

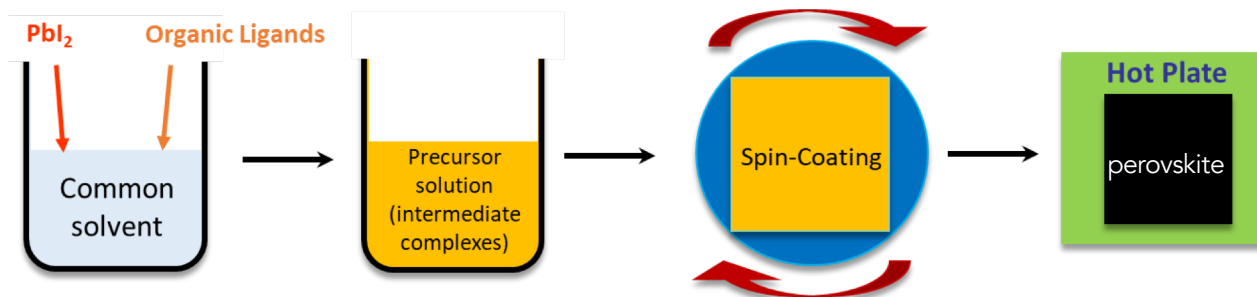
understanding the roles solvents play in perovskite processing

yueh-lin (lynn) loo

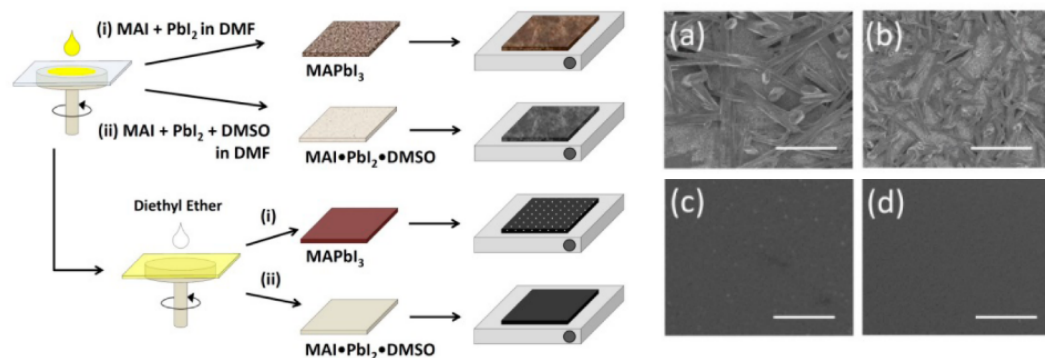
theodora d. '78 & william h. walton III '74 professor in engineering
andlinger center for energy + the environment
chemical & biological engineering department
loogroup.princeton.edu
 @loo_group

with clay hamill, xiaoming zhao, petr khlyabich, tianran liu, fengyu zhang, jeff schwartz + antoine kahn
collaboration primarily funded by DoE EERE SETO DE-EE0008560

solvents play a critical role in perovskite processing



+ lewis-base (DMSO) as processing additive



n. ahn, d.-y. son, i.-h. jang, s.m. kang, m. choi, n.-g. park, *j. am. chem. soc.* 27, 8696, 2015.

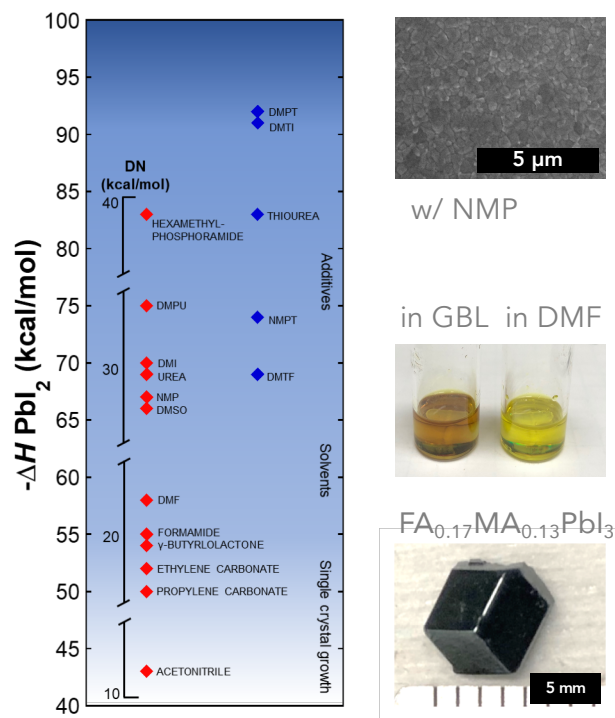
+ solvent-precursor reactions



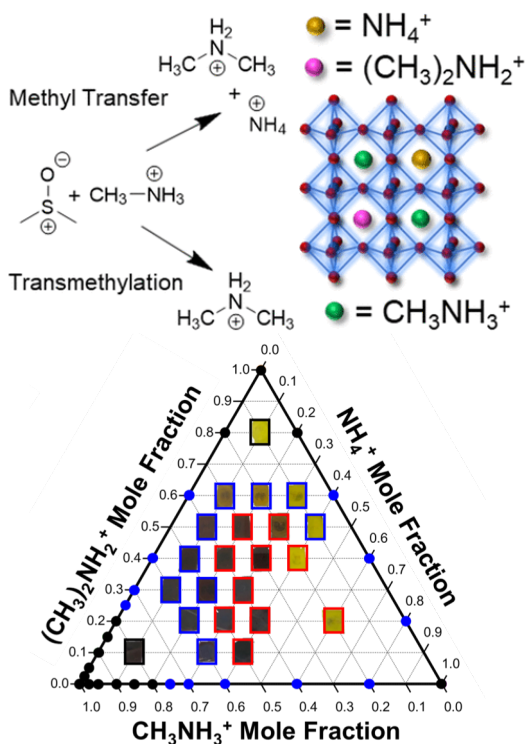
b. dou, l.m. wheeler,
j.a. christians, d.t. moore,
s.p. harvey, j.j. berry, f.s. barnes,
s.e. shaheen, m.f.a.m. van hest.
acs energy lett. 3, 979, 2018.

