A Route To Low-Cost Flexible Solar Cells: Rational Design of the Organic Charge Transport Layer

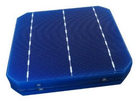
Tracy H. Schloemer[1], Dr. Jonathan Tinkham[1], Dr. Zhen Li[2], Dr. Kai Zhu[2], and Dr. Alan Sellinger[1]
[1]Colorado School of Mines, Golden, CO; [2]National Renewable Energy Lab, Golden, CO

Introduction

Why perovskite solar cells?

To meet growing demand for energy, we must offset some of the traditional greenhouse gas-based power production with renewables, such as solar.

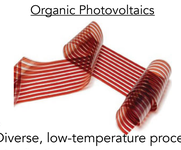
Silicon/CdTe



https://www.nrel.gov/pv/assets/images/efficiency-chart.png; https://www.alibaba.com/wholesale-monocrystalline-silicon-wafer.html

- ✓ Power conversion efficiencies (PCEs) up to 21.7%
- ✗ Relatively high production costs

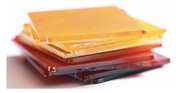
Organic Photovoltaics



https://www.greentechmedia.com/articles/read/konarka-gets-45m-from-total-5373

- ✓ Diverse, low-temperature processing with flexible substrates
- ✗ Lower stabilities and efficiencies

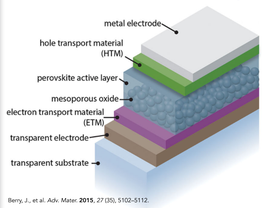
Perovskite Solar Cells (PSC)



https://cleantechnica.com/2015/10/07/oxford-pv-raises-19-million-for-perovskite-solar-cell-rd/

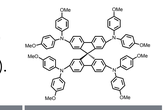
- ✓ Solution-processable
- ✓ PCEs up to 22.1% in <10 years of R & D

However, to realize widespread commercialization there are barriers to overcome.



Berry, J., et al. *Adv. Mater.* **2015**, *27* (35), 5102–5112.

Our focus is upon optimizing hole-transport materials (HTM).

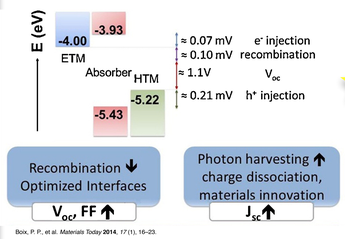


The dominant HTM is Spiro-OMeTAD. It:
- is labor intensive/expensive to synthesize,
- has decent thermal properties, and
- has decent energetic match to transport positive charge-carriers only upon doping.

	Spiro-OMeTAD
Cost	~$300/g to synthesize and purify
T_g	124 °C (but can crystallize at rt)

Malinauskas, T.; et al. *ACS Appl. Mater. Interfaces* **2015**, *7* (21), 11107–11116.
Teh, C. H.; et al. *J. Mater. Chem. A* **2016**, *4* (41), 15788–15822.

Goals



Boix, P. P., et al. *Materials Today* **2014**, *17* (1), 16–23.

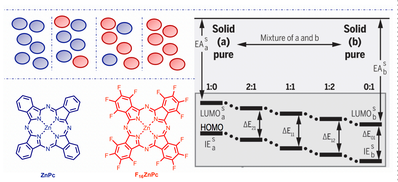
To support future commercialization of perovskite solar cells, our group is:

- ★ Developing a cross-linkable, energetically tunable HT system via alloying of conjugated carbazole- and fluorine-cored HTMS to achieve desired E_{HOMO} levels, and
- Elucidating interactions among HTM and perovskite to design materials that reduce electrode corrosion, and
- Exploring HTM electron density-device property relationships.

Viability of Alloying within EH44 HTM Family

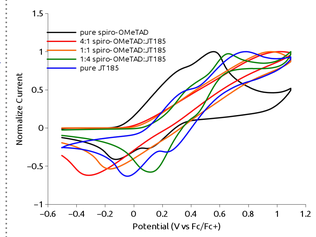
What is alloying?

It is the blending of organic molecules with different energy levels to tune band energies via long-range Coulombic interactions.



Schwarze, M., et al. *Science* **2016**, *352* (6292), 1446–1449.; Ueno, N. *Science* **2016**, *352* (6292), 1395–1396.

Proof of Principle Spiro-OMeTAD and JT185

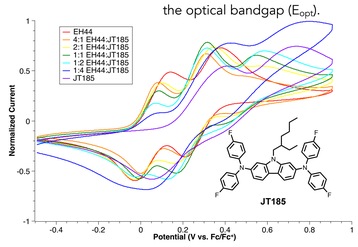


	E_{HOMO} (eV)
spiro	-4.73
4:1	-4.78
1:1	-4.86
1:4	-4.89
JT185	-4.89

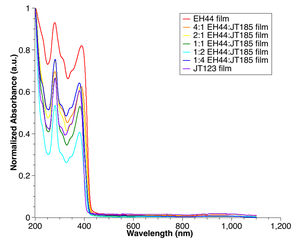
Data courtesy of Dr. Jonathan Tinkham.

EH44 and JT185

E_{HOMO} does not significantly change upon change in blend ratio. UV-Vis shows good mixing and negligible impact the optical bandgap (E_{opt}).

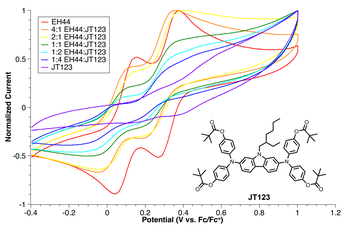


	E_{HOMO}	E_{opt} (eV)
EH44	-4.78	2.93
4:1	-4.77	2.95
2:1	-4.76	2.95
1:1	-4.77	2.98
1:2	-4.75	3.00
1:4	-4.74	2.98
JT185	-4.95	3.06

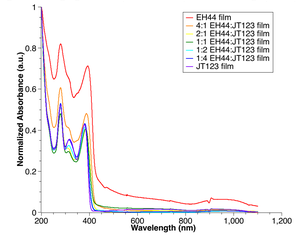


EH44 and JT123

E_{HOMO} increases upon increase of JT123. UV-Vis shows good mixing and negligible impact the optical bandgap (E_{opt}).



	E_{HOMO}	E_{opt} (eV)
EH44	-4.83	2.90
4:1	-4.78	2.95
2:1	-4.80	2.98
1:1	-4.77	3.00
1:2	-4.75	3.04
1:4	-4.72	3.05
JT123	-4.95	3.08



Preliminary Device Results

Will V_{oc} increase with increasing JT185 content?

Standard Device Architecture

Perovskite: Methylammonium Lead Iodide
From MAI/MACl precursor, "FA85 + Cl"

HTM	PCE (%, forward)	PCE (%,reverse)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF
spiro	14.3 ± 0.3	16.9 ± 0.2	22.4	1.02	0.63
9:1 spiro:JT185	14.8 ± 0.1	17.3 ± 0.2	23.0	1.01	0.62
8:2 spiro:JT185	15.0 ± 0.3	16.2 ± 0.2	22.1	1.04	0.67
7:3 spiro:JT185	13.7 ± 0.5	15.7 ± 0.4	22.4	1.03	0.61

Perovskite: Methylammonium Lead Iodide From MAI precursor

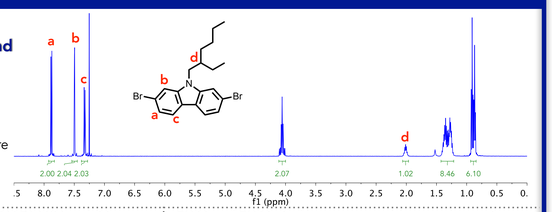
HTM	PCE (%, forward)	PCE (%,reverse)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF
spiro	15.7 ± 0.1	16.8 ± 0.2	21.6	1.08	0.68
9:1 spiro:JT185	15.1 ± 0.2	16.1 ± 0.2	21.4	1.06	0.67
8:2 spiro:JT185	13.9 ± 0.3	14.7 ± 0.4	21.1	1.06	0.62
7:3 spiro:JT185	13.5 ± 0.9	14.4 ± 0.9	21.1	1.07	0.62

While the V_{oc} does not significantly change with increasing JT185 content, device performance is comparable to the spiro control and there appears to be reduced hysteresis in the FA85 + Cl 20% JT185 system.

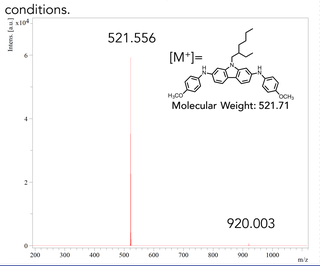
Sample HTM Characterization

Characterization includes: ^{1}H-, ^{19}F- and ^{13}C-NMR, COSY, MALDI-MS, UV-Vis, TGA, and DSC.

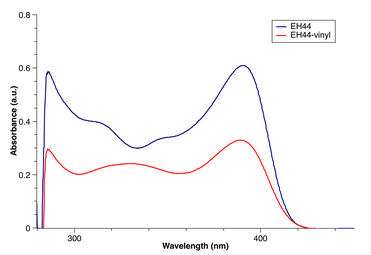
^{1}H-NMR to affirm structure of key intermediate for EH44 HTM family.



High purity affirmed via MALDI-MS in addition to NMR. Peak at 920.003 likely due to experimental conditions.



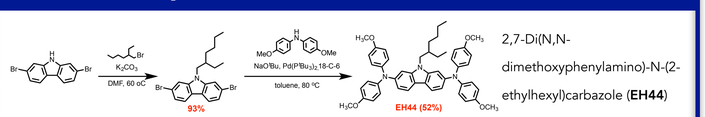
EH44 and EH44-vinyl have comparable optoelectronic properties.



Synthesis

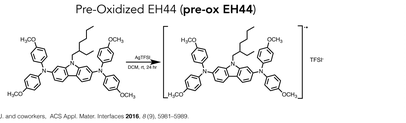
	Spiro-OMeTAD
Cost	~$150/g to synthesize and purify
T_g	52ºC

Teh, C. H.; et al. *J. Mater. Chem. A* **2016**, *4* (41), 15788–15822.



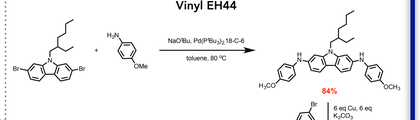
2,7-Di(N,N-dimethoxyphenylamino)-N-(2-ethylhexyl)carbazole (**EH44**)

Pre-Oxidized EH44 (**pre-ox EH44**)

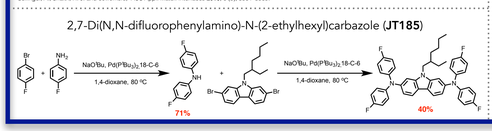


Sellinger, A.; Snaith, H. J. and coworkers. *ACS Appl. Mater. Interfaces* **2016**, *8* (9), 5981–5989.

Vinyl EH44



2,7-Di(N,N-difluorophenylamino)-N-(2-ethylhexyl)carbazole (**JT185**)



Conclusions and Future Work

	From our Data…	Further Investigation…
Alloying	• Cyclic voltammetry model studies narrowed down potentials for device integration, and preliminary device studies have been conducted.	• Explore potential hysteresis reduction, • Try different alloy systems (JT123/spiro; EH44/spiro).
Synthesis of EH44 HTM family	• A cross-linkable EH44 derivative was synthesized and characterized.	• Optimize synthesis, • Tune structure to afford polymerization <120 °C, and • Synthesis of HTM library for structure-device
Ion Migration	• Model studies indicate either (a) limited interaction among HTM/iodide in solution or (b) solution-phase models are not appropriate for this investigation.	• ^{1}H-NMR with methylammonium iodide/formamidinium iodide, and • Pursue solid-state characterization.

Acknowledgements

- **Professor Alan Sellinger**
- **The Sellinger Group,** especially:
  - Dr. Jonathan Tinkham
- **NREL Collaborators:**
  - Dr. Kai Zhu
  - Dr. Zhen Li - devices were made together
- **Funding:**
  - Poate Fellowship, Department of Chemistry
  - Colorado School of Mines, Department of Chemistry

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