

**Table 1:** Photoluminescent properties of mixed-halide tin perovskite nanoplates in toluene (excitation at 400 nm).  
[Reproduced from Ref. 3]

Compound	QY/Lifetime, $\tau_1$ , $\tau_2$ , $\tau_3$ [%]/[ns]	FWHM [nm]	Peak [nm]
PEA <sub>2</sub> SnI <sub>4</sub>	6.40 ± 0.14 (0.10/2.57/17.88)	36.0	640.6
PEA <sub>2</sub> Sn(Br <sub>0.15</sub> I <sub>0.85</sub> ) <sub>4</sub>	2.19 ± 0.16 (0.09/1.26/9.06)	36.2	610.9
PEA <sub>2</sub> Sn(Br <sub>0.3</sub> I <sub>0.7</sub> ) <sub>4</sub>	1.03 ± 0.03 (0.12/1.19/8.06)	44.5	590.4
PEA <sub>2</sub> Sn(Br <sub>0.625</sub> I <sub>0.375</sub> ) <sub>4</sub>	0.36 ± 0.01 (0.15/0.83/5.23)	56.2	557.8
PEA <sub>2</sub> SnBr <sub>4</sub>	0.10 ± 0.01 (-/0.32/2.94)	79.6	550.2

The photostability was also significantly improved for PEA<sub>2</sub>SnI<sub>4</sub> prepared with 3-methylbutanoic acid. Upon irradiation of PEA<sub>2</sub>SnI<sub>4</sub> at 406 nm (10 mW cm<sup>-2</sup>) for 120 h in degassed toluene, the emission intensity decreased only 25% compared to the original value. In contrast, under identical conditions, pristine PEA<sub>2</sub>SnI<sub>4</sub> synthesized without added carboxylic acids showed a loss ≈ 77% of the emission intensity. The observed degradation of PEA<sub>2</sub>SnI<sub>4</sub> was attributed to the oxidation of Sn<sup>2+</sup> toward Sn<sup>4+</sup>. Taken together, upon mixing iodo- and bromo- precursors, the emission wavelength was successfully tuned from 640 nm (PEA<sub>2</sub>SnI<sub>4</sub>) to 550 nm (PEA<sub>2</sub>SnBr<sub>4</sub>), with a corresponding emission quantum yield 0.16–6.40% and FWHM 36–80 nm. The results demonstrate a major advance in the emission yield and tunability of tin-halide perovskites. (Reported by Yu-Jong Wu)

*This report features the work of Ching-Wen Chiu, Hao Min Chen, Pi-Tai Chou and their collaborators published in Adv. Mater. **30**, 1706592 (2018).*

#### TLS 01C2 SWLS – X-ray Powder Diffraction

- X-ray Powder Diffraction
- Materials Science

#### References

1. T. C. Jellicoe, J. M. Richter, H. F. J. Glass, M. Tabachnyk, R. Brady, S. E. Dutton, A. Rao, R. H. Friend, D. Credgington, N. C. Greenham, M. L. Böhm, J. Am. Chem. Soc. **138**, 2941 (2016).
2. M. C. Weidman, M. Seitz, S. D. Stranks, W. A. Tisdale, ACS Nano **10**, 7830 (2016).
3. M. Y. Chen, J. T. Lin, C. S. Hsu, C. K. Chang, C. W. Chiu, H. M. Chen, P. T. Chou, Adv. Mater. **30**, 1706592 (2018).

