Molecular Conductivity Dopants and Charge Transfer Materials for High Efficiency OLEDs

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Pacific Northwest National Laboratory

OLED Materials for Lighting and Displays

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Outline

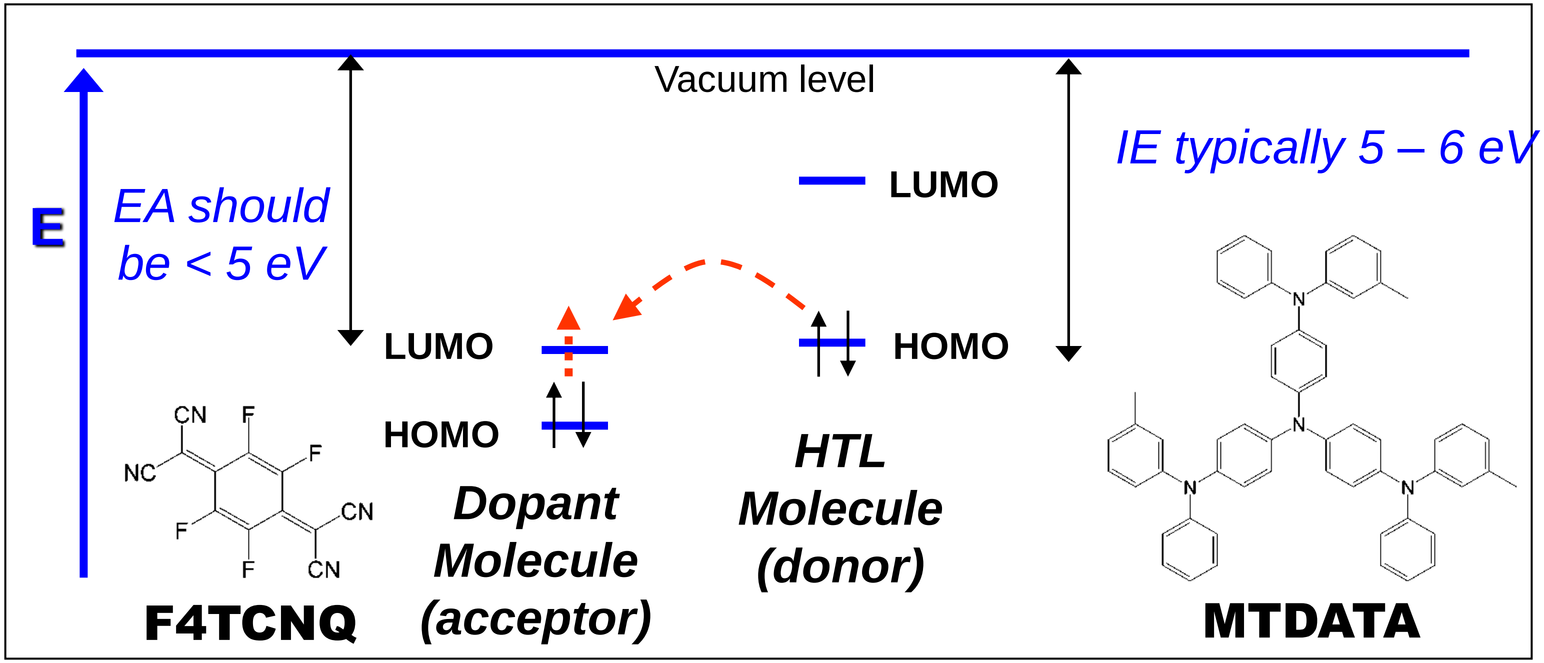
- **Conductivity doping**
- New charge transport layers
- Summary

The role of charge transport in producing efficient charge transport

- Efficiency
  - Reduced injection barriers at interfaces
  - Good charge transport
  - Potential to reduce surface plasmon polariton coupling

- Cost
  - Wider process window
  - Potential for both solution and vacuum thermal processing

How do conductivity dopants work?



- Donate/accept electron to/from HTL/ETL to increase carrier density
- Mobility still governed by HTL (or ETL)
- Can be ionic (i.e., $CsCO_3$) or molecular (i.e., F4TCNQ)

Challenges associated with some conductivity dopants

- Very reactive by nature
- Volatility and stability before, during and after deposition
- Must match energies appropriately
  - $HOMO_{dopant}$ to $LUMO_{HTL}$
  - $LUMO_{dopant}$ to $HOMO_{ETL}$
- Device stability – reduce dopant mobility in device (i.e., diffusion)

- One approach – add ‘anchor’ to improve stability

Initial project concept

ANCHORED MOLECULAR DOPANT

Molecular Acceptor

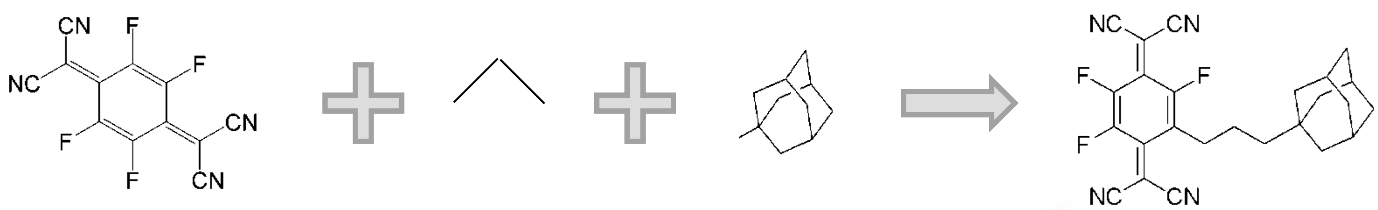
σ -connecting unit

Molecular Anchor

Derivatize without sacrificing high electron affinity

Vary length & rigidity

1) Inert to charge transfer reactions
2) Rigid (solid state stability)



F3TCNQ-Ad1

12 steps!

