Solvent engineering approaches for green printable perovskite formulations

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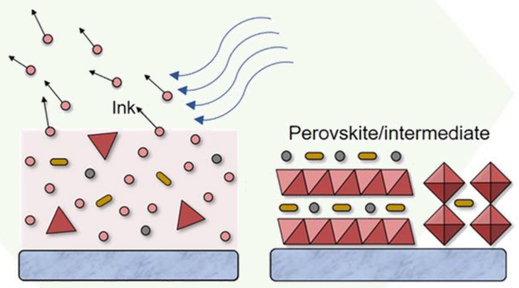
OBJECTIVE

Solution processed perovskite materials are still based on toxic and/or hazardous solvents that, despite giving rise to an optimum control on crystallization for a wide range of compositions and deposition techniques, limit both their processing and scalability for future commercialization. Our objective is to perform a comprehensive solubility study of perovskite precursors in non-hazardous no-toxic solvents that allows achieving green printable perovskite formulations, compatible at industrial level.

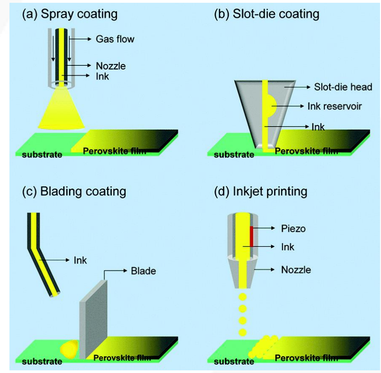


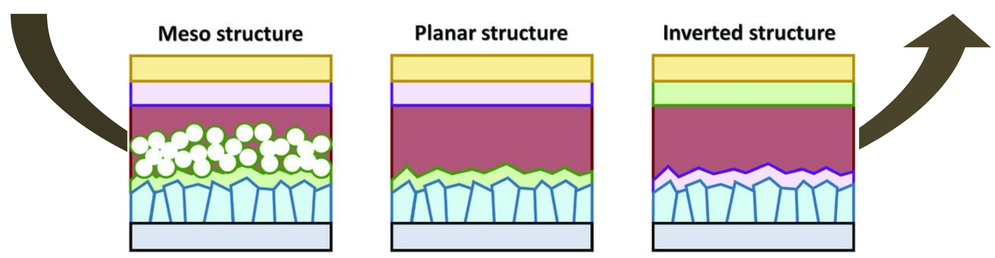
High efficiency and stable perovskite solar cells

Compositional engineering

Interface engineering

Deposition technique parameters





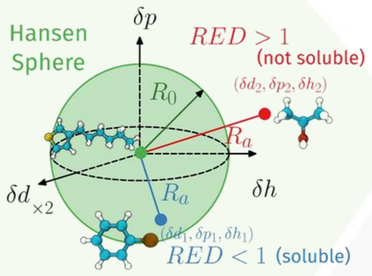
SOLVENT ENGINEERING APPROACHES

Hansen solubility parameters (HSP)

- ✓ tool to describe and predict the solubility of organic molecules based on the principle of "*like dissolves like*"
- ✓ interactive energies between solvent and solute are governed by three components: dispersion forces (δD), polar forces (δP) and Hydrogen bond forces (δH)

Main limitation:

- ○ ionic forces and coordination interactions are not taken into account



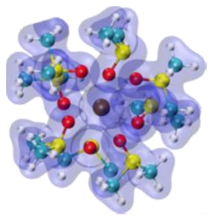
Mayer bond order (MBO) and Guttman donor number (GDN)

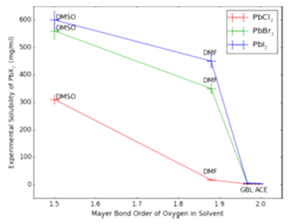
MBO

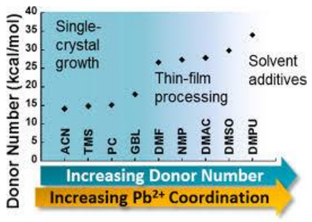
- ✓ solubility dominated by complexation and governed by the electronic state of solvent's dative bonding atoms
- ✓ quantification of the electronic state of solvent's most electronegative atom