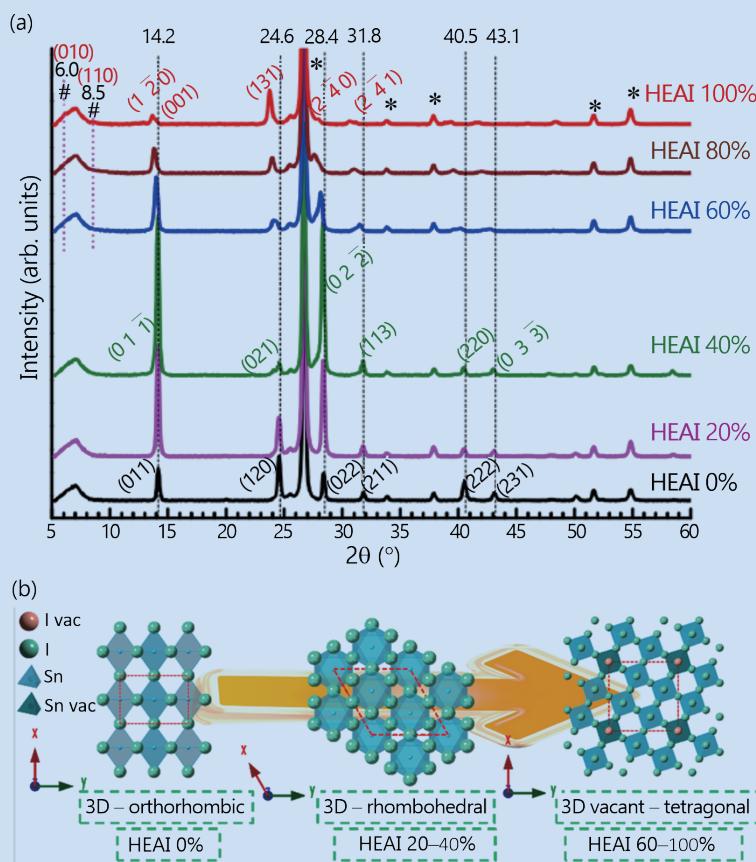
## A New Series of Tin-Based Perovskite Materials

*Hybrid HEA<sup>+</sup>/FA<sup>+</sup> organic cations can tune the optoelectronic properties and band structures on varying the HEAI proportions.*

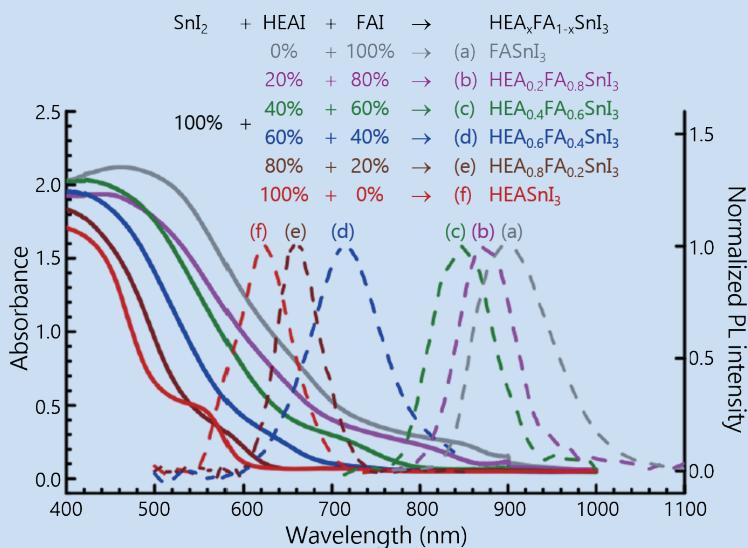
Perovskite solar cells (PSC) possess the advantages of cheap fabrication, versatile configurations and large expected efficiency of power conversion, which lead them to become the most promising next-generation photovoltaic devices.<sup>1</sup> Conventional perovskite materials containing toxic element lead (Pb) have evoked the development of lead-free PSC and become an important issue for future commercialization of PSC. In the same group of the periodic table, tin (Sn) is hence a promising candidate to replace lead in PSC, but a problem of reproducibility was discovered for tin-based PSC in recent tests. Sn<sup>2+</sup> is readily oxidized to Sn<sup>4+</sup>, which increases the density of defects. Previous investigations tried to improve the performance and stability of tin-based devices generally on

varying the B and X components of the typical formula ABX<sub>3</sub>, in which A represents site ions on the corners of the lattice, B represents site ions on the center of the lattice and X is halogen.

A research team from National Chiao Tung University recently tried to modify the energy levels by altering A upon mixing two organic cations, formamidinium (FA<sup>+</sup>) and 2-hydroxyethylammonium (HEA<sup>+</sup>), to improve the performance and the stability of a tin-based PSC.<sup>2</sup> With chemical formula HEA<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3</sub>, the authors found that, as x increases, the crystal structure alters from orthorhombic ( $x = 0$ ) to rhombohedral ( $x = 0.2$ –0.4), and then to tetragonal ( $x = 0.6$ –1.0), as shown in Fig. 1.



**Fig. 1:** (a) X-ray diffraction patterns of HEAxFA<sub>1-x</sub>SnI<sub>3</sub> perovskites deposited on mesoporous FTO/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/C device substrates with varied HEAI:FAI ratios as indicated. The intense signals marked \* correspond to contributions from the carbon layer and the FTO substrate; small diffraction signals at 6.0° and 8.5° are marked #. (b) Kinetically preferred perovskite structures of single crystals with HEAI proportions 0, 40, and 80% represented from left to right. A 3D-vacant perovskite was produced at  $x = 0.6\text{--}1.0$ . [Reproduced from Ref. 2]



**Fig. 2:** Absorption (solid curves) and normalized PL (dashed curves) spectra of HEAxFA<sub>1-x</sub>SnI<sub>3</sub> films deposited on mesoporous Al<sub>2</sub>O<sub>3</sub>/glass substrates with varied HEAI:FAI ratios ( $x = 0\text{--}1$ ) controlled by stoichiometric proportions of HEAI:FAI precursors. [Reproduced from Ref. 2]

They found also that the band-gap energy systematically increased with increasing proportion of HEAI. The performance of the HEA<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3</sub> devices increased from PCE 0.8% ( $x = 0$ ) to PCE 2.5% ( $x = 0.4$ ), and decreased with  $x > 0.4$ . In addition, the absorption and photoluminescent spectra of HEA<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3</sub> show the variation of the bandgap; increasing the proportion of HEAI shifted the emission from 900 nm ( $x = 0$ ) to 623 nm ( $x = 1$ ) and the absorption edges from 925 nm ( $x = 0$ ) to 614 nm ( $x = 1$ ), as shown in Fig. 2. This result indicates that HEA<sup>+</sup> plays a key role to modify the crystal structures for the observed variation of the bandgaps in this series.

Ultraviolet photoelectron spectral measurements on the HEAxFA<sub>1-x</sub>SnI<sub>3</sub> series determined the work function and the energy difference between the work function and the valence-band maximum. These results support the modification of energy levels on varying the proportions of HEAI precursors; a strong *n*-type characteristic matching  $E_{\text{CB}}$  of TiO<sub>2</sub> for electron transfer from perovskite to the TiO<sub>2</sub> layer was found in the sample at HEAI 40%. In addition, upon replacing MA<sup>+</sup> with FA<sup>+</sup> or Cs<sup>+</sup>,  $E_g$  values varied within 0.3 eV, whereas the crystal structure altered from 3D to 2D or formed a hollow perovskite with more than 0.6 eV tunability of the bandgap on replacing A with BA<sup>+</sup> or PEA<sup>+</sup>. Taken together, varying HEAI proportions can alter the lattice structure that results in varying the optoelectronic properties and band structures in the hybrid HEA<sub>x</sub>FA<sub>1-x</sub>SnI<sub>3</sub> PSC. The discovery of new 3D-vacant and 2D tin-based PSC opens a new door for further development of lead-free PSC. (Reported by Yu-Jong Wu)

This report features the work of Eric Wei-Guang Diau and his collaborators published in ACS Energy Lett. **3**, 2077 (2018).

#### TLS 24A1 BM – (WR-SGM) XPS, UPS

- Ultraviolet Photoelectron Spectroscopy
- Chemical Materials

#### References

1. J. Bisquert, G. Garcia-Belmonte, A. Guererro, Impedance Characteristics of Hybrid Organometal Halide Perovskite Solar Cells. Springer International Publishing, Switzerland, 163 (2016).
2. C.-M. Tsai, Y.-P. Lin, M. K. Pola, S. Narra, E. Jokar, Y.-W. Yang, E. W.-G. Diau, ACS Energy Lett. **3**, 2077 (2018).