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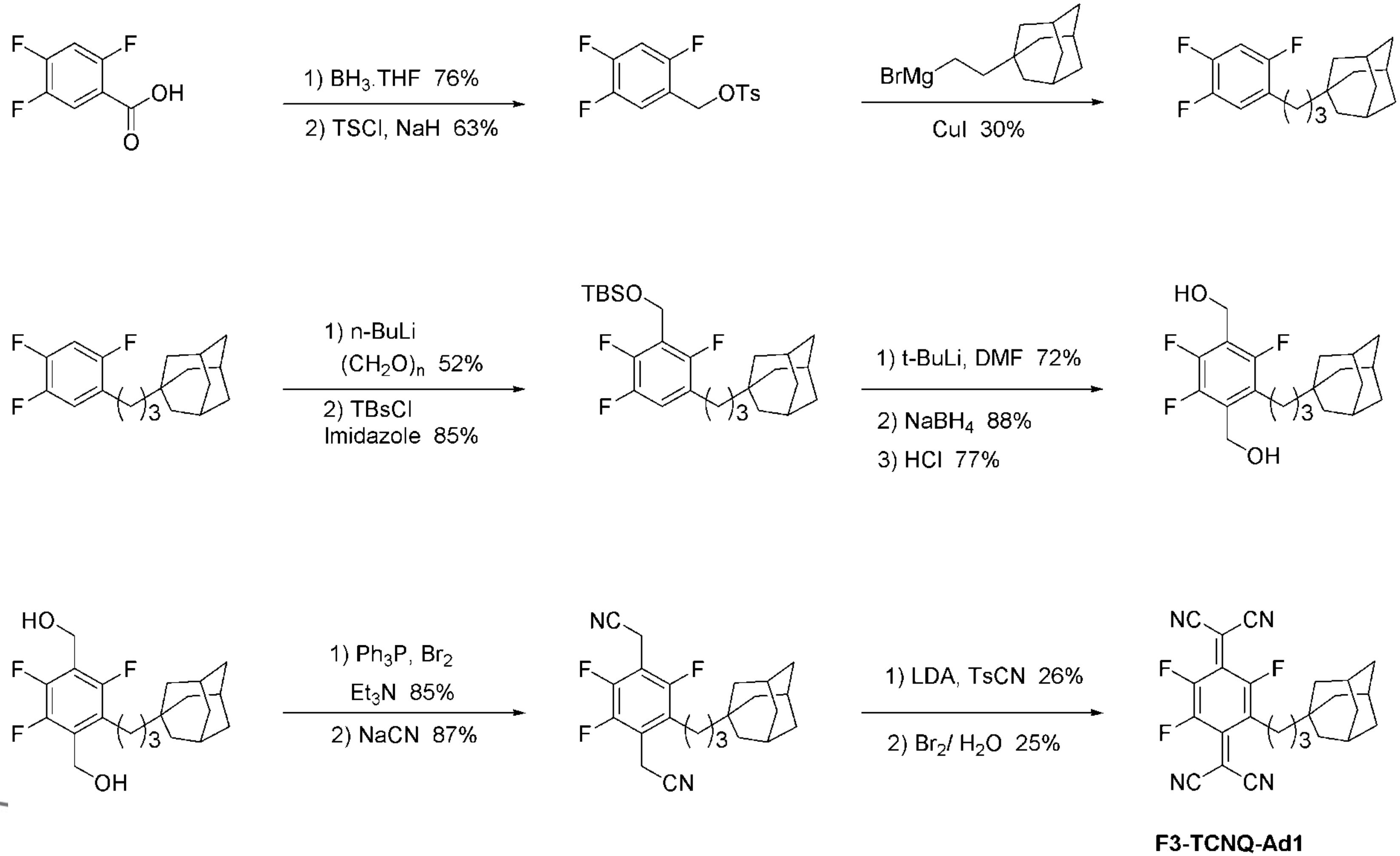
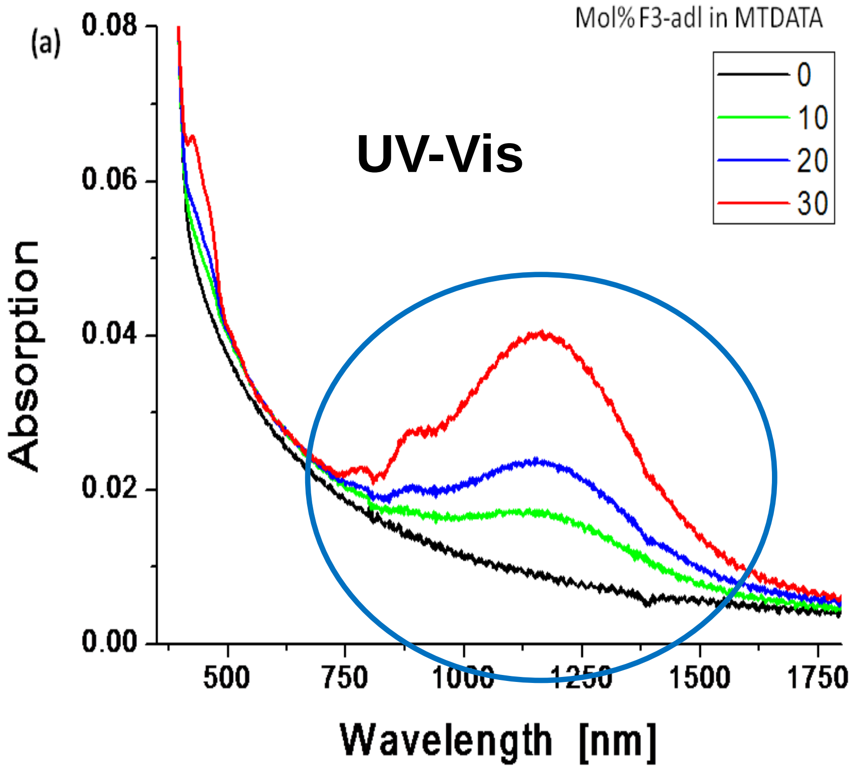
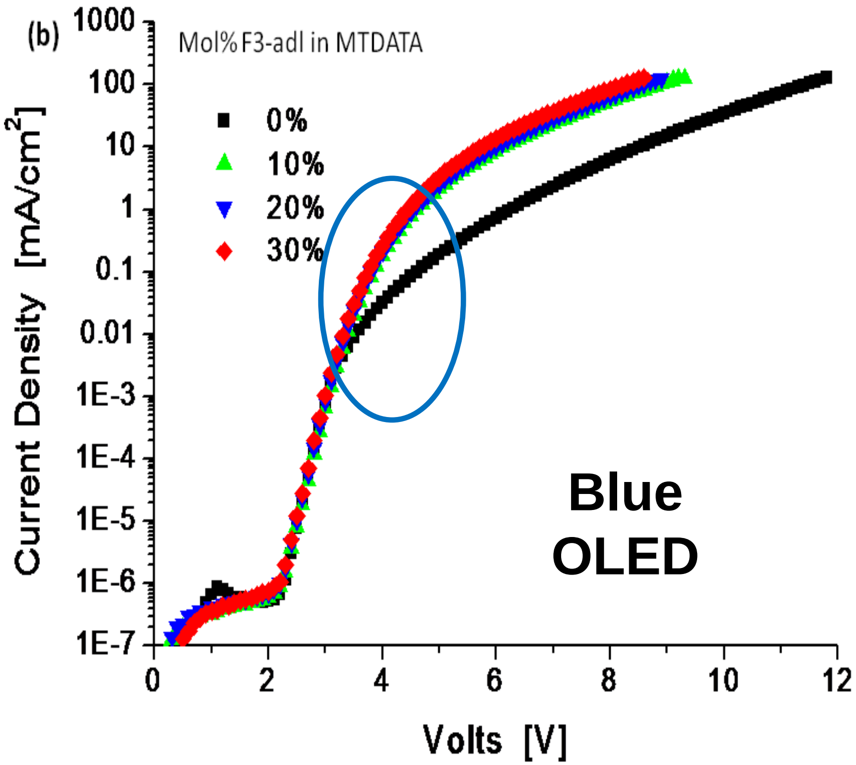
Synthesis and scale up of F3-TCNQ-Ad1



Anchored p-dopant generates charge complex and increases transport rate





UV-Vis absorption spectra for solution-processed HTL (MTDATA:F3TCNQ-adl)

ITO/60 nm HTL:x mol% F3TCNQ-adl/5 nm TCTA/15 nm HM-A1:5 wt% FIrpic/50 nm PO15/1 nm LiF/100 nm Al

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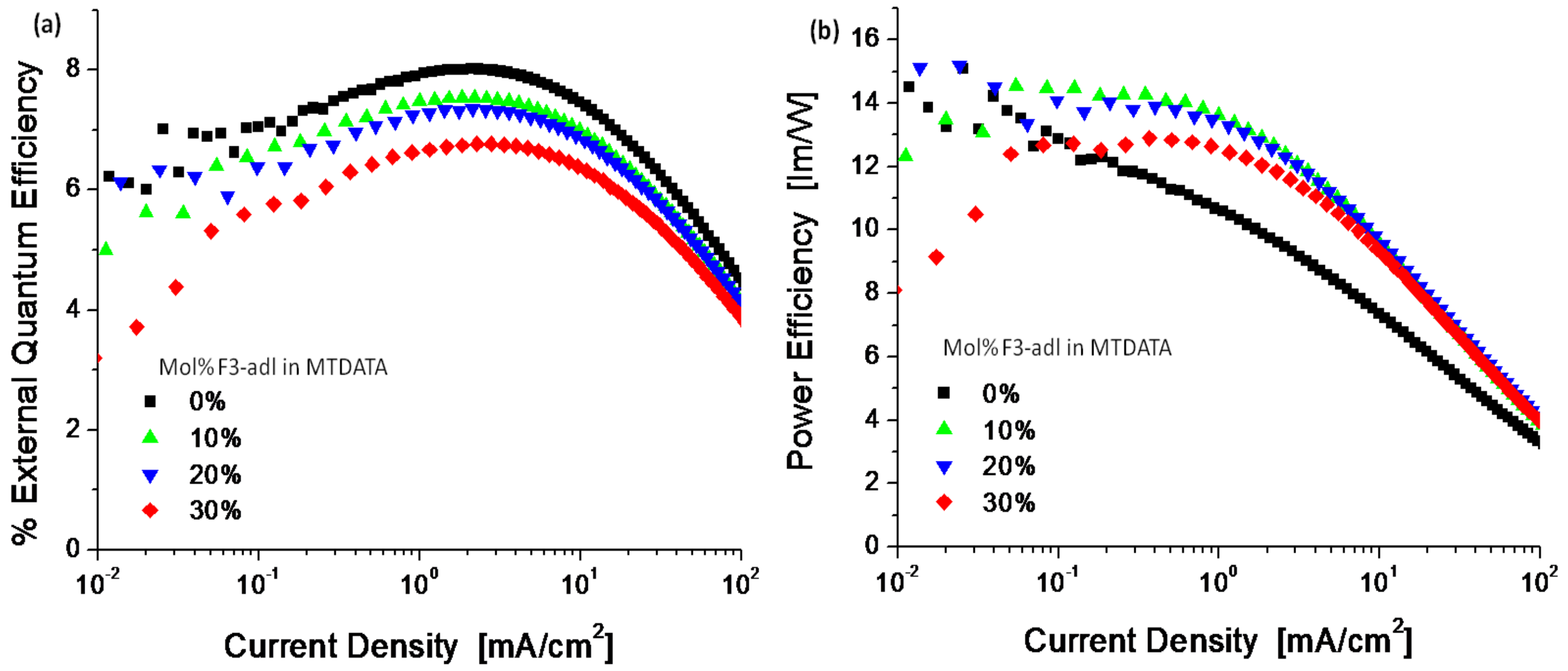
EQE and power efficiency blue OLED using anchored dopant F3TCNQ-adl