GDN

- ✓ solubility dominated by the coordination ability of the solvent with Pb^{+2}
- ✓ quantification of Lewis basicity of the solvent

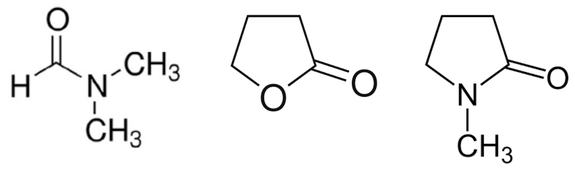






Alternative approach

- ✓ solvent alternatives based on functional groups with similarities to DMF, GBL and NMP



DMF **GBL** **NMP**

Solvent screening methodology

Solvent database (1247)

Selection criteria according to HSP, MBO and GDN (RED≤1; bond unsaturation 0,1-0,4; GDN>18 Kcal)

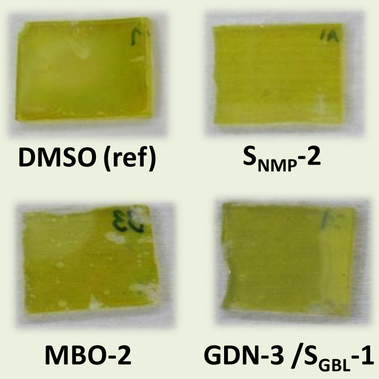
Exclusion of solvents classified as GS06, GS08, GS09 + MP≤25 C and BP≤200 C

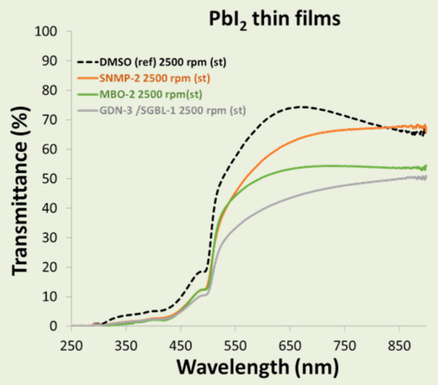
MAIN RESULTS

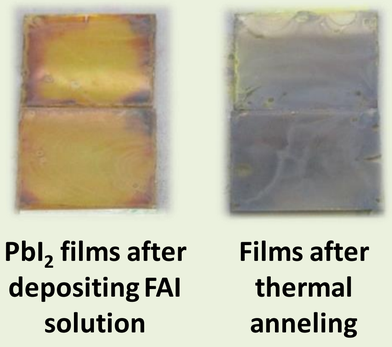
- ✓ Solubility tests of PbI_2 were experimentally performed on more than 30 green solvents and more than 85 green solvents mixtures, at concentrations ranging from 40 mg/ml to 400 mg/ml
- ✓ None of the pure solvents achieved to dissolve PbI_2 at 400 mg/ml, but 14 solvent combinations were successful using 10-20 vol% of DMSO. Ternary mixtures are being evaluated to completely remove DMSO volume fraction
- ✓ First trials on perovskite formation based on 3 green solvent alternatives showed very promising results

PbI_2 solubility 400mg/ml	HSP-1	MBO-1	MBO-2	GDN-1	GDN-2	GDN-3 /S_{GBL}-1	S_{GBL}-2	S_{GBL}-3	S_{NMP}-1	S_{NMP}-2	S_{DMF}-1	S_{DMF}-2	S_{DMF}-3	S_{DMF}-4
Pure solvent	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
+ DMSO	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 10% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.	OK 20% vol.
+ MAI (1:1)	NA	NA	OK **Without DMSO**	NA	NA	OK **Without DMSO**	NA	NA	NA	OK **Without DMSO**	NA	NA	NA	NA

Spin-coated PbI_2 films, transmittance spectra and $FAPbI_3$ formation







PbI_2 films after depositing FAI solution **Films after thermal anneling**

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 763989. This publication reflects only the author's views and the European Union is not liable for any use that may be made of the information contained therein.