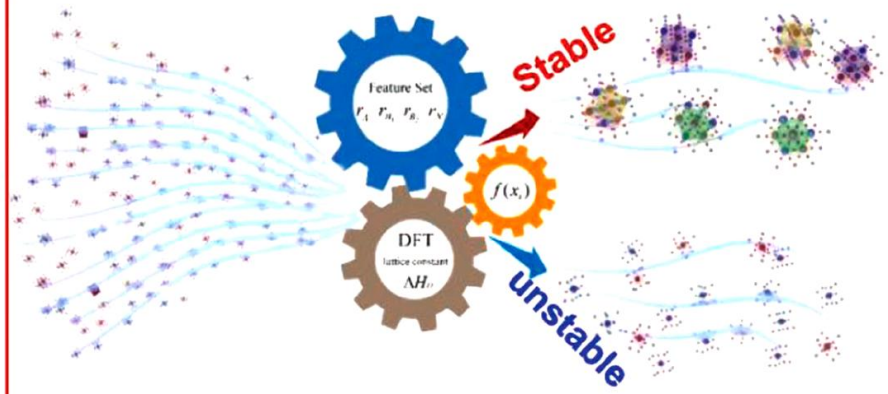


A = Na, K, Rb, Cs
B1 = Na, K, Rb, Cu, Ag, In, Tl
B2 = Sb, Bi, Ga, In
X = Cl, Br, I

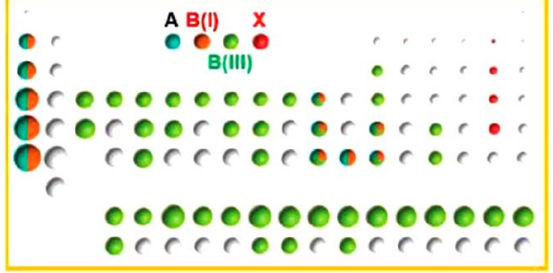
Physics Intuition

Descriptor	Phys. Mean.	Stab. Acc.	Form. Acc.	RMSE (meV/atom)
$\mu = R_B / R_X$	t	Framework stability	85%	77%	54
$t = (R_A + R_X)/\sqrt{2}(R_B + R_X)$	μ	Octahedral stability (Pauling's first rule)	49%	60%	96
$\eta = (\frac{4}{3}\pi R_A^3 + \frac{4}{3}\pi R_B^3 + 4\pi R_X^3)/V_{cell}$	η	Packing Fraction	59%	61%	97
	$(t+\mu)^n$	Ref. 30	88%	84%	27

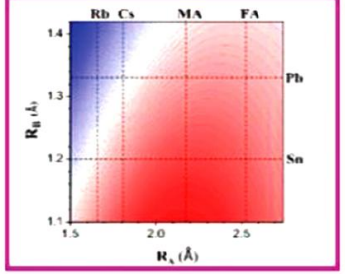
Machine Learning

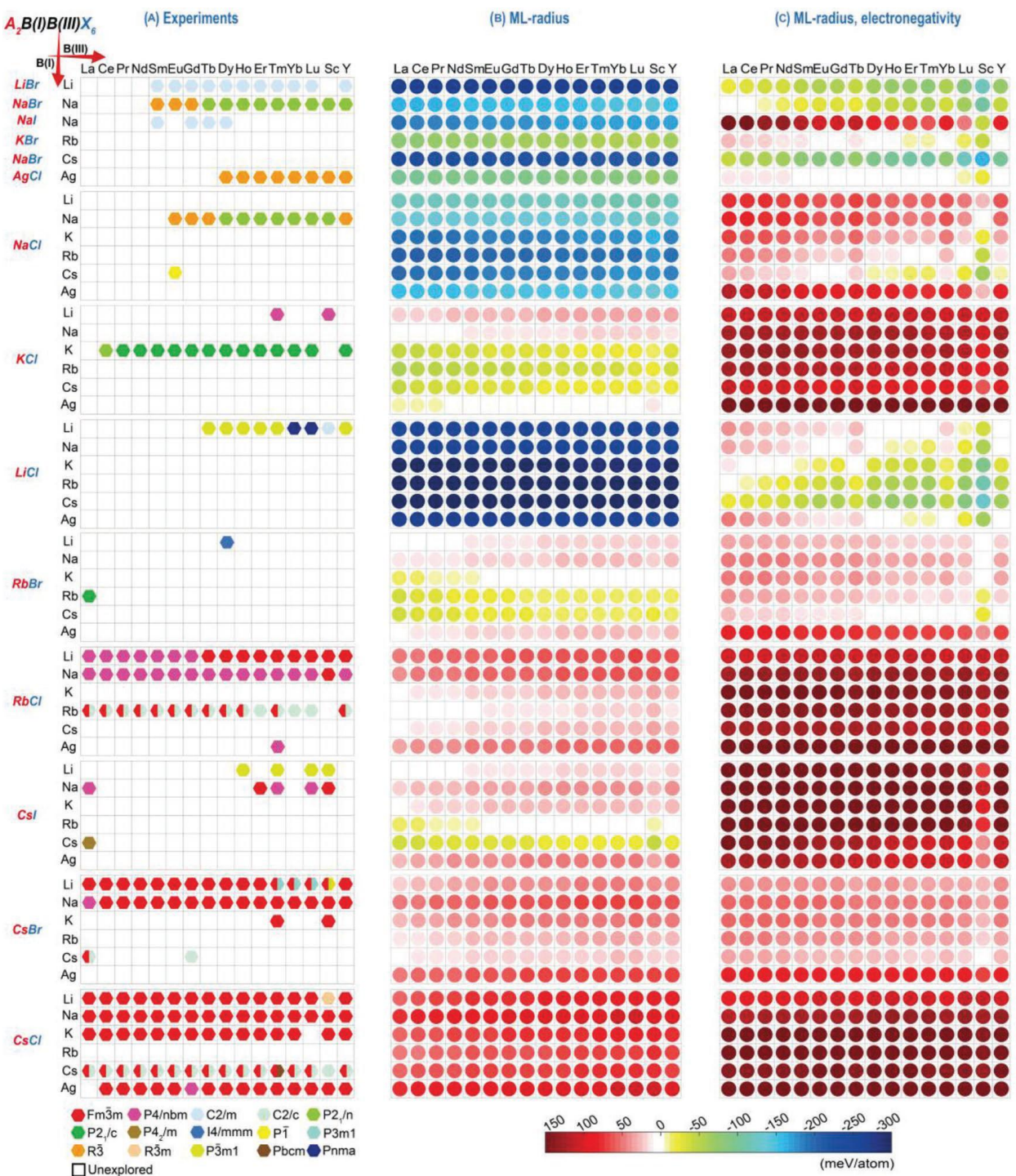


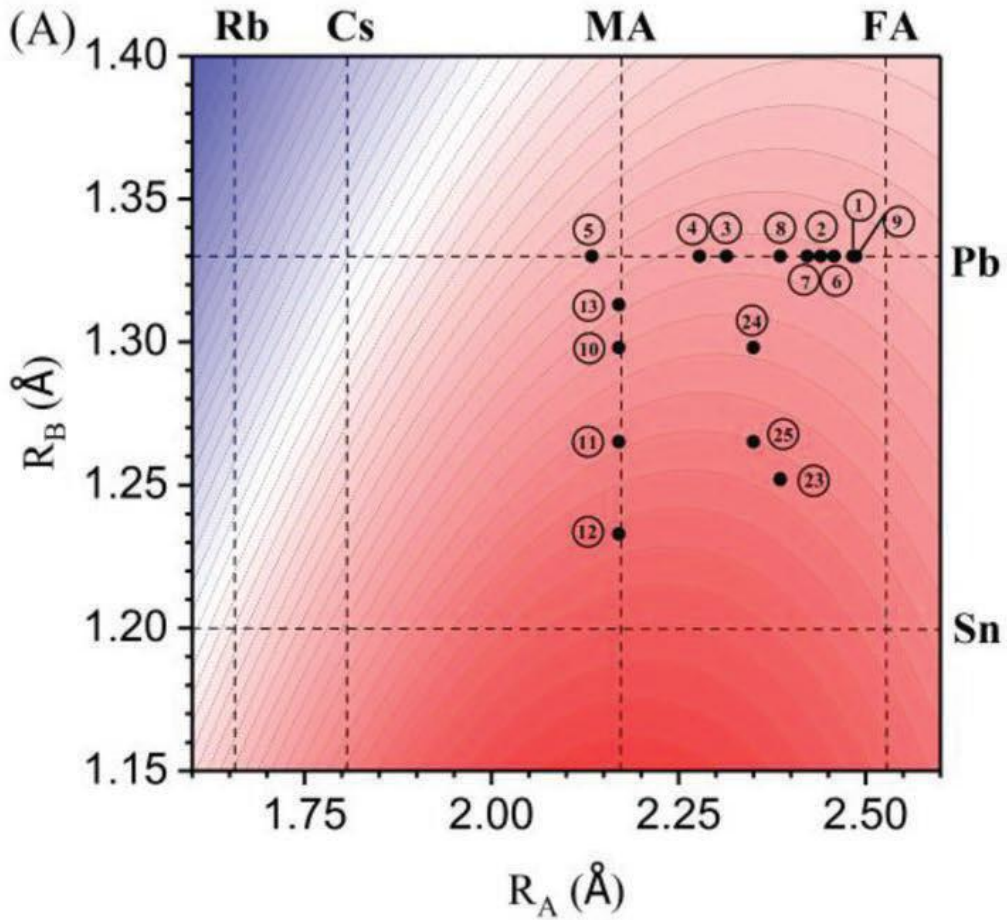
~10⁴ Double Halide Perovskites



Mixed Perovskites



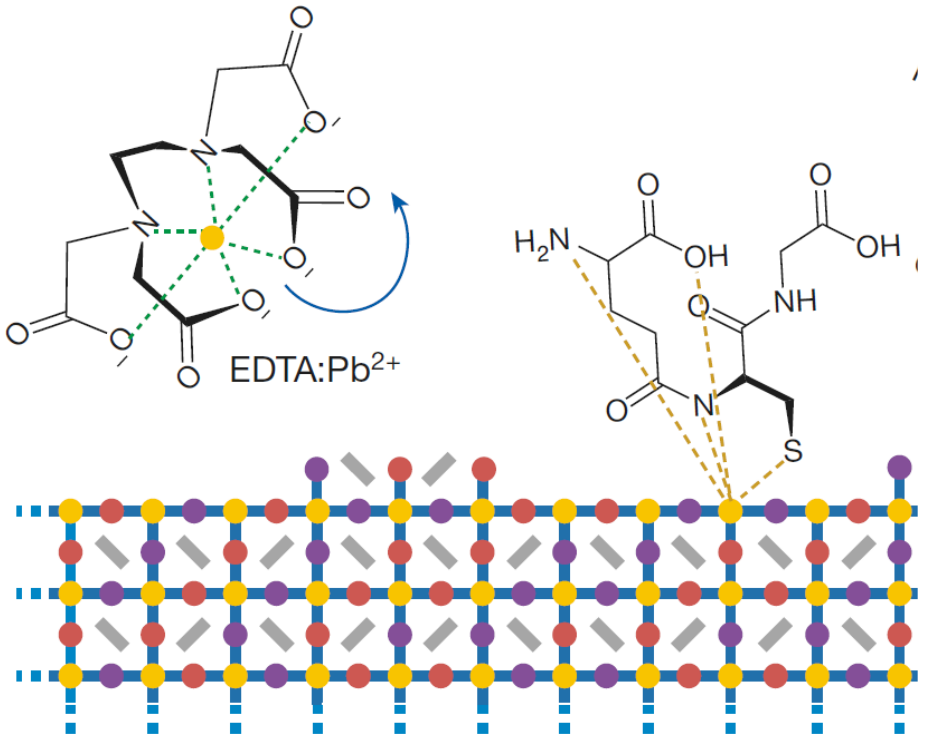




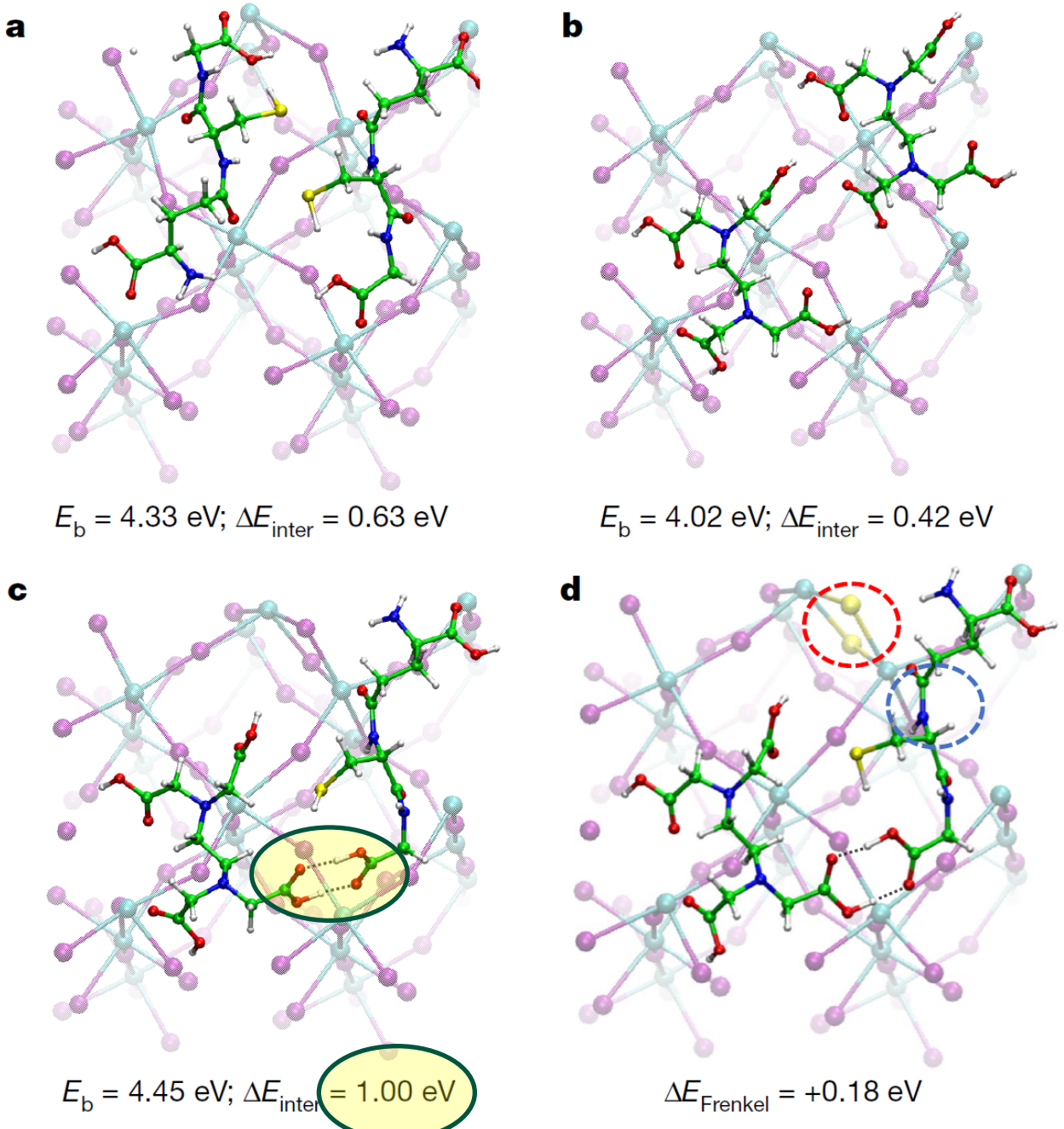
Predict stable compositions but lose physical meaning of descriptors

Exploting intermolecular interactions for surface passivation

EDTA **Glutathione**



Hassan Y. et al. "Ligand-engineered bandgap stability in mixed-halide perovskite LEDs" *Nature*, **2021**, 591, 72–77



Computational Laboratory for Hybrid/Organic Photovoltaics

CNR-SCITEC



E. Mosconi


G. Vitillaro


D. Meggiolaro

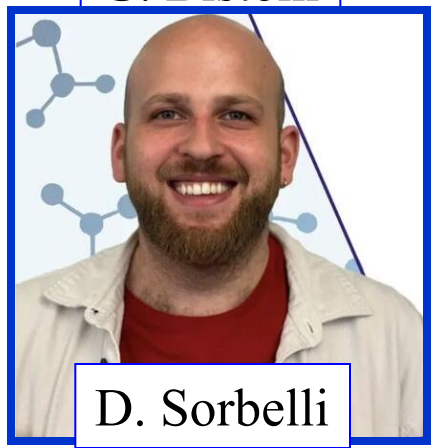

L. Belpassi

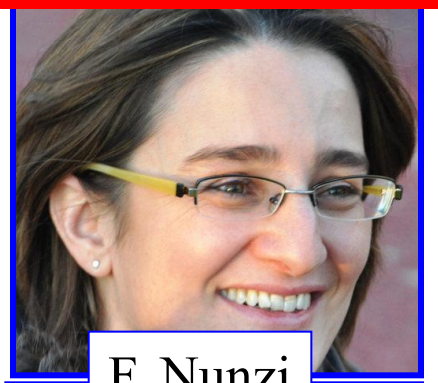

S. Fantacci

UNIPG-DCBB


P. Belanzoni


G. Bistoni


D. Sorbelli


F. Nunzi

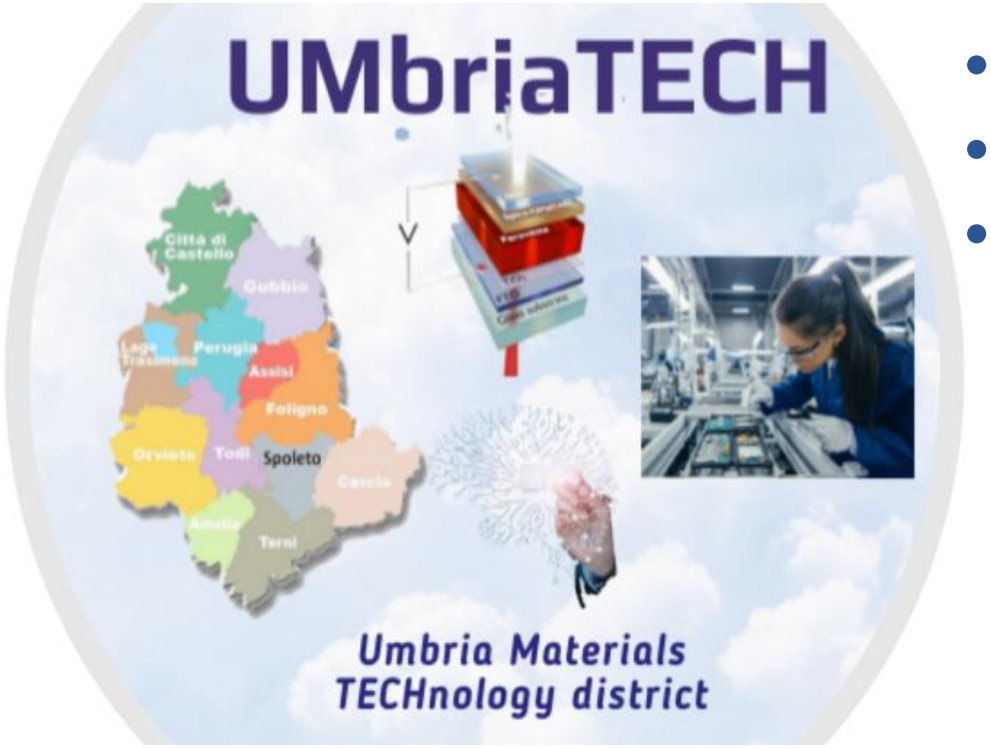

E. Ronca


L. Gregori

Conclusions

- Lessons learnt from DSSCs have boosted research on PSCs

Trying to make an inpact



- UNIPG-DCBB
- CNR- SCITEC
- MISTER SMART INNOVATION S.c.r.l.

Technology transfer center funded with 5M€

Scale up PVSK technology

Prolabin – Solertix - Eni