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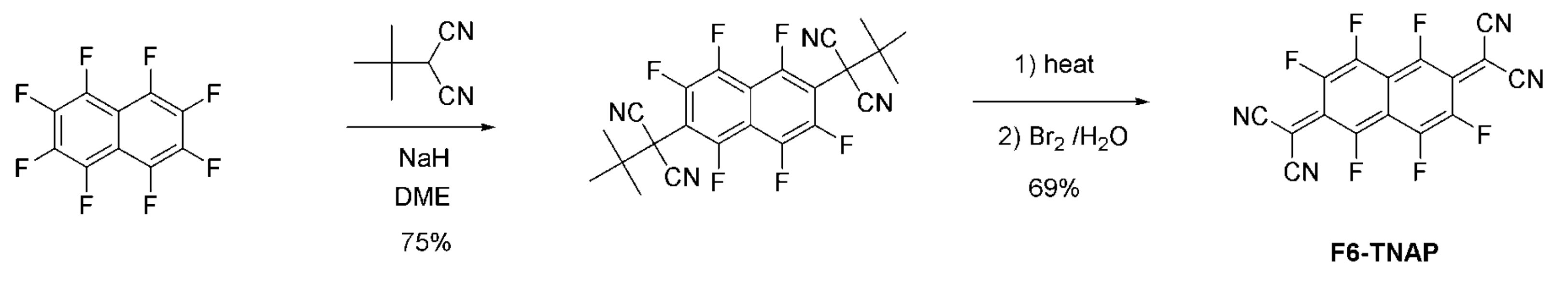
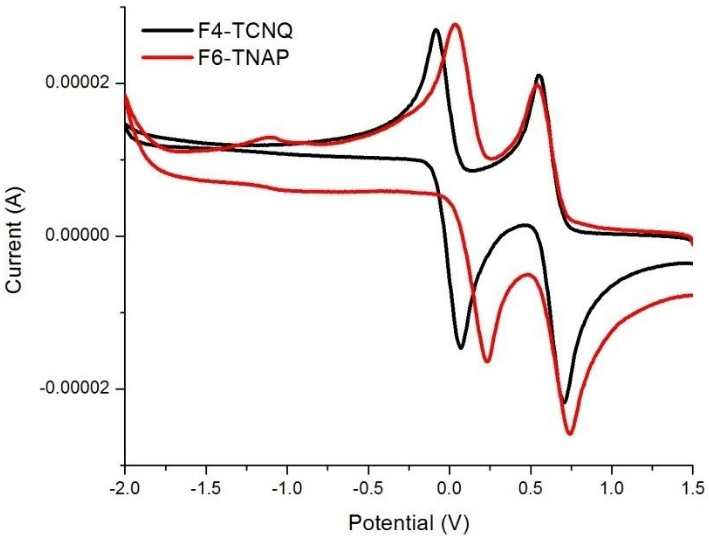
Or, increase MW…

- Structural analog to F4TCNQ
- F6-TNAP is obtained in 3 steps in good yield – amenable to scaleup
  - Sublimes well
  - Less volatile than F4TCNQ



P.K. Koech, A.B. Padmaperuma, et al., *Chem. Mater.*, **2010**, *22* (13), 3926–3932

Solution electrochemistry is similar to F4TCNQ

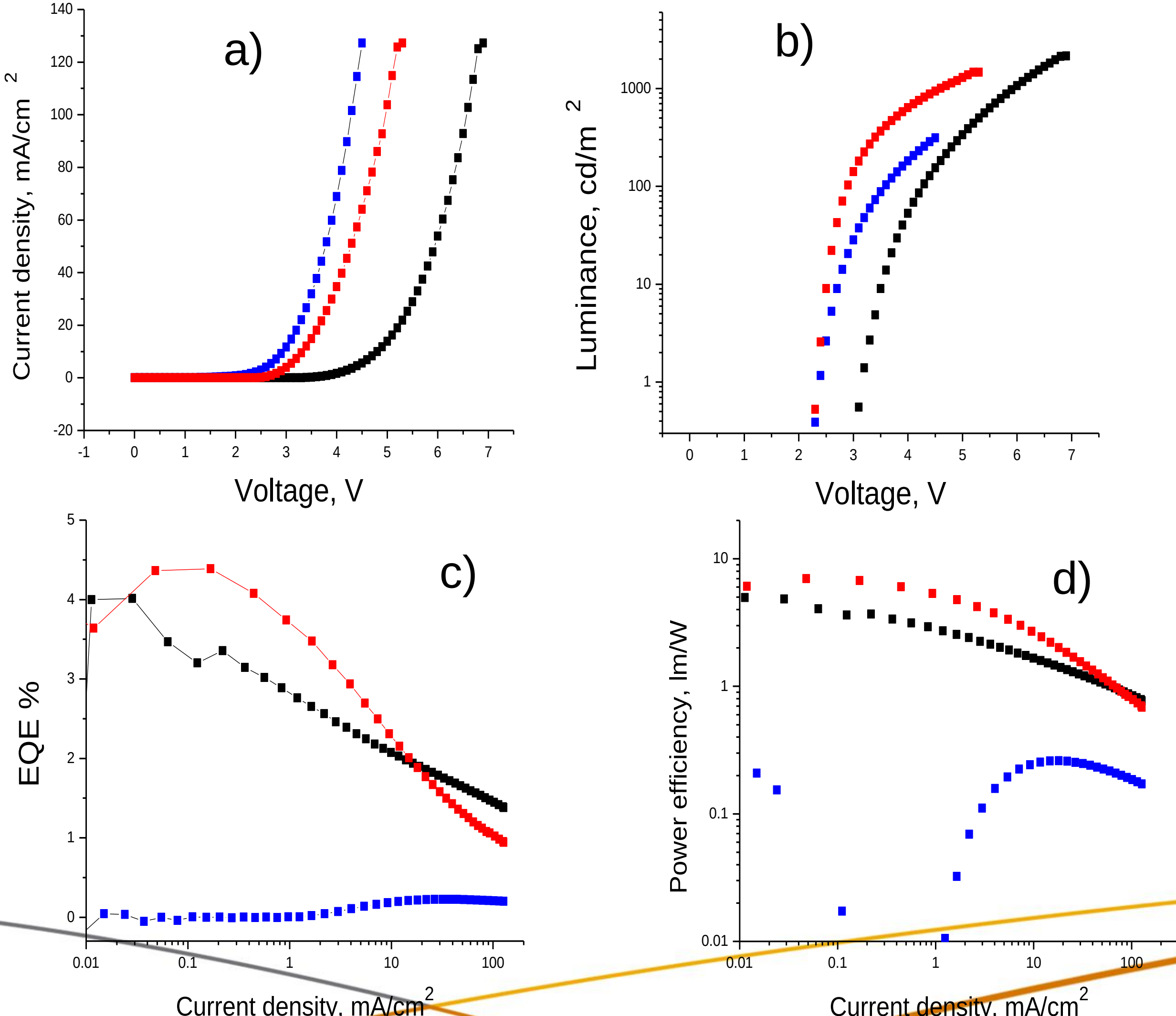


	From Experiment				Theory	
	E_{red} (V)	E_g (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)
F4-TCNQ	0.63	2.98	- 5.35	- 8.33	- 5.51	- 7.96
F3-TCNQ-Ad1	0.50	2.86	- 5.22	- 8.08	- 4.95	- 7.36
F6-TNAP	0.65	2.10	- 5.37	- 7.47	- 5.57	- 7.48

$$E_{LUMO} = - 4.72 - E_{red};\ E_{HOMO} = E_{LUMO} - E_g$$

- E_{LUMO} is similar to F4TCNQ – should dope, e.g., MTDATA

Red p-i-n OLEDs using F6-TNAP have better EQE, efficiency



Device structures:
HTL 30 nm*/EML 15 nm/ETL 50 nm*/ cathode 100nm
**excluding 5 nm buffers when applicable*

Undoped:
ITO/MTDATA/
CBP:5%PQIr/
BPhen/LiF/Al

p-i-n doped:
ITO/MTDATA:2%F6-TNAP/
CBP:5%PQIr/
BPhen:2%Cs_2CO_3/Al

p-i-n doped, with buffers:
ITO/MTDATA:2%F6-TNAP/5nm MTDATA/
CBP:5%PQIr/
5nm BPhen/BPhen:2%Cs_2CO_3/Al

