Sulfur-donor solvents preferentially coordinate Pb^{2+} in perovskite precursor solutions

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Loo group

Collaborators

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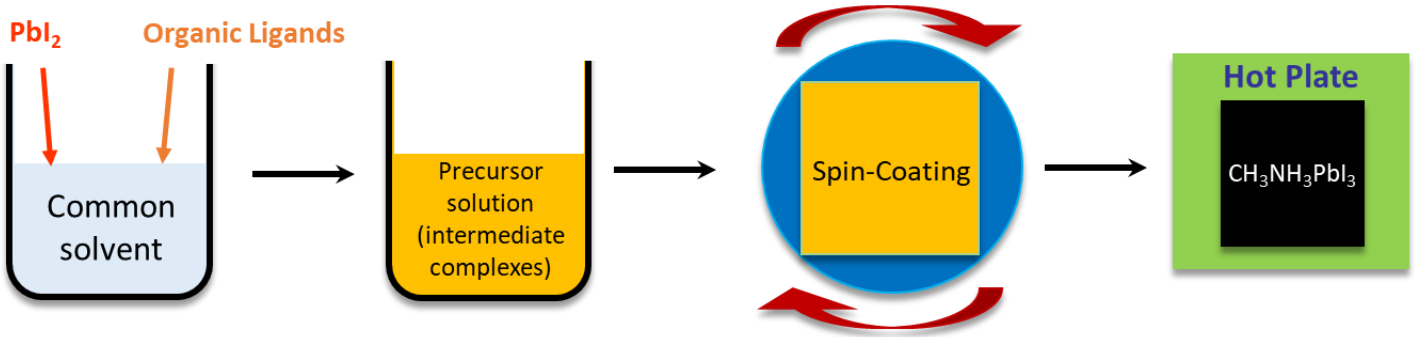
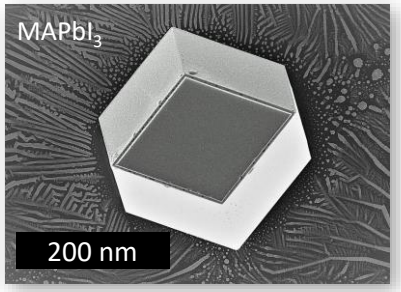
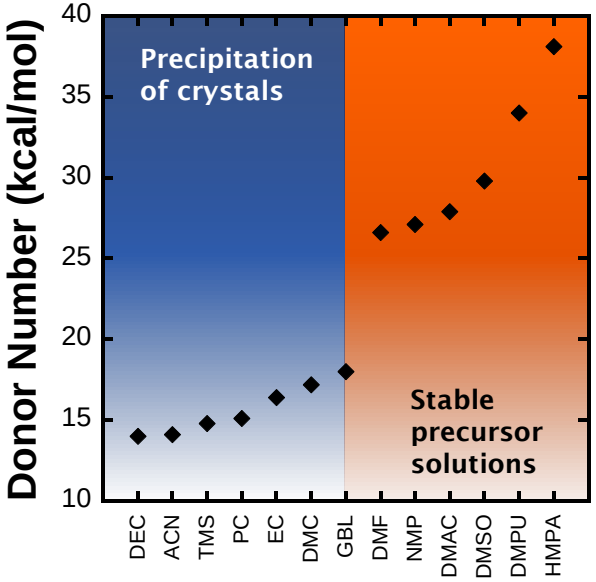
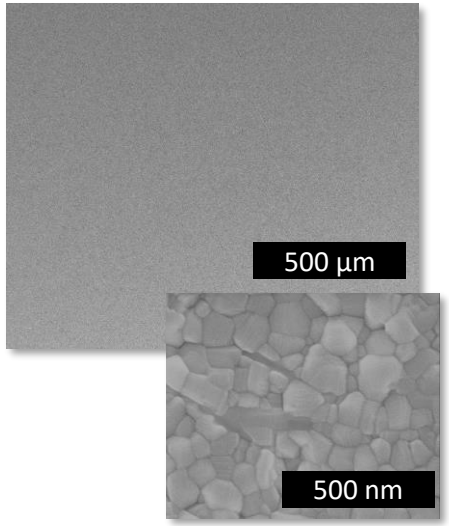
Coordination/reactions affect film structure, composition, and morphology



+ Precursor-solvent *coordination*



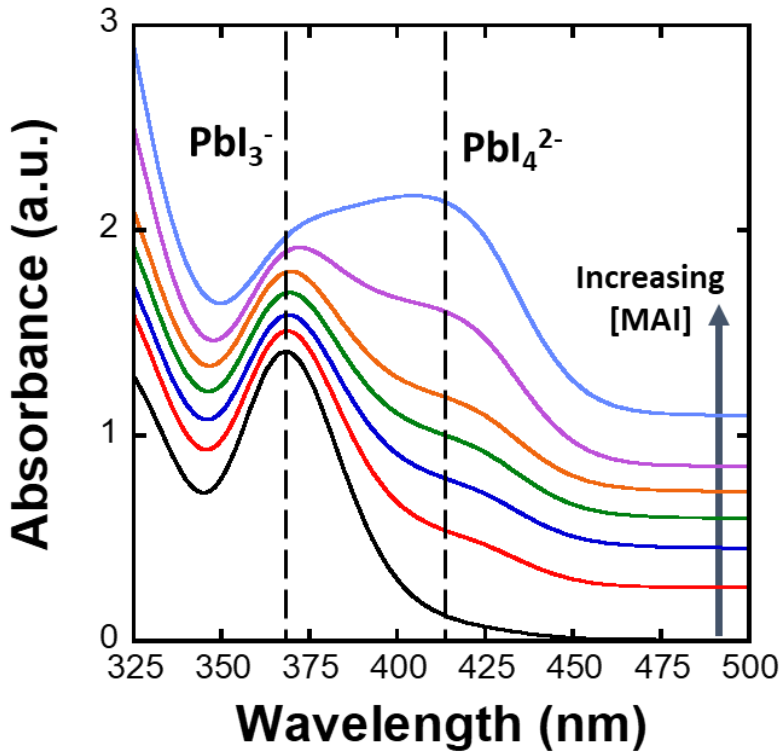


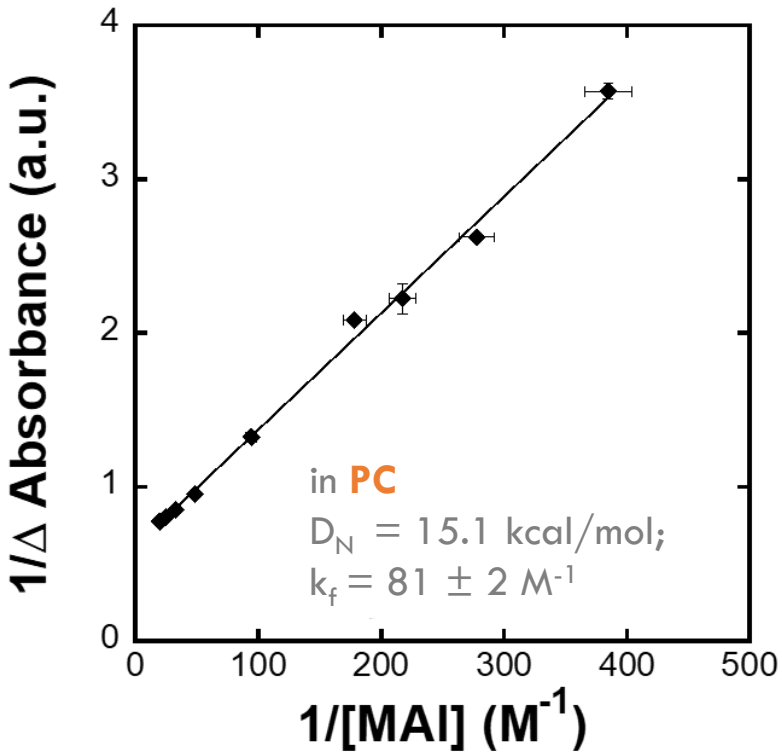


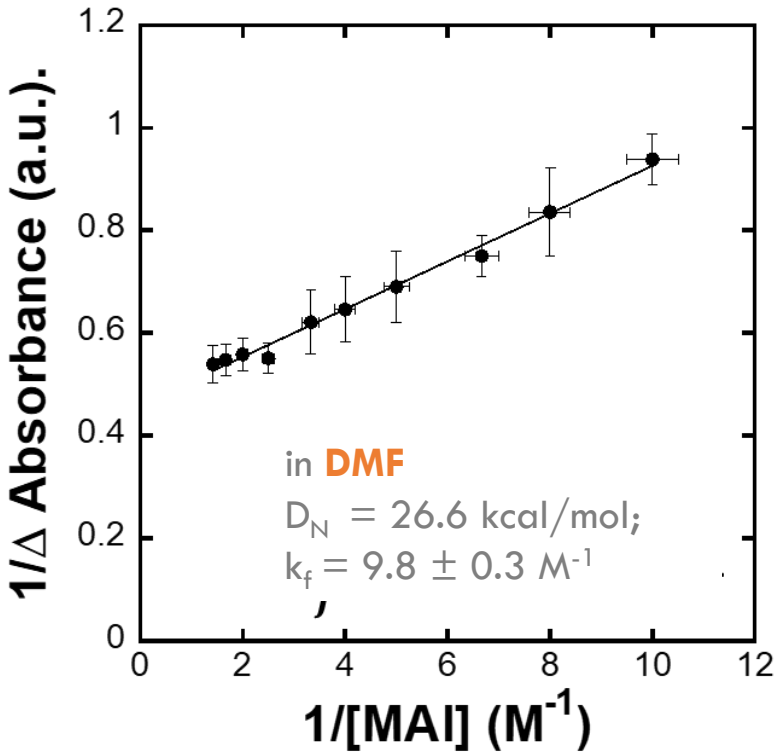
Strongly coordinating Lewis-base additive necessary to tune morphology and crystallization kinetics.

J. C. Hamill, J. Schwartz, Y.-L. Loo. *ACS energy lett. 3.* 92, 2018.

Examining the strength of Pb^{2+}-solvent interactions



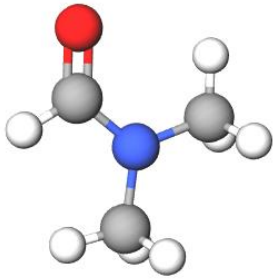




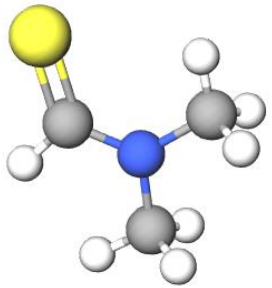
+ Lower K_f for PbI_4^{2-} formation constant implies ***stronger*** solvent coordination with Pb^{2+}
+ **Higher D_N = stronger coordination**

J. C. Hamill, J. Schwartz, Y.-L. Loo. *ACS energy lett. 3.* 92, 2018.

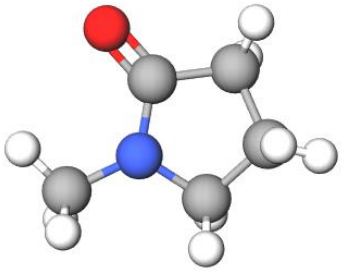
Choice of O-donor and S-donor solvent pairs



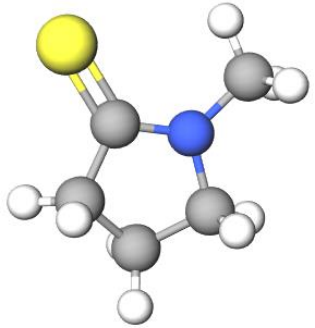
N,N-dimethylformamide
(DMF)



N,N-dimethyl***thio***formamide
(DMTF)

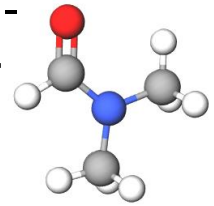


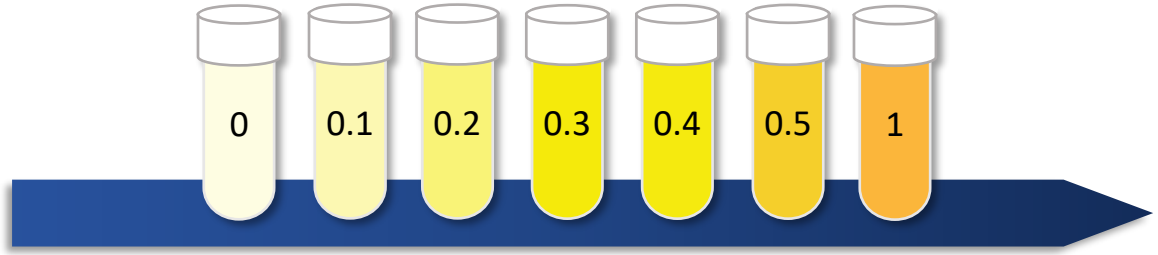
N-methyl-2-pyrrolidone
(NMP)



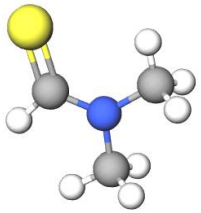
N-methyl-2-pyrrolidone
thione (NMPT)

Pure O-donor





Increasing mole fraction S-donor

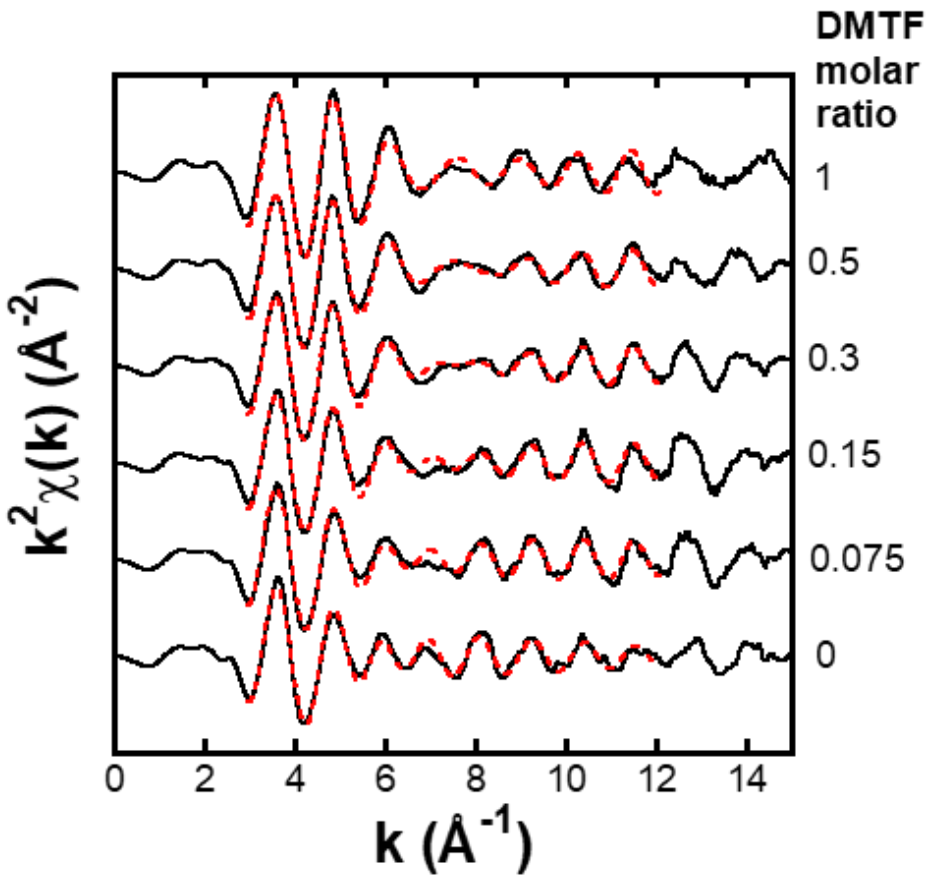


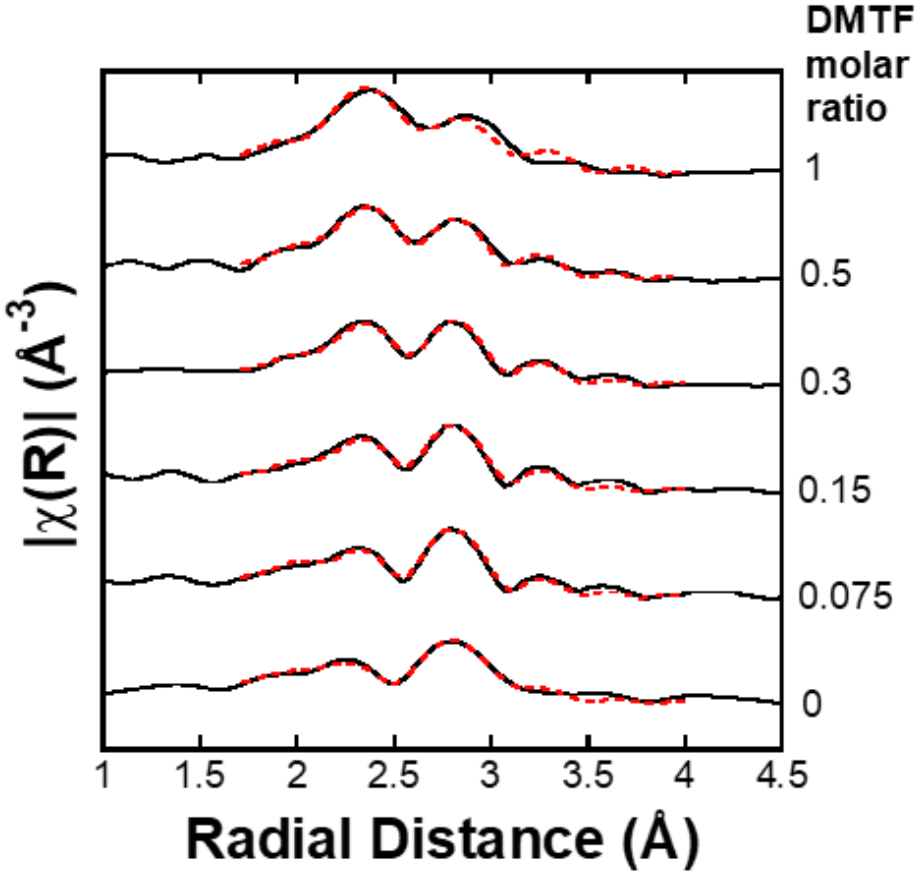
Pure S-donor

- Extended X-ray absorption fine structure (EXAFS) spectroscopy used to determine the number and identify of atoms coordinated to Pb^{2+} in solution

J. C. Hamill, O. Romiluyi, S. Thomas, J. Schwartz, M. F. Toney, P. Clancy, Y. –L. Loo. In prep.

Collection and fitting of EXAFS data





Fitting parameters include **coordination number/identity** of coordinating atoms, **bond distance**, and **degree of disorder** around the absorber.

EXAFS performed at Pb L_{III} absorption edge
Samples flash frozen and measured at 10 K to minimize thermal disorder

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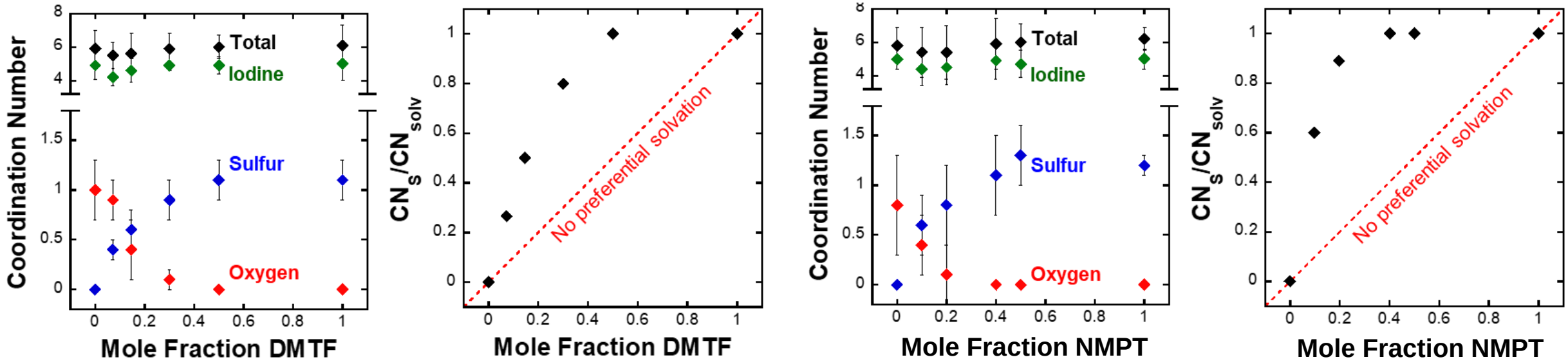
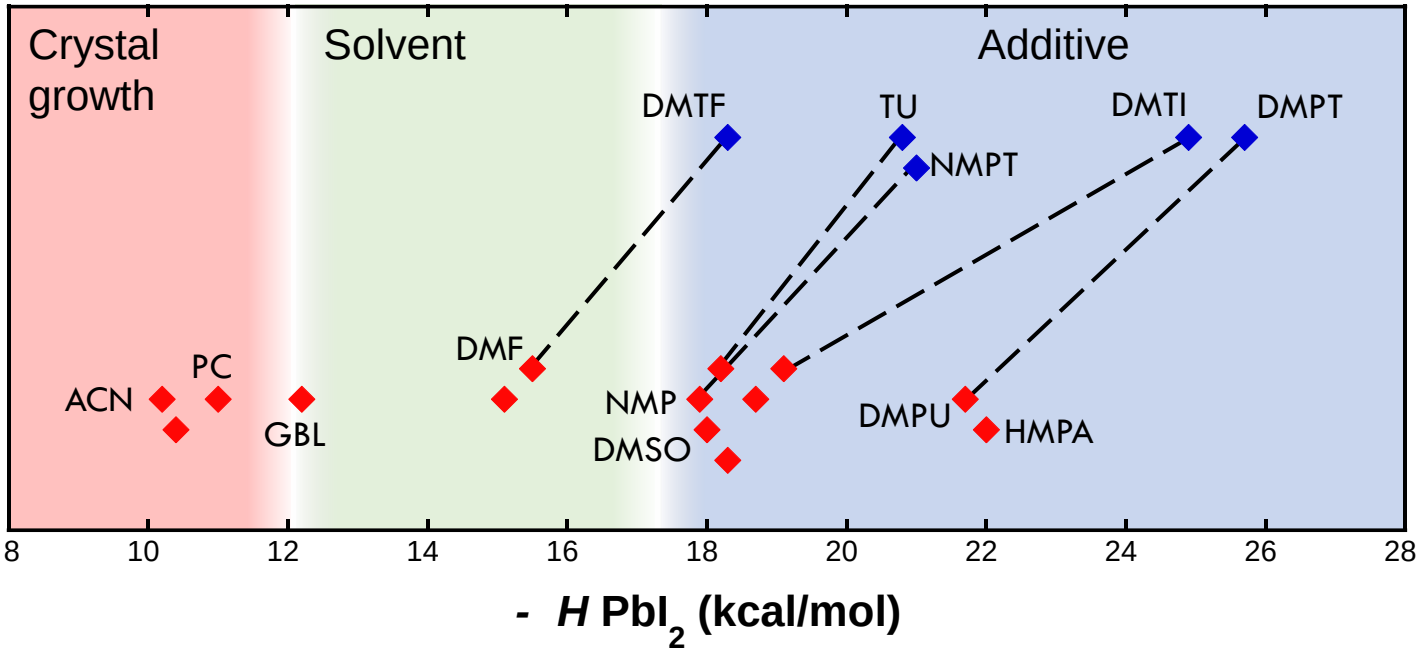
EXAFS proves preferential coordination of Pb^{2+} by S-donor



- **For both DMF/DMTF and NMP/NMPT solutions, stronger propensity to coordinate Pb^{2+} by S-donor**
- **Fraction of S-coordinated Pb^{2+} is always *higher* than expected if no preferential solvation**
- **Conclude Pb^{2+} prefers coordination to S-donor**

J. C. Hamill, O. Romiluyi, S. Thomas, J. Schwartz, M. F. Toney, P. Clancy, Y. –L. Loo. In prep.

Calculations provide Pb^{2+}-solvent binding energies



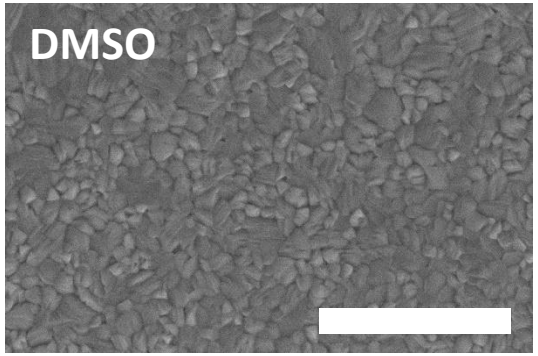
+ **S-donors "clustered" on high end of the scale, suggesting may be useful as *additives* to precursor solutions**
+ **Change in BE is always *higher* for S-donor, indicating stronger coordination between solvent and Pb^{2+}**

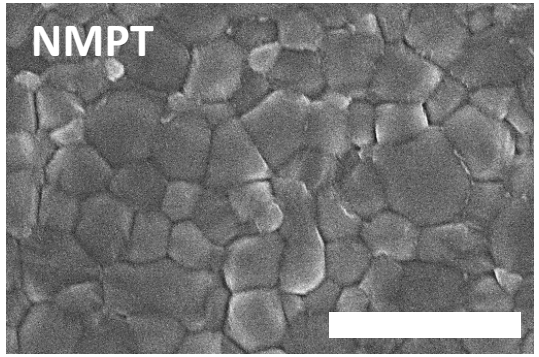
*PW6B95 dispersion-corrected model utilizing def2-TZVP basis set.

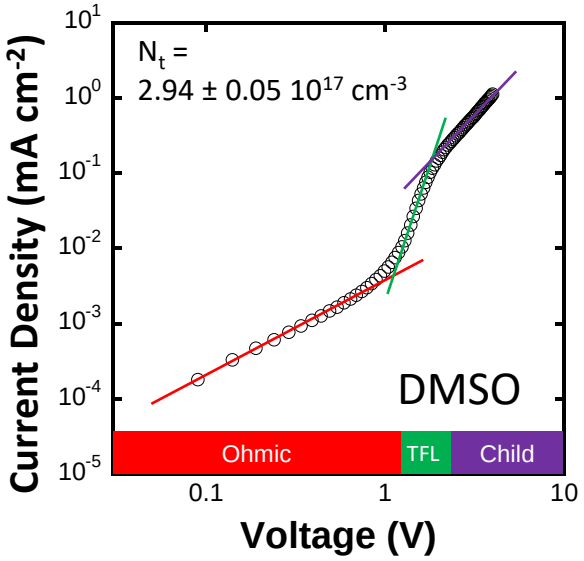
J. C. Hamill, O. Romiluyi, S. Thomas, J. Schwartz, M. F. Toney, P. Clancy, Y. –L. Loo. In prep.

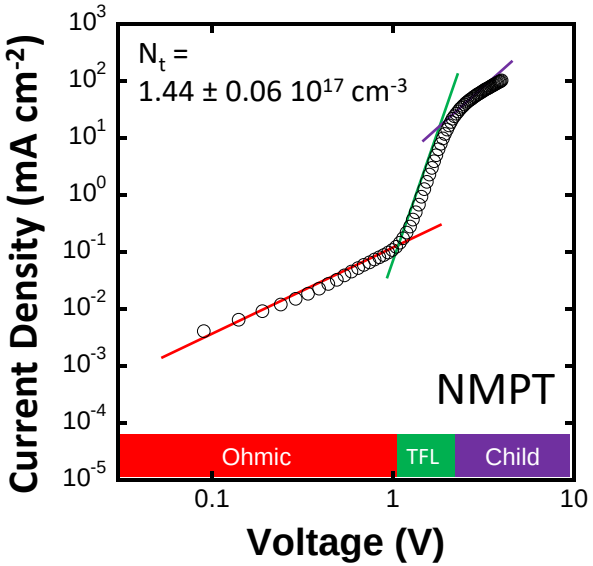
Conclusions and outlook

- **EXAFS studies confirm that for two solvent pairs tested, S-donor preferentially coordinates Pb^{2+} in perovskite precursor solutions**
- **Calculations confirm larger change in enthalpy as a result of solvent-PbI_2 binding for S-donors relative to O-donors for multiple O-donor/S-donor pairs**
- **High binding enthalpies, coupled with our experimental results, suggest that S-donors useful as *additives* to perovskite precursor solutions**





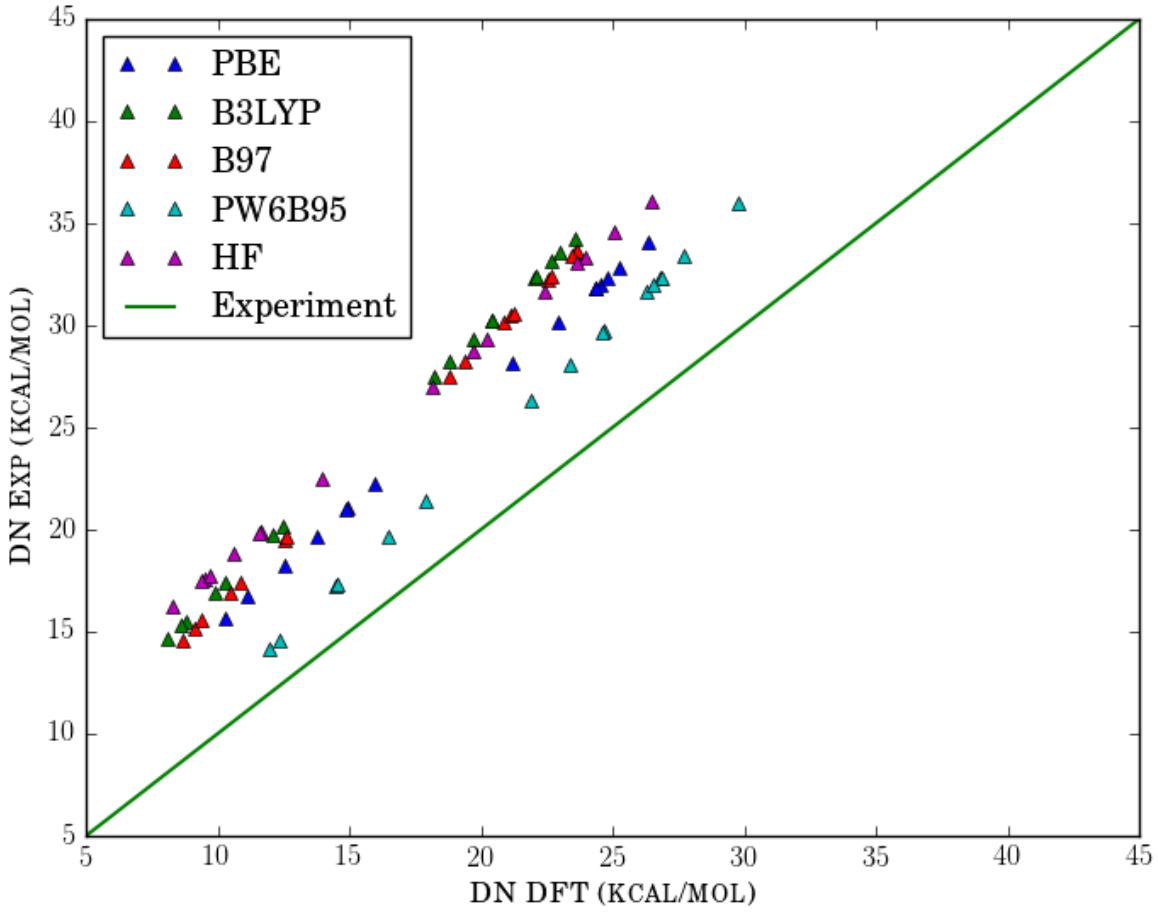


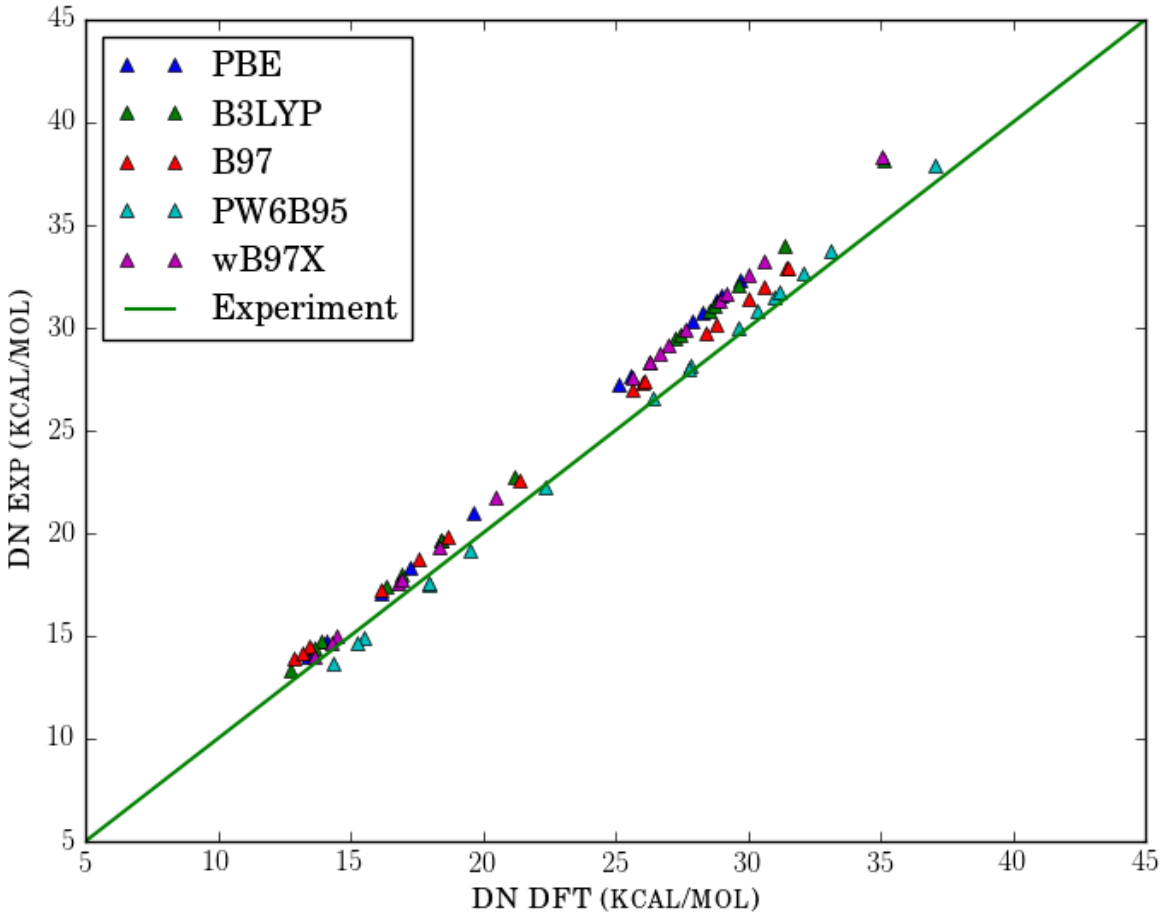


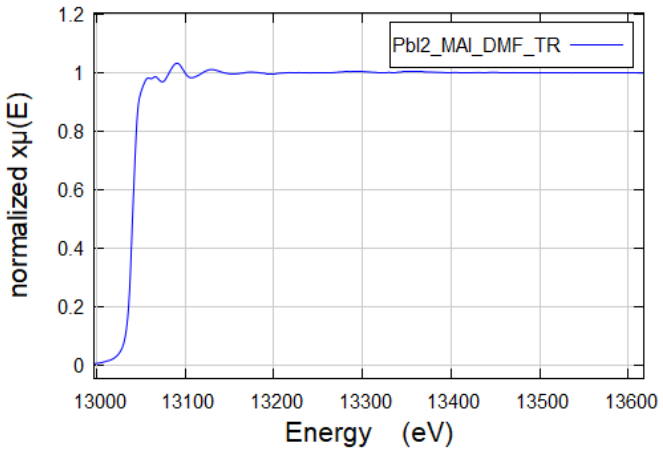
F. Zhang, J. C. Hamill, A. Kahn, Y.-L. Loo. *Unpublished.*

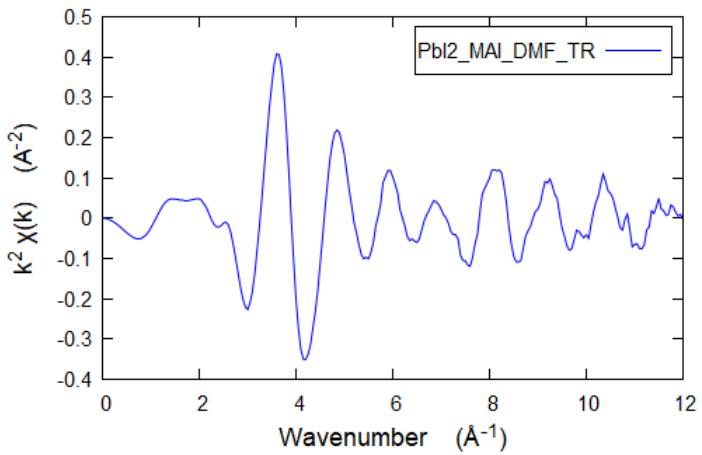
Supplementary Slides

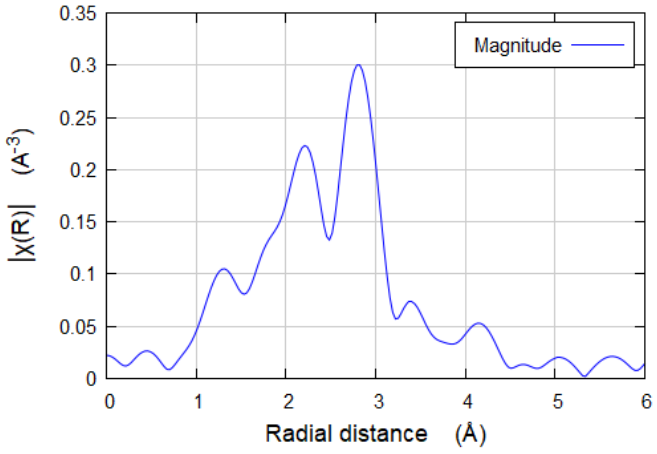
Necessity of dispersion corrections











EXAFS spectrum can be written as sum of contribution of scattering paths:

$$\chi(k) = \sum_{i=1}^{n} \chi_i(k)$$

With each path represented as:

$$\chi_i(k) = \frac{N_i S_0^2 F(k)}{k R_i^2} \sin[2kR_i + \varphi_i(k)]\, e^{-\sigma_i^2 k^2}\, e^{-\frac{2R_i}{\lambda(k)}}$$

Parameters varied for fitting:

(1) N – coordination number
(2) σ^2 – the disorder term – static and thermal
(3) ΔE_0 – the change in absorption edge of model vs. data
(4) ΔR_i – the change in interatomic distance

A. Sharenko, C. Mackeen, L. Jewell, F. Bridges, M. F. Toney. *Chemistry of Materials* **2017**, *29*, 1315.
J. C. Hamill, O. Romiluyi, S. Thomas, J. Schwartz, M. F. Toney, P. Clancy, Y. –L. Loo. In prep.