three vignettes

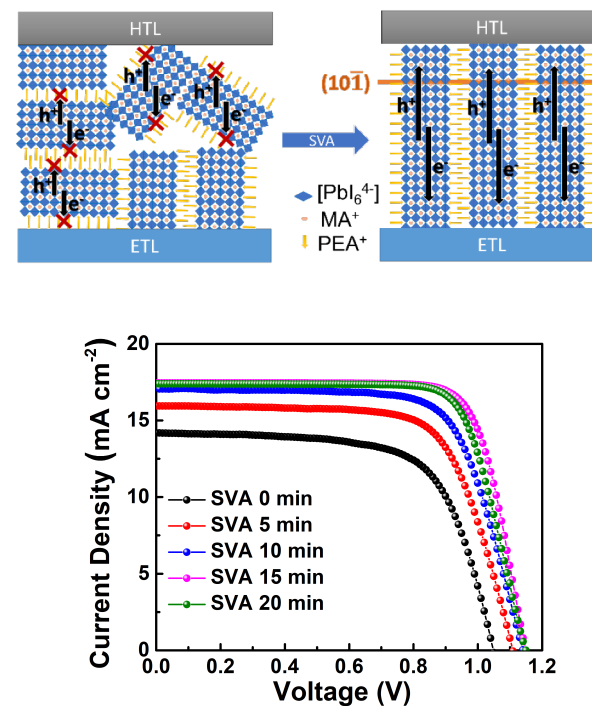
+ solvent-Pb²⁺ coordination



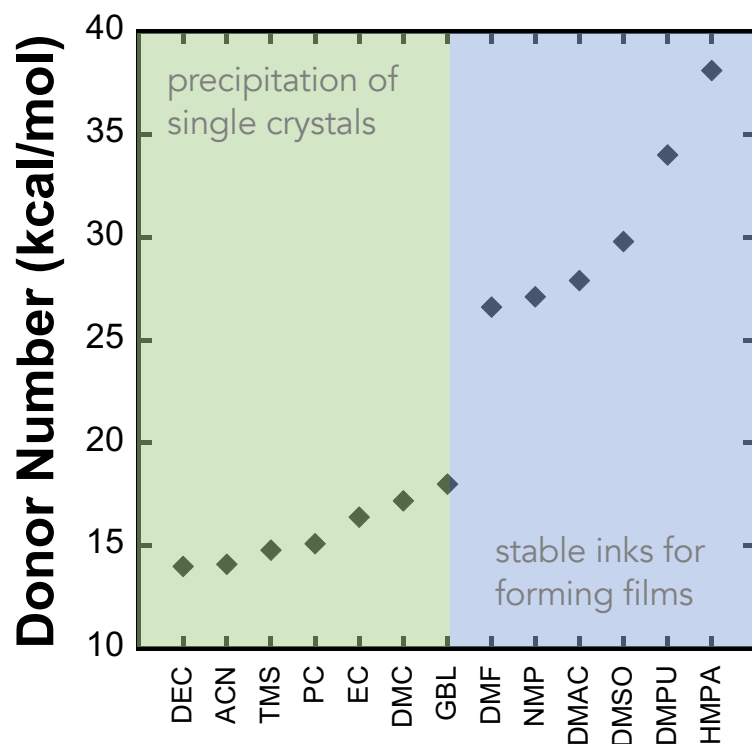
+ additive-precursor reactions



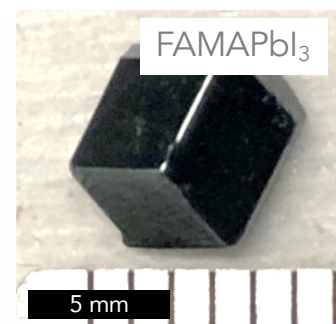
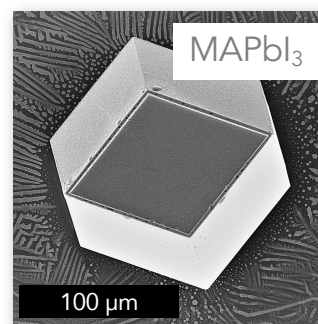
+ post-deposition processing



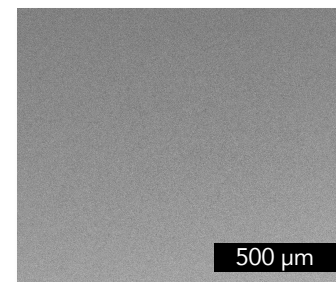
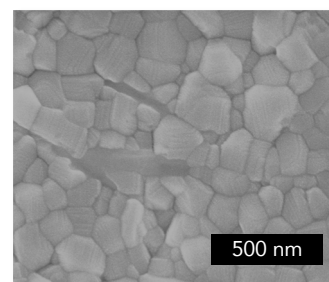
quantifying strength of solvent-Pb²⁺ interaction



+ single crystals from PC

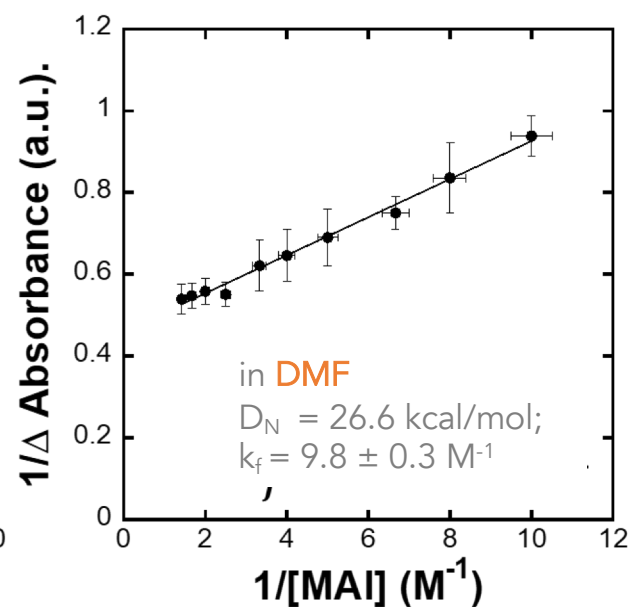
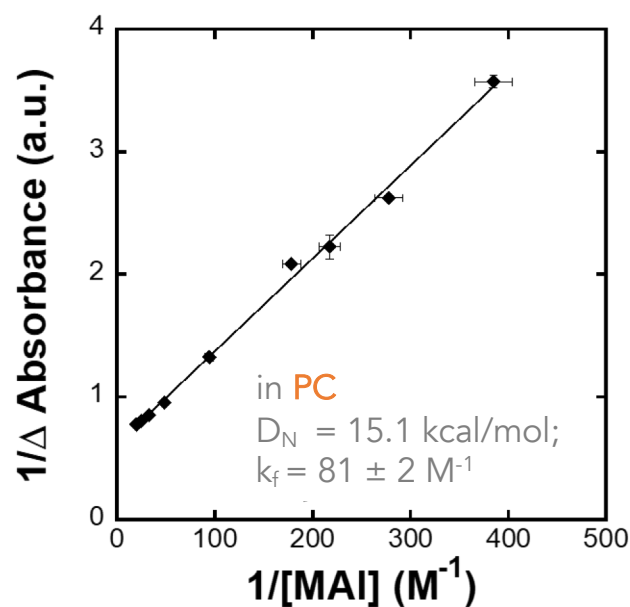
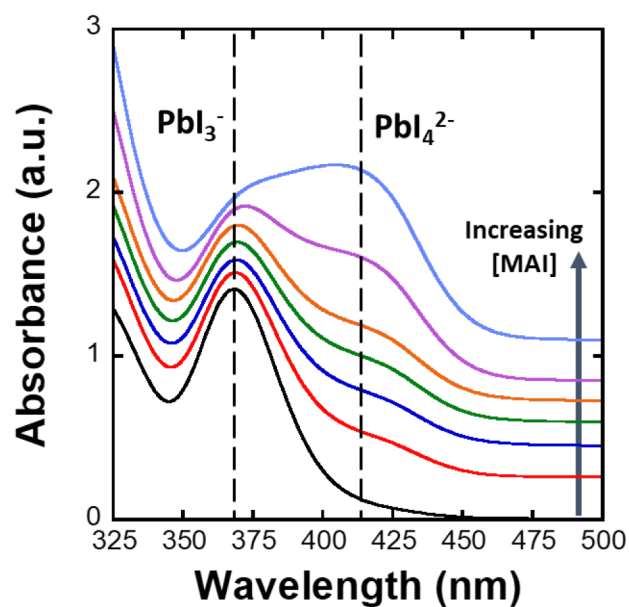


+ thin films with DMPU as additive



j.c. hamill, j. schwartz, y.-l. loo. *ACS energy lett.* 3, 92, 2018.

benesi-hildebrand analysis quantifies strength of complexation



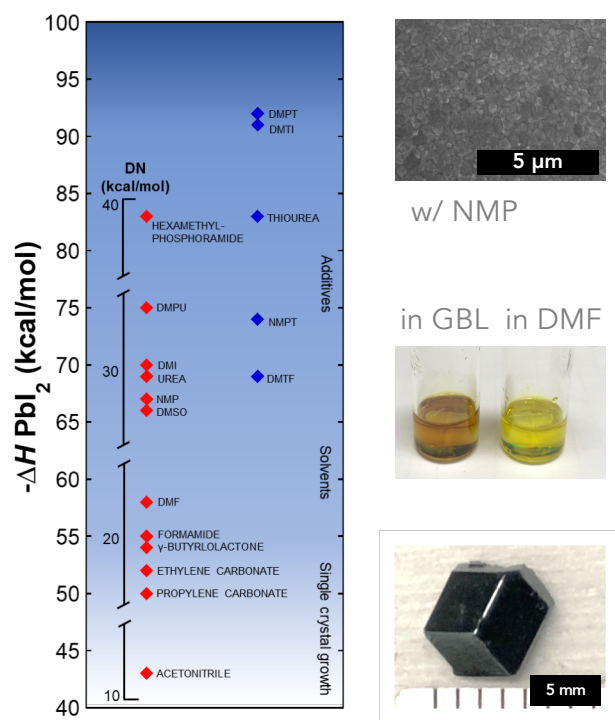
j.c. hamill, j. schwartz, y.-l. loo. ACS energy lett. 3, 92, 2018.

- + lower k_f indicates lower tendency to form PbI_4^{2-} with increasing MAI concentration
- + D_N correlated positively with coordination strength of solvent to Pb^{2+}

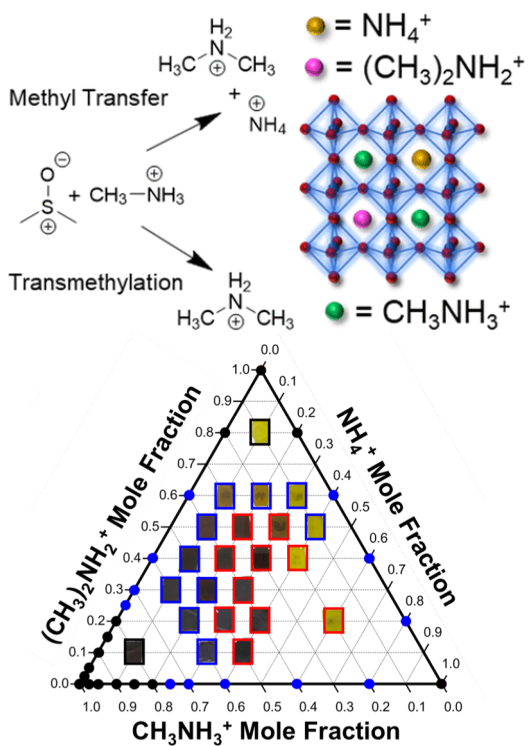
see clay hamill's talk [EN09.15.07; 12/6 @ 3:45pm] on sulfur-donor solvents

three vignettes

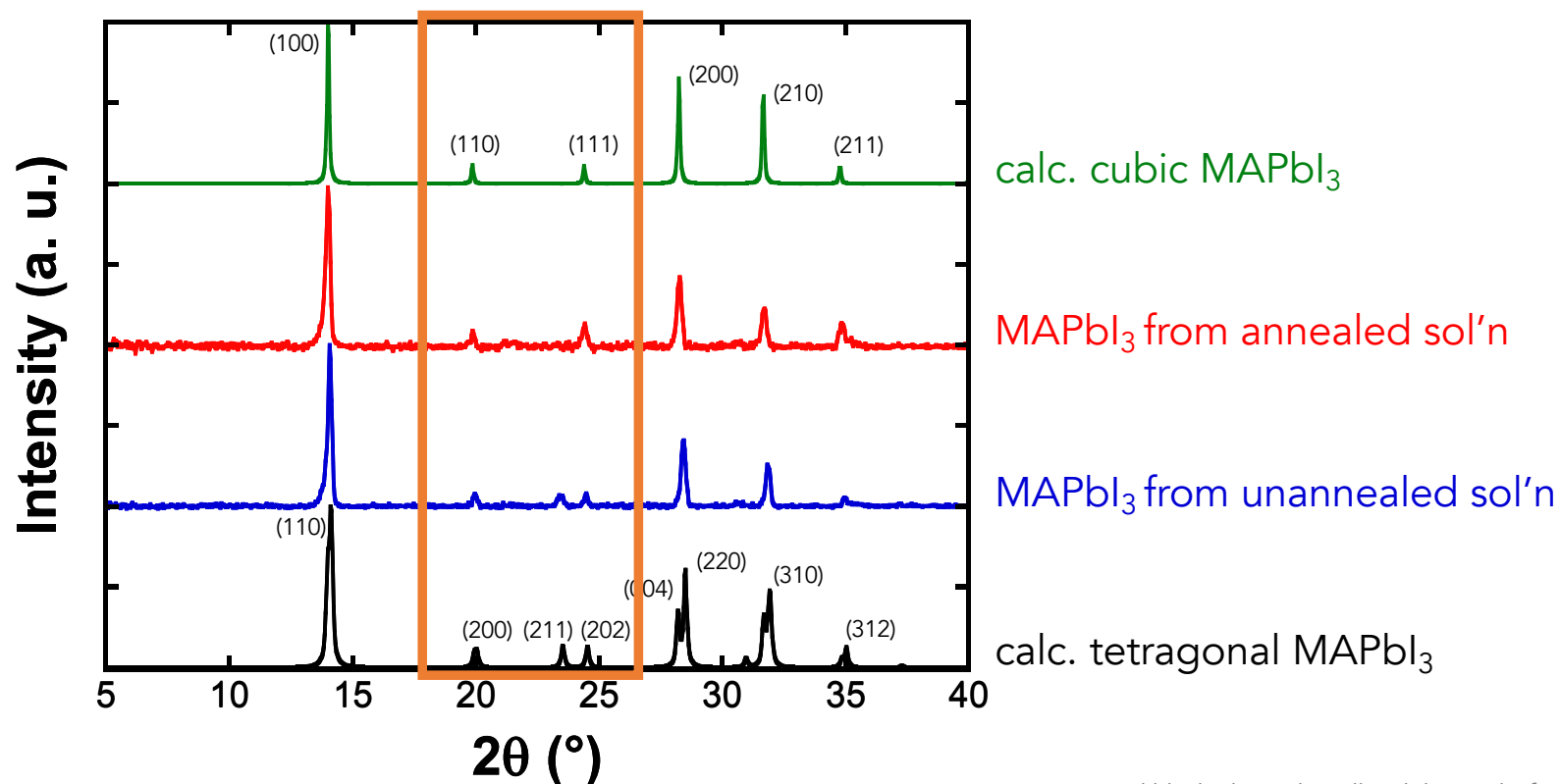
+ solvent-Pb²⁺ coordination



+ additive-precursor reactions

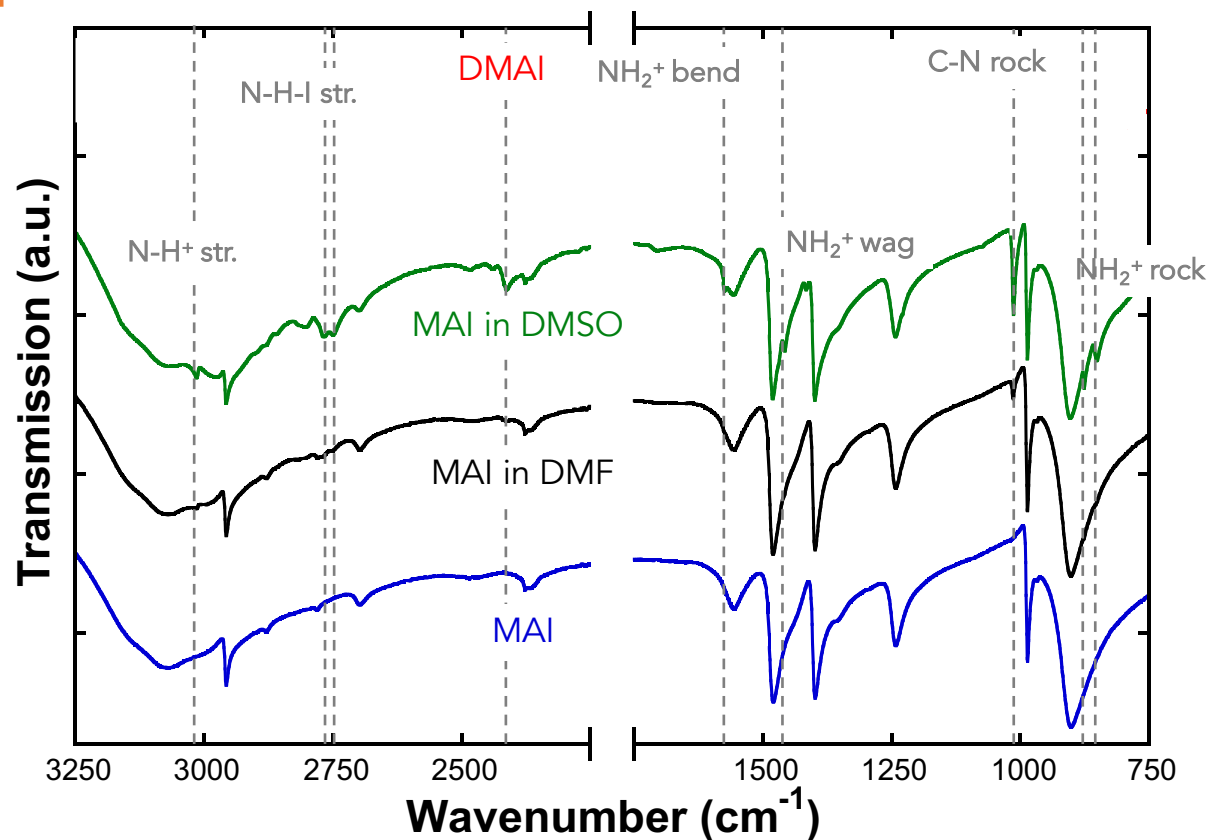


annealing of precursor solution alters solid-state structure



p.p. khlyabich, j.c. hamill, y.-l. loo, *adv. func. mater.* 28, 1801508, 2018.

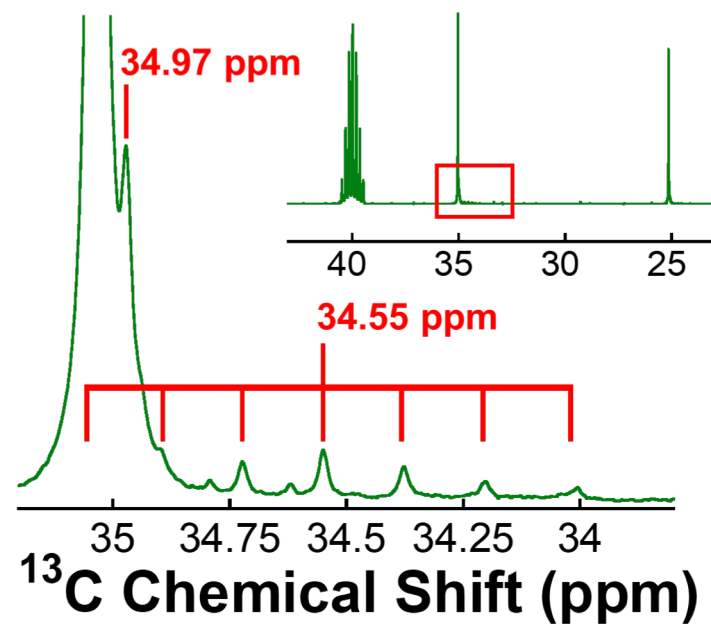
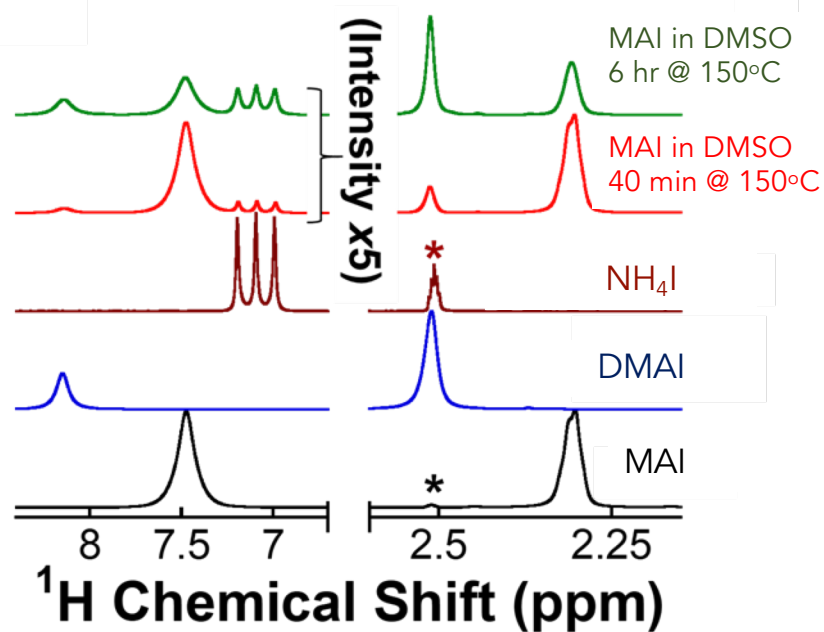
infrared spectroscopy indicates solvent reaction with MAI



- + MAI is heated for 40 mins @ 150 °C in DMF, DMSO
- + new modes detected corresponding to reference spectrum of DMAI; suggests DMA⁺ formation on annealing
- + conversion to DMA⁺ 6x faster in DMSO than in DMF

j. c. hamill, j. sorli, i. pelczer, j. schwartz, y.-l. loo, *chem. mater.* 31, 2114, 2019.

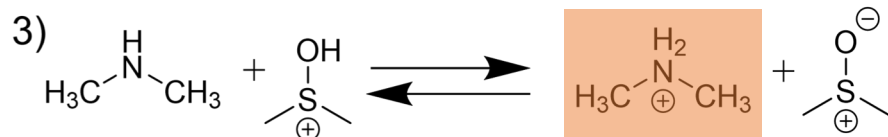
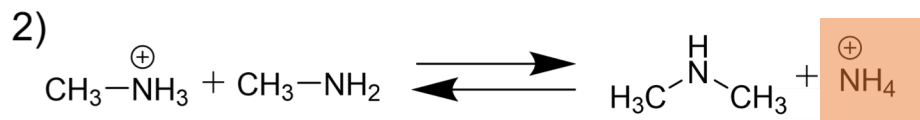
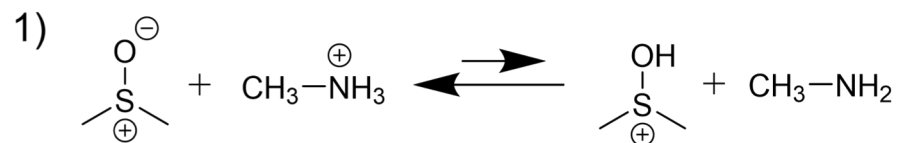
annealing MA⁺ in DMSO [+ also DMF] forms DMA⁺ + NH₄⁺



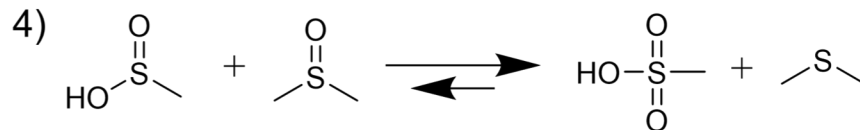
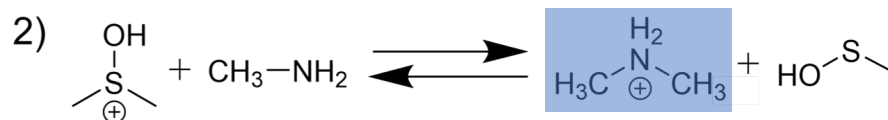
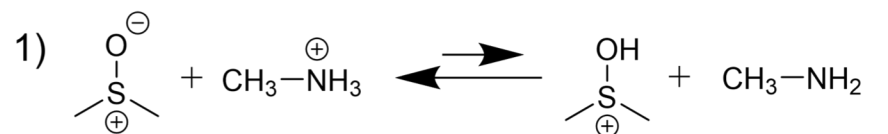
j. c. hamill, j. sorli, i. pelczar, j. schwartz, y.-l. loo, chem. mater. 31, 2114, 2019.

+ heating in DMSO-d₆ results in formation of NH₄⁺ + two populations of DMA⁺

proposed side reactions between MA⁺ + DMSO



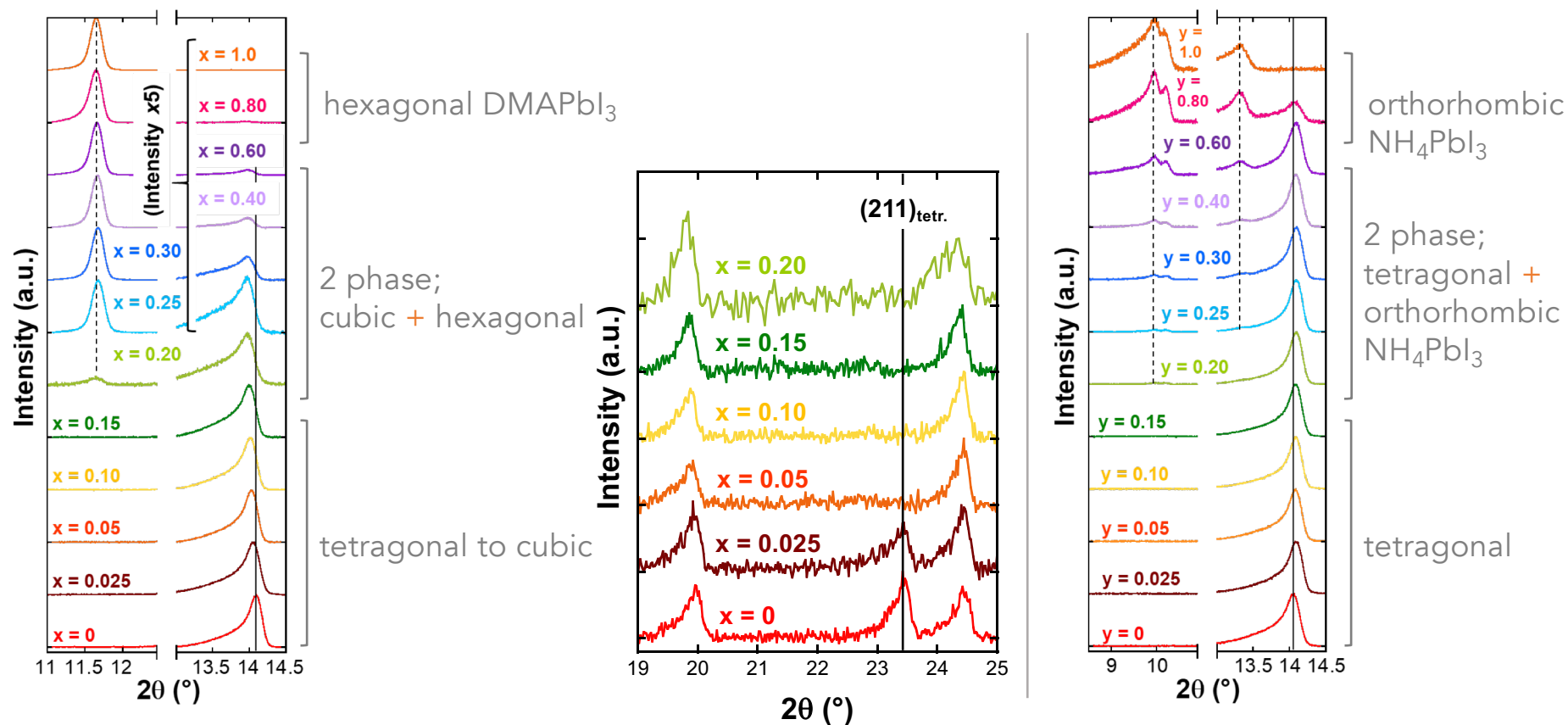
- + DMSO is protonated
- + DMSO acts as proton shuttle
- + MA⁺ disproportionates; forms NH₄⁺ + DMA⁺



- + DMSO is protonated
- + DMSO can methyl transfer to MA⁺; yields DMA⁺, sulfi(e,o)nic acid + (CH₃)₂S

j. c. hamill, j. sorli, i. pelczer, j. schwartz, y.-l. loo, *chem. mater.* 31, 2114, 2019.

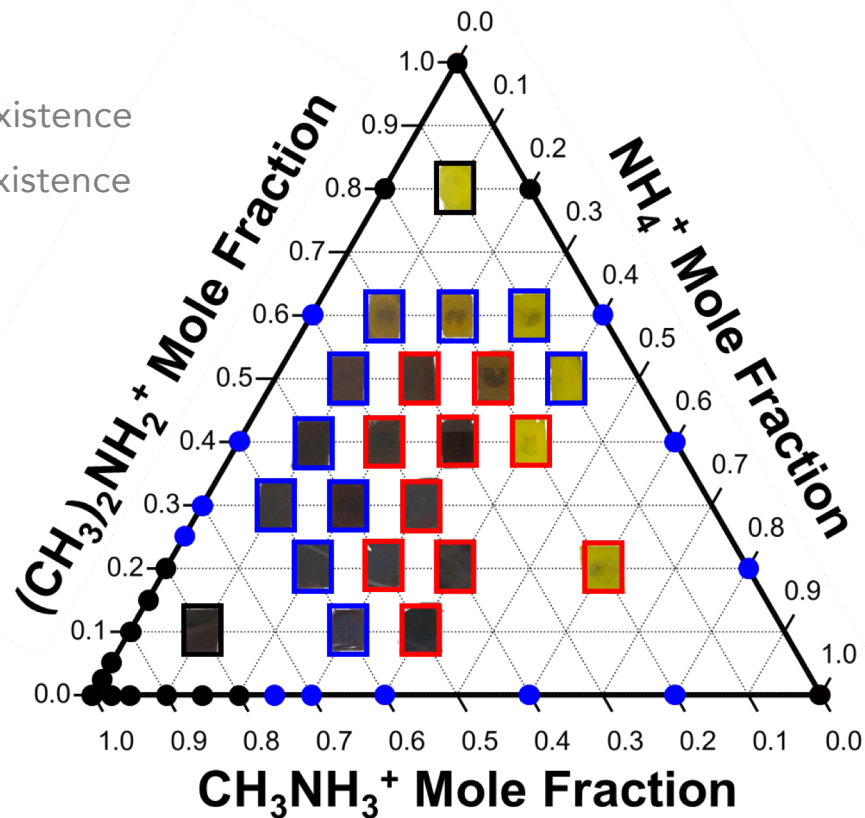
DMA⁺ + NH₄⁺ incorporation affects structure of MA_{1-x-y}DMA_x(NH₄)_yPbI₃



J. C. Hamill, J. Sorli, I. Pelczar, J. Schwartz, Y.-I. Loo, Chem. Mater. 31, 2114, 2019.

a partial ternary phase diagram of $\text{MA}_{1-x-y}\text{DMA}_x(\text{NH}_4)_y\text{PbI}_3$

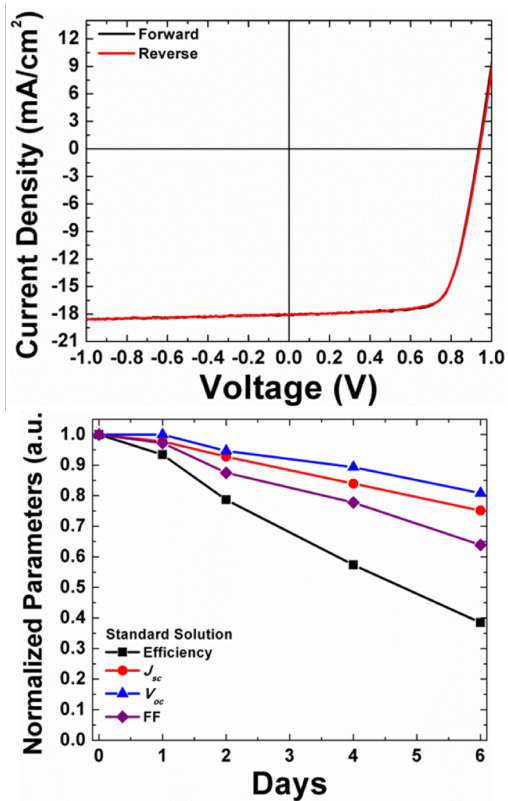
- = 1 phase
- = 2-phase coexistence
- = 3-phase coexistence



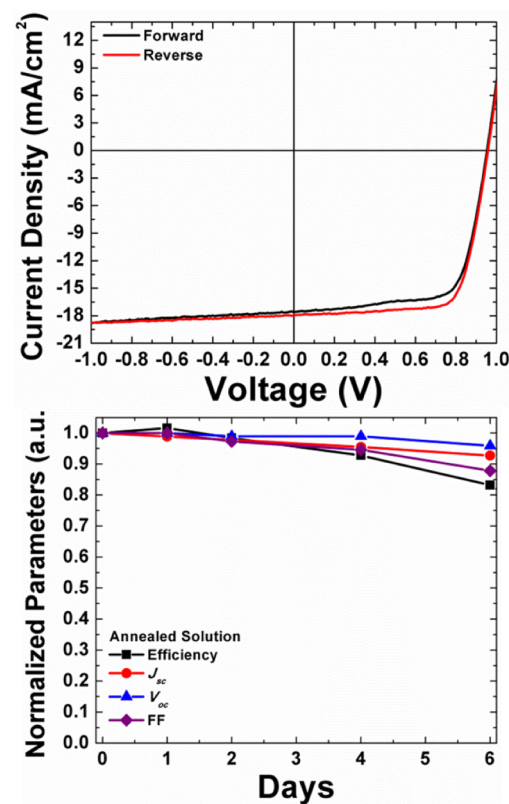
j. c. hamill, j. sorli, i. pelczer, j. schwartz, y.-l. loo,
chem. mater. 31, 2114, 2019.

implications on device stability

+ from unannealed precursor solution



+ from annealed precursor solution



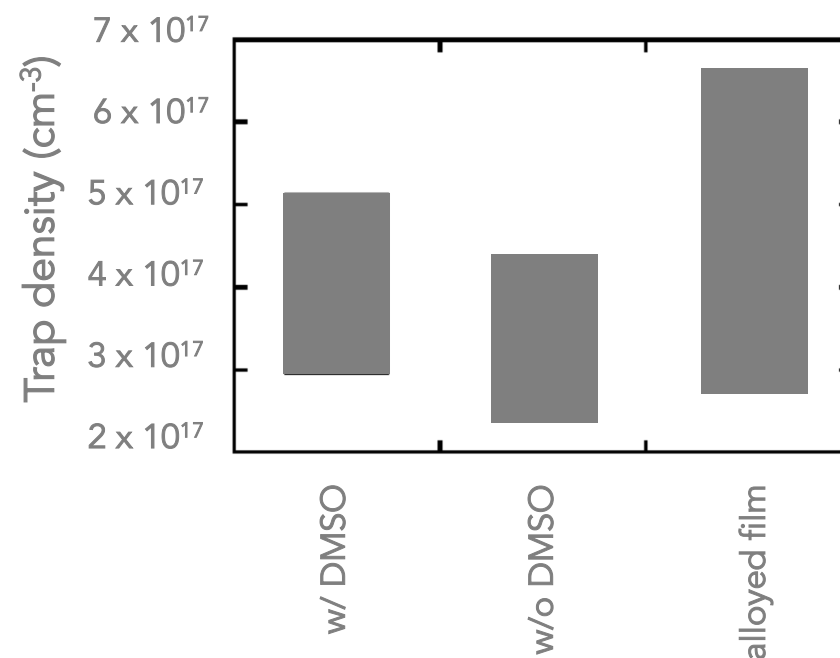
P.P. Khyabich, J.C. Hamill, Y.-L. Loo, Adv. Func. Mater. 28, 1801508, 2018.

on device performance

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency (%)
Standard Solution (FS)	19.1 ± 0.7 (19.7)	0.92 ± 0.01 (0.93)	0.70 ± 0.02 (0.73)	12.2 ± 0.6 (13.0)
Standard Solution (RS)	20.0 ± 0.6 (20.7)	0.92 ± 0.01 (0.93)	0.77 ± 0.02 (0.79)	14.1 ± 0.2 (14.4)
Annealed Solution (FS)	18.8 ± 0.1 (18.9)	0.87 ± 0.01 (0.87)	0.71 ± 0.01 (0.71)	11.6 ± 0.1 (11.6)
Annealed Solution (RS)	19.2 ± 0.1 (19.3)	0.87 ± 0.01 (0.88)	0.71 ± 0.01 (0.72)	12.0 ± 0.1 (12.1)

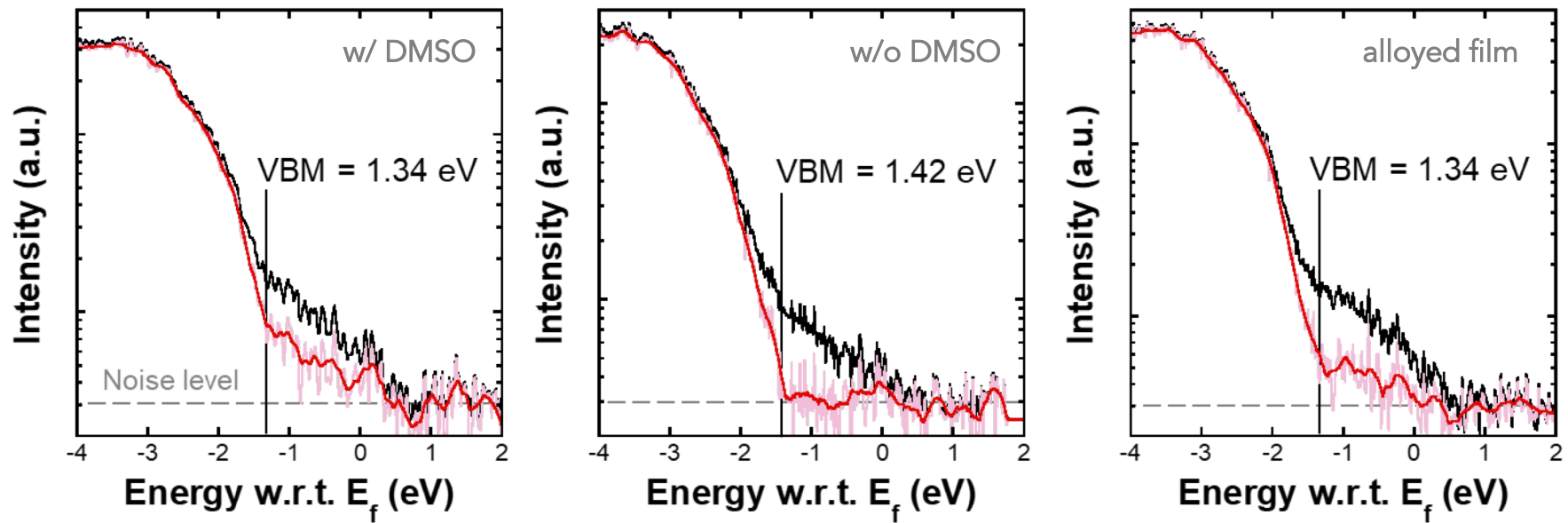
p.p. khlyabich, j.c. hamill, y.-l. loo, *adv. func. mater.* 28, 1801508, 2018.

+ SCLC measurements; trap density extraction



clay hamill, unpublished data, (2019).

trap states can be directly observed

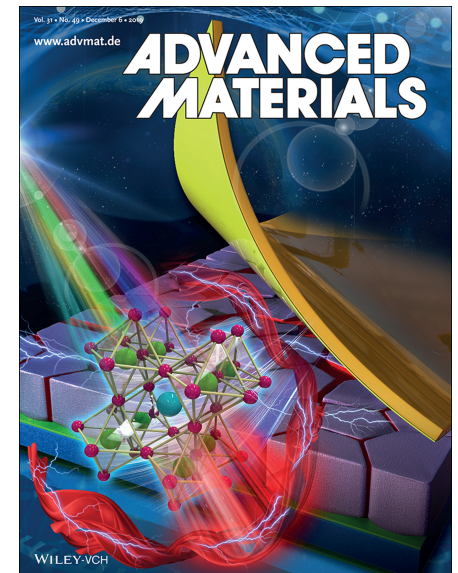


unpublished data; UPS measurements carried out by fengyu zhang, antoine kahn

see fengyu zhang's talk [EN09.11.06; 12/5 @ 9:45am]

summary

- + solvent-precursor interaction/complexation can be exploited for perovskite processing; strength quantified through **binding enthalpy**
- + solvents + solvent additives can readily **react** with precursors; incorporation of byproducts can impact solid-state structuring + optoelectronic properties
- + post-deposition **solvent-vapor annealing** can be a general approach to improve organization of 2D perovskites, markedly improving solar cell performance + stability



x. zhao, c. yao, t. liu, j.c. hamill, g.o. ngongang ndjawa,
g. cheng, n. yao, h. meng, y.-l. loo, *adv. mater.* 31,
1904494, 2019.

xiaoming zhao, EN08.06.06
tuesday 8:00pm

acknowledgements



- + clay hamill
- + petr khlyabich | now nike
- + xiaoming zhao
- + tianran liu

- + jeff schwartz | chemistry
- + istvan pelczer | chemistry
- + fengyu zhang + antoine kahn | electrical engineering
- + oluwaseun romiluyi + paulette clancy | JHU
- + mike toney | SSRL