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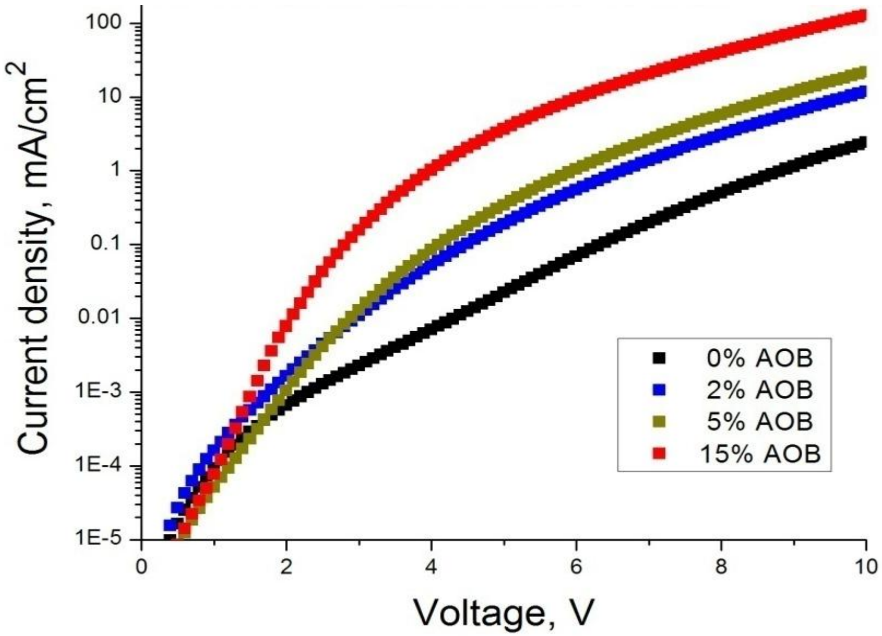
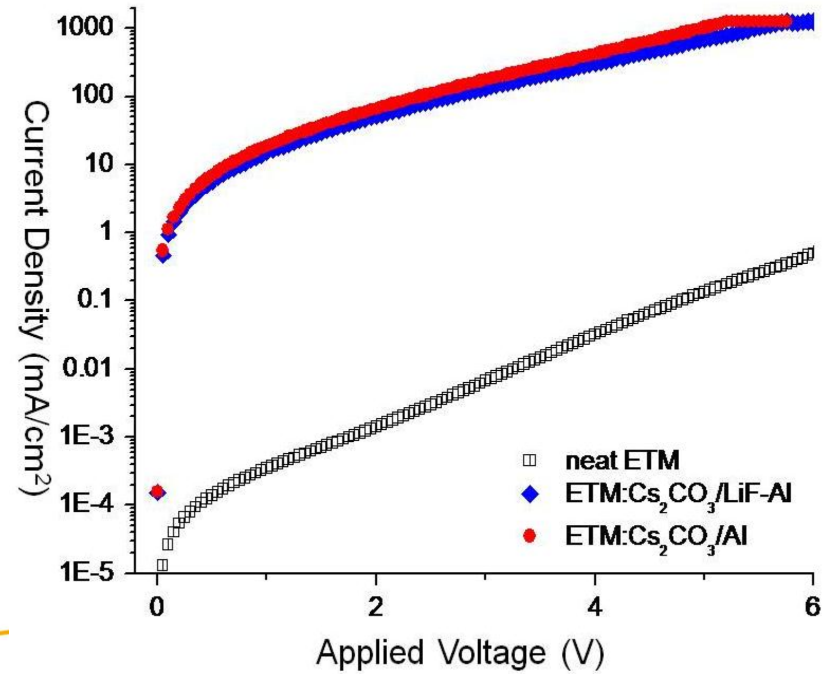
ETM1

- Synthesized new ETL material with good yield
- Stable in air, as complex
- Vacuum deposited
- Electron-only devices - **ITO/20 nm Al/100 nm ETL1:x% dopant/LiF/Al**

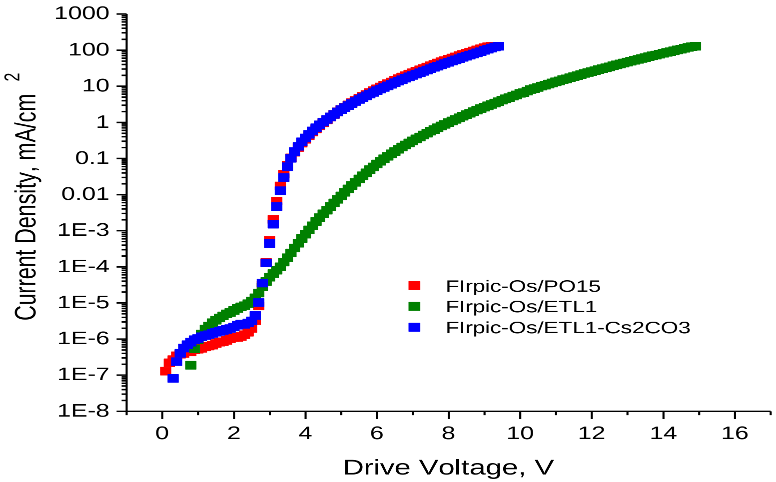


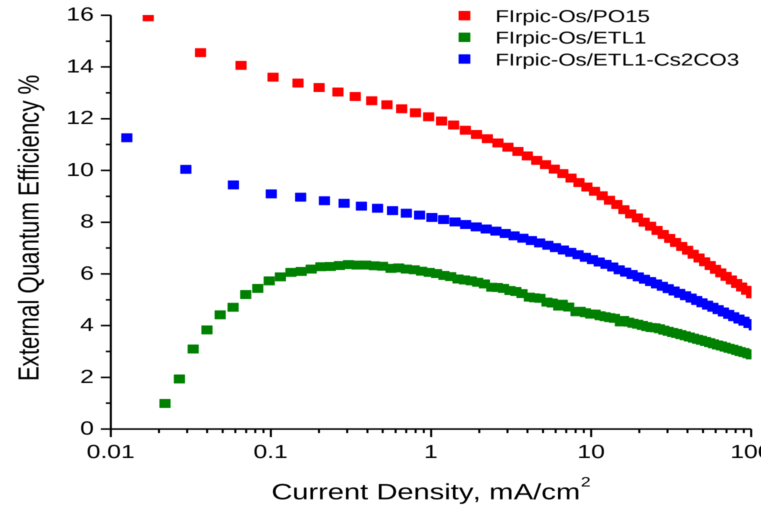


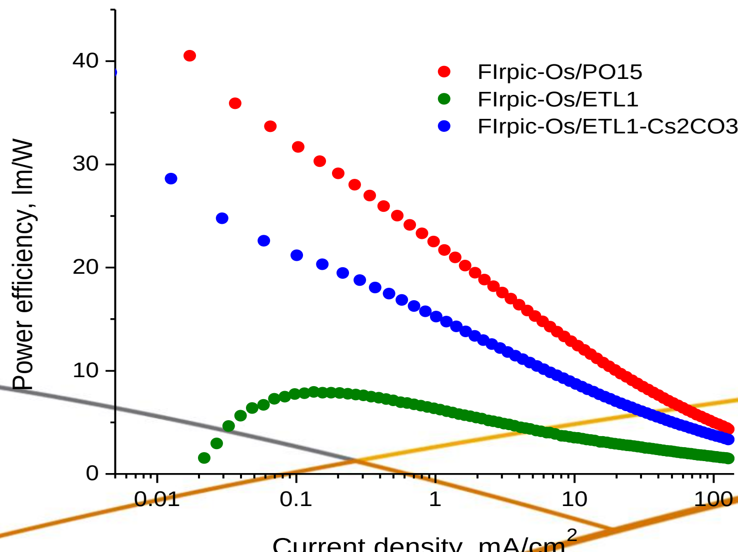
White n-doped OLED with ETL1 vs. PO15

ITO/390 NPD/50 TCTA/150 HMA1:5% Firpic/50 HMA1:1% Os-Orange/100 PO15/400 ETL/Al

ETL: **PO15/LiF, ETL1** or **ETL1:CsCO$_3$**







- ETL1:CsCO$_3$ equals PO15 I-V performance
- Lower EQE for device not yet optimized

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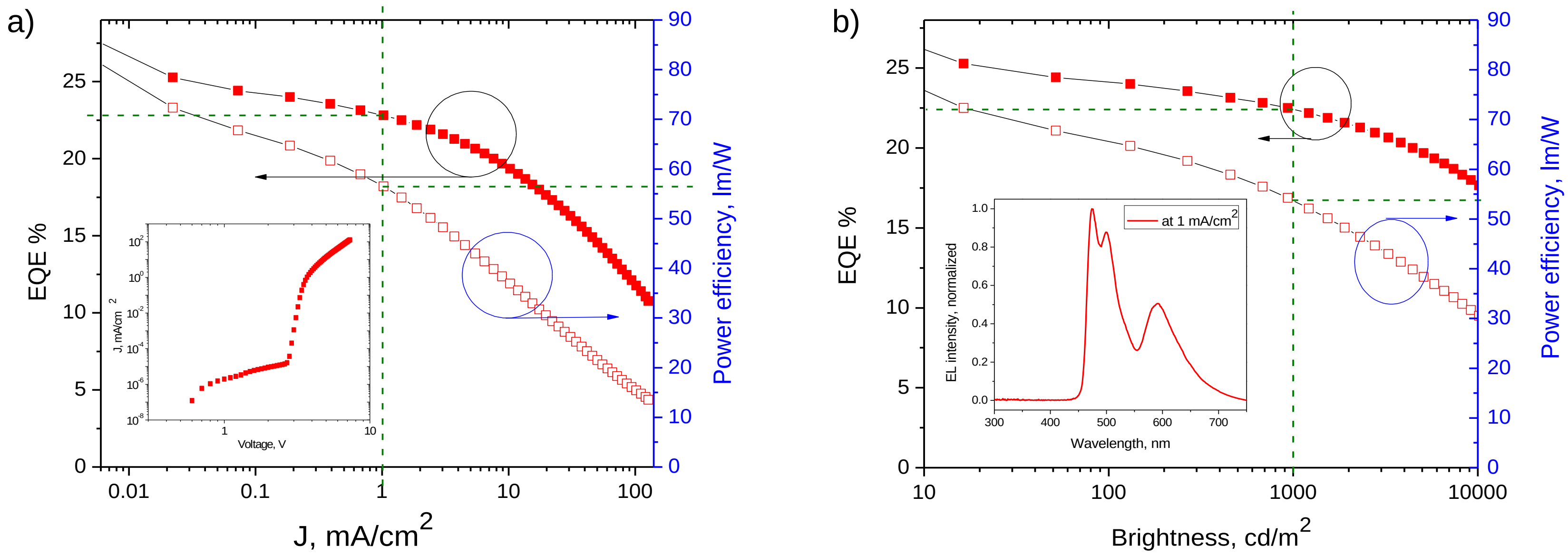
White *p-i-n* device demonstrates good power efficiency (with outcoupling)



ITO/570 Å TPD:1% F3-TCNQ-Adl/300 Å NPD/50 Å TCTA/80 Å HMA1:10% Firpic:0.5% Os-Orange/100 Å PO15/350 Å BPhen/50 Å ETM:8%Cs_2CO_3/10 Å LiF/1000 Å Al

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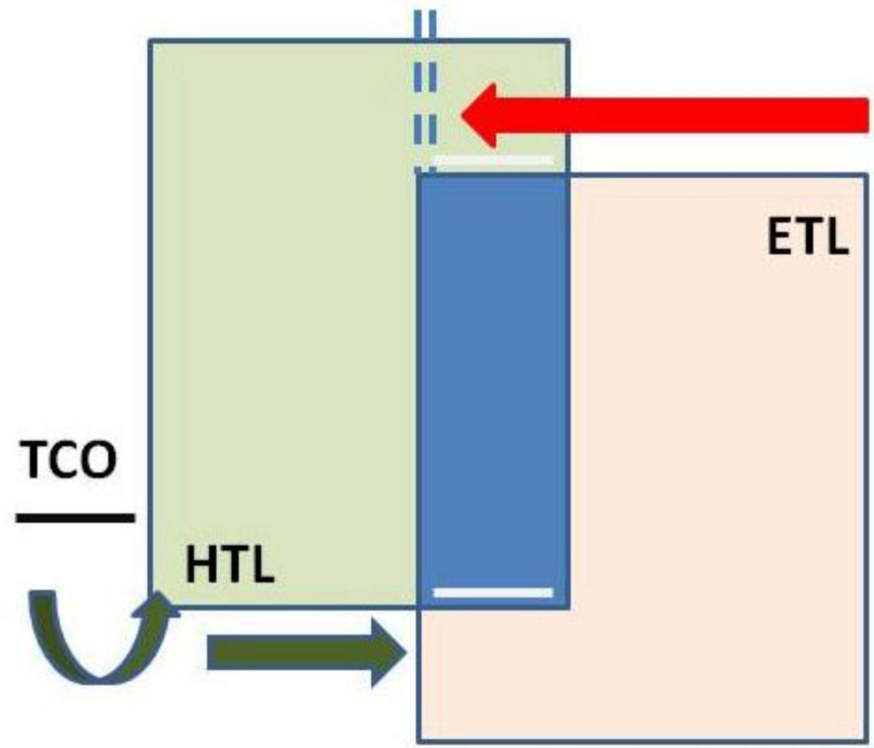
Outline

- Conductivity doping
- **New charge transport layers**
- Summary

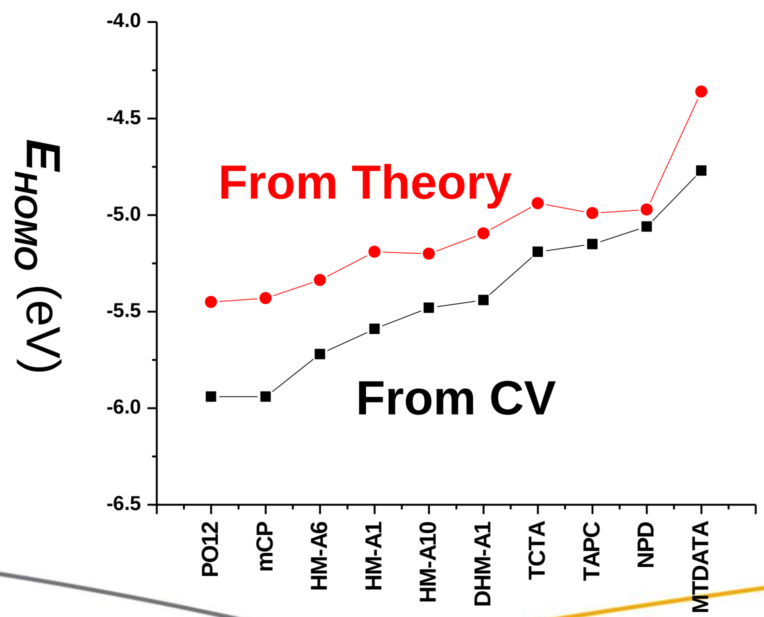
Design Rules
- Hole transport materials

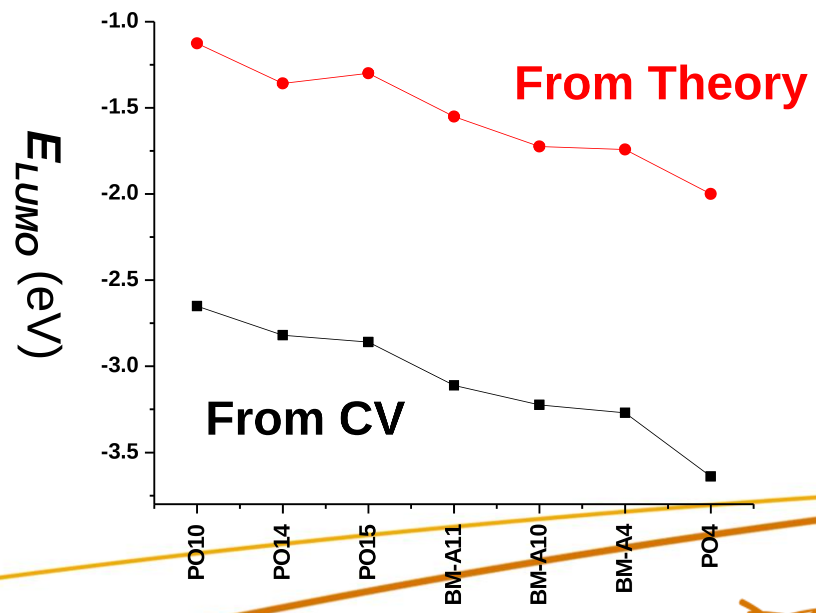
- Hole injection
  - Shallow E_{HOMO}
- Hole transport
  - High hole mobility
- Electron blocking
  - Shallow E_{LUMO}
- Prevent exciton quenching
  - High triplet energy



Computational Design
- HOMO/LUMO energies

- Geometry optimized at B3LYP/6-31G* level
- *NWChem* computational package





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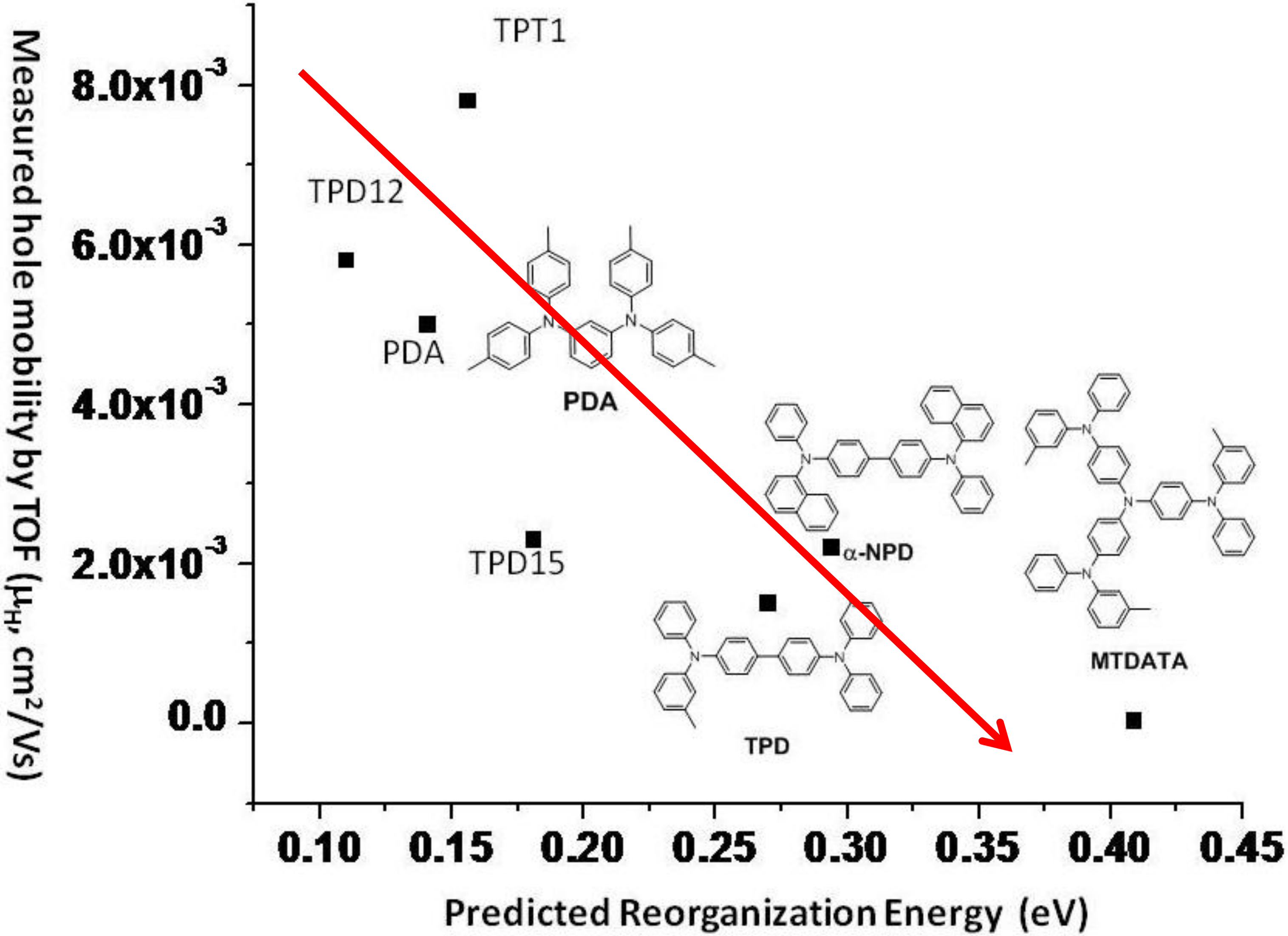
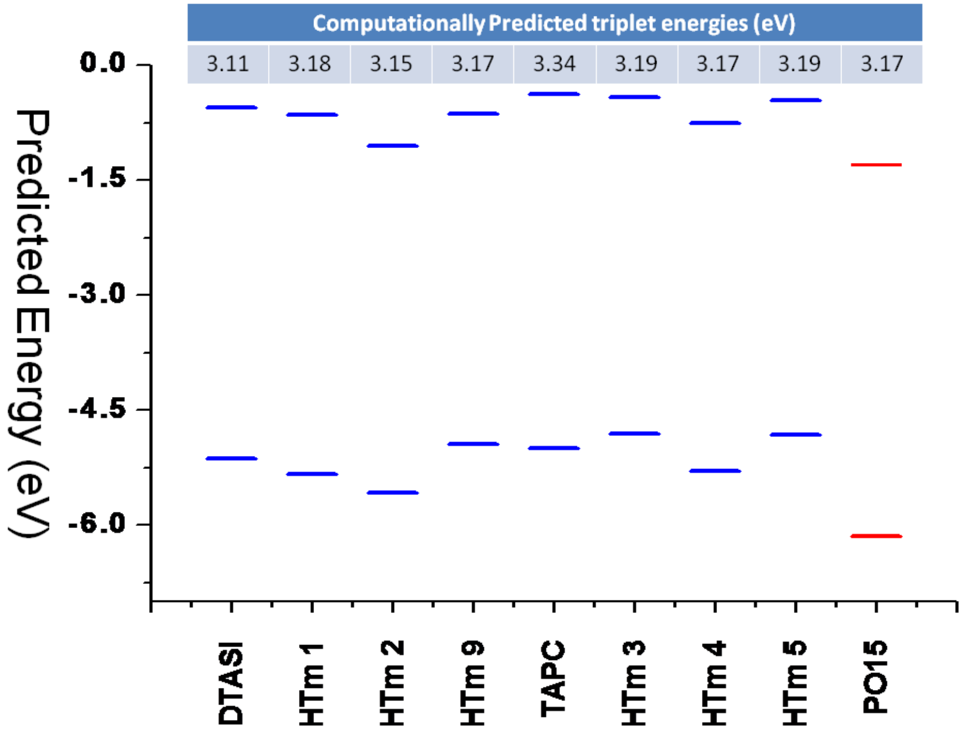
Computational Design
- reorganization energy vs. mobility



Rational Design of HTMs

- Two classes of HTms based on TAPC and DTASI were studied

- Predicted three parameters:
  - Reorganization energy (λ_i)
  - E_{HOMO} / E_{LUMO}
  - E_T



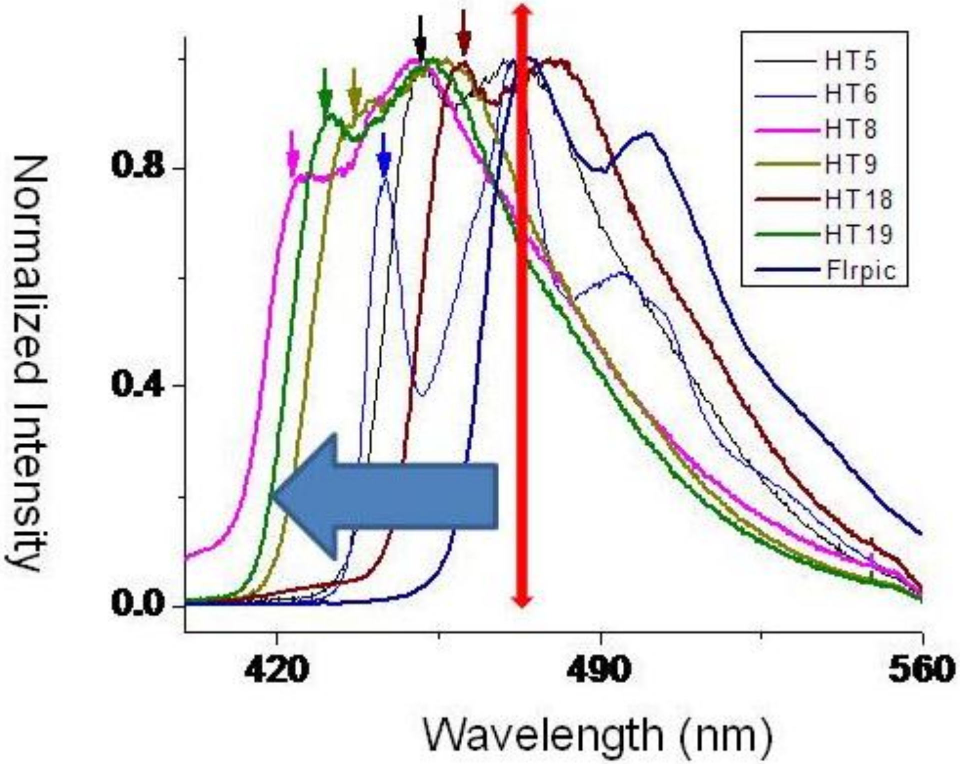
Reorganization Energies

DTASI	0.095	TAPC	0.104
HTm 1	0.104	HTm 3	0.070
HTm 2	0.064	HTm 4	0.059
HTm 9	0.057	HTm 5	0.072

E_T calculated as described by Bredas *Chem. Mater.*, **2010**, *22* (1), 247–254

Measured electronic structure for new HTMs

	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)
TAPC	**-1.7**	**-5.2**	**3.5**
HTM 5	-1.7	-5.3	3.6
HTM 6	-1.7	-5.2	3.6
HT8	-1.6	-5.1	3.5
DTASI	**-1.8**	**-5.3**	**3.4**
HTM 9	-1.8	-5.2	3.5
HTM 18	-1.9	-5.4	3.5
HTM 19	-1.9	-5.4	3.5
PO15	**-2.9**	**-6.6**	**3.7**



All HTm have $E_T > E_T$ of FIrpic

$$E_{LUMO} = E_{HOMO} + E_g$$

$$E_{HOMO} = (1.4 \pm 0.1) \cdot (qVCV)\ \ (4.6 \pm 0.08)\ \text{eV}$$

D' Aandrade Organic Electronics 6 (2005) 11–20

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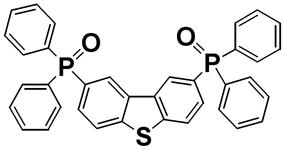
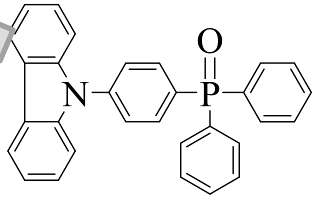
Summary and Future Work



PO15

Electron transporting Host

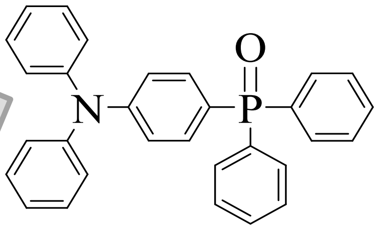
EQE ~ 10% at 20% FIrpic doping



PO12

Ambipolar Host

EQE ~ 8% at 5% FIrpic doping



HM-A1

Ambipolar Host

EQE ~ 16%
PE – 38 lm/W
Improved hole injection
Hole rich

Mixed host structure

EQE ~ 17%
PE > 50 lm/W
Improved charge balance

Mixed host structure

Develop new HTMs
Improve
- Charge balance
- Stability

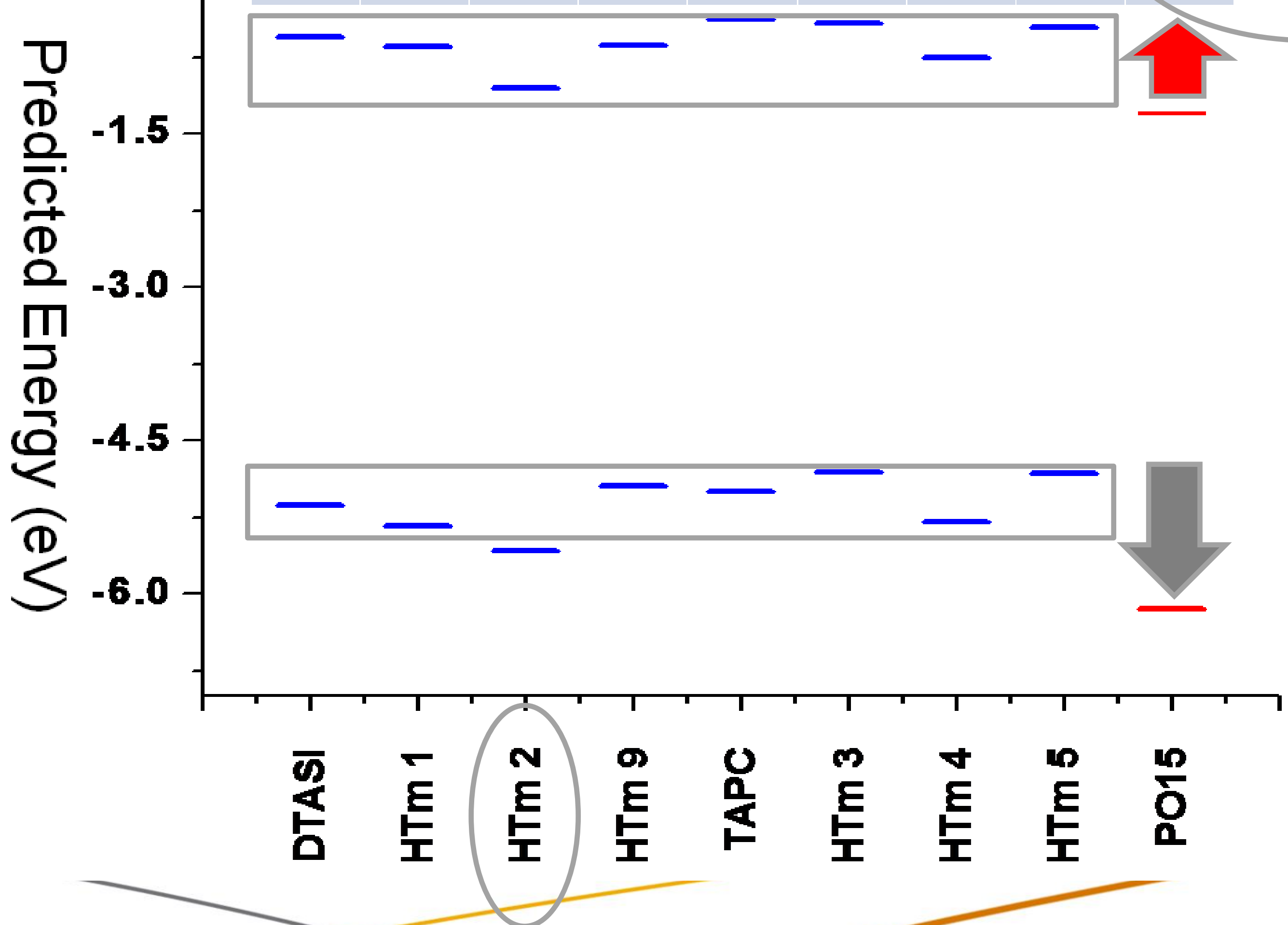
Charge transport materials

- Goal: Add to the toolbox of stable charge transport materials suitable for blue OLEDs
  - Reduce roll-off
  - Improve charge balance in EML
  - Improve process window
- Examples – HTLs, ambipolar hosts

Rational Design of charge transport materials

Computationally Predicted triplet energies (eV)								
3.11	3.18	3.15	3.17	3.34	3.19	3.17	3.19	3.17

Exp E_T > 3eV



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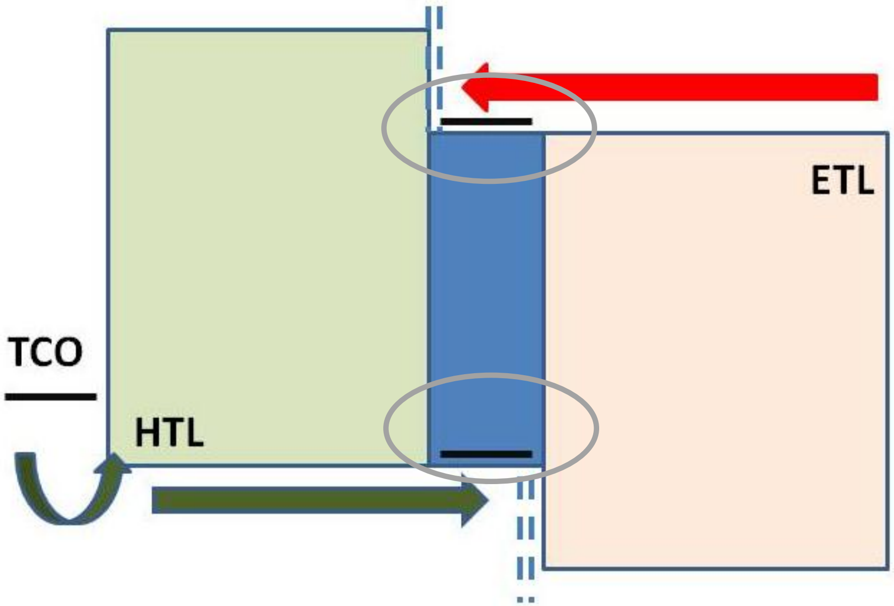
Design rules for ambipolar hosts

- Hole injection
  - Shallow E_{HOMO}
- Charge transport
  - High hole mobility
  - High electron mobility
- Prevent exciton quenching
  - High triplet energy
- Prevent charge trapping



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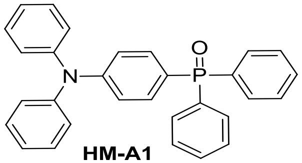
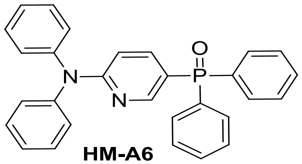
Alter device properties by molecular design of ambipolar hosts

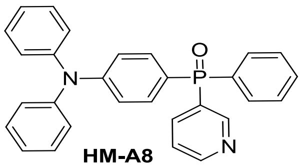
- Simple changes to the structure
  - Change E_T
  - Change E_{HOMO}/E_{LUMO}
  - Change packing
  - Change transport
- Affect the charge balance in the EML
- Affect the device efficiency



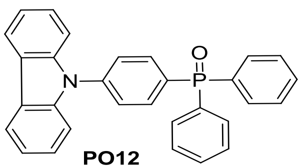
HM-A1



HM-A6



HM-A8

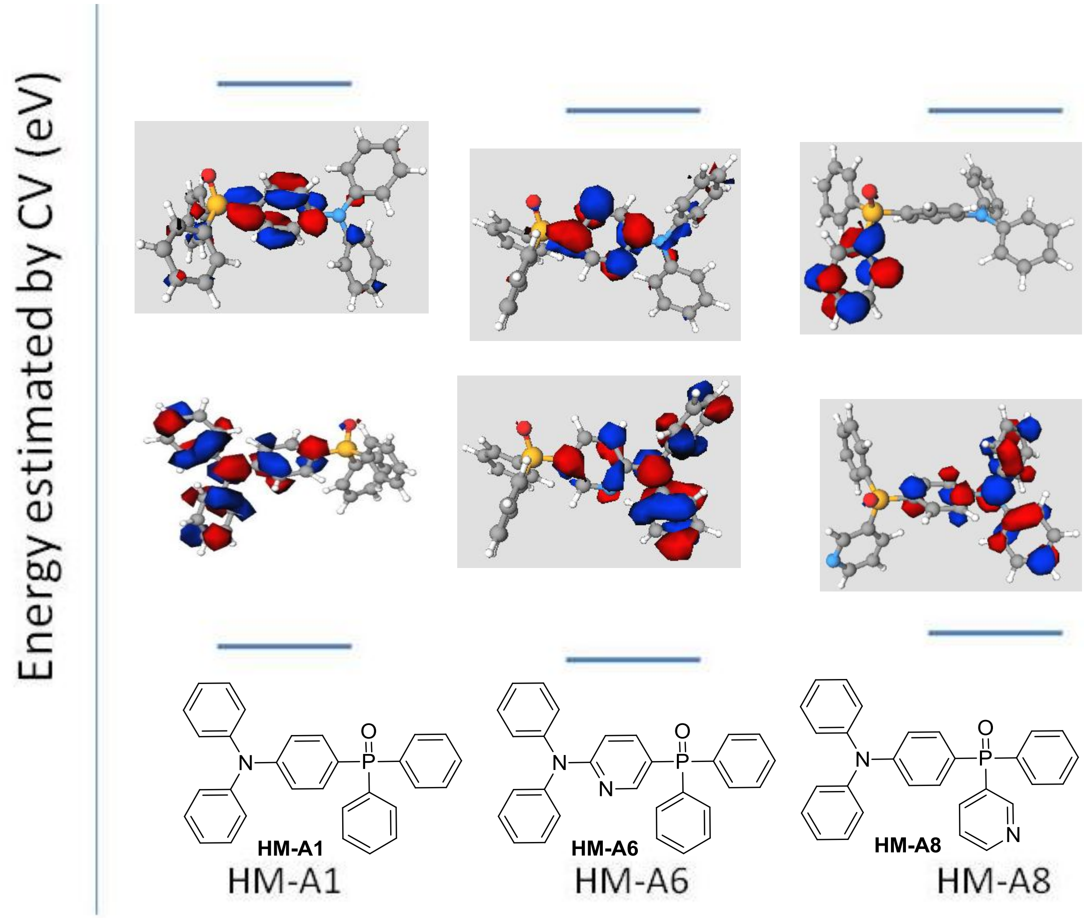


PO12

	E_{HOMO}, *eV*	E_{LUMO}, *eV*	E_T, *eV*
PO12	-5.70	-2.52	3.00
HM-A1	-5.45	-2.56	2.80
HM-A6	-5.54	-2.68	2.80
HM-A8	-5.39	-2.69	2.82

Tuning hole transport: phenyl vs. pyridyl moieties

- HTm = TPA
- HM-A6 and HM-A8 have similar LUMO energies
- LUMO changes
- HM-A8:
  - The HTm does not contain an electron deficient ring



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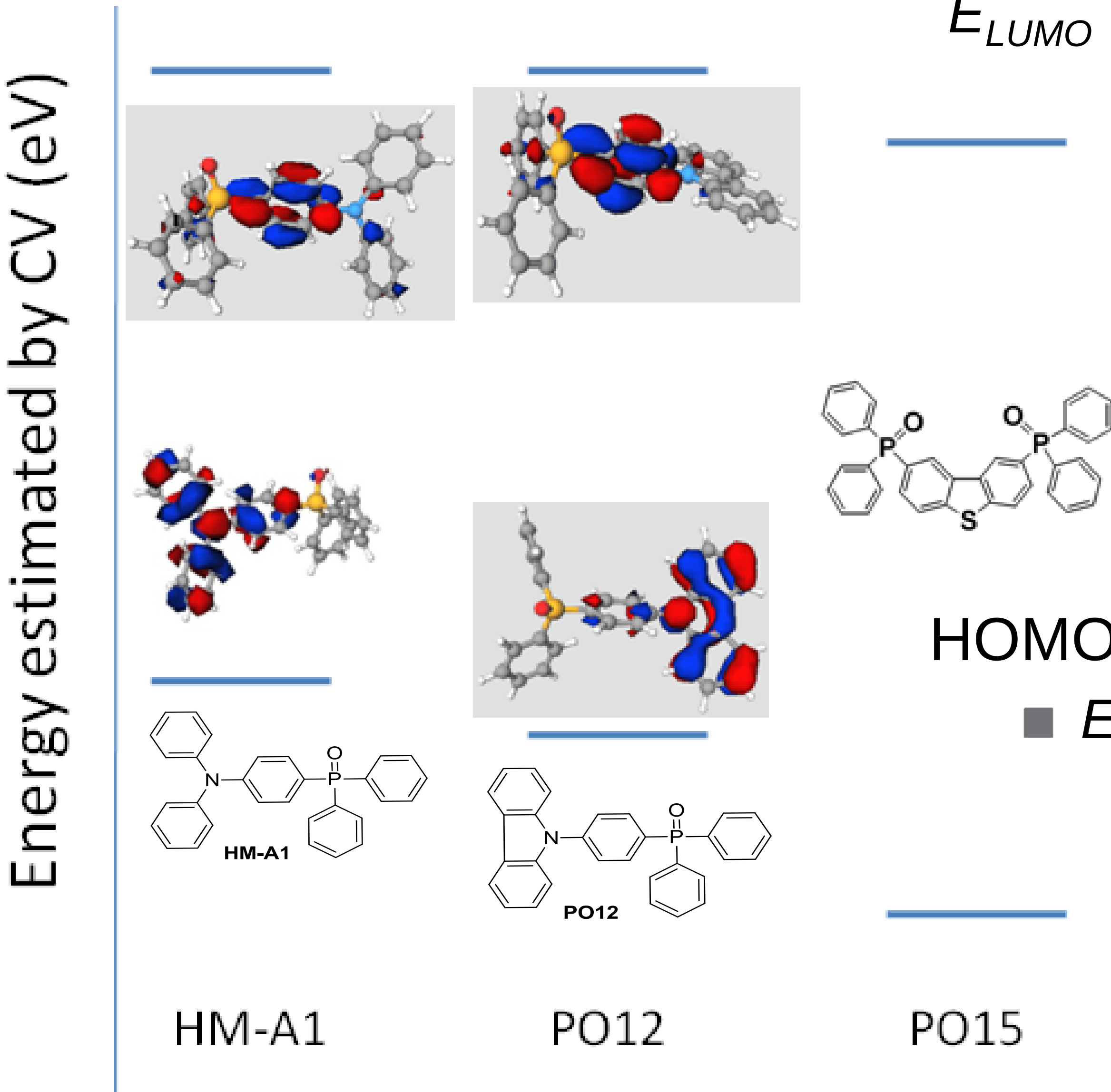
Tune electronic structure by changing the HTm - CBz vs. TPA

E_{LUMO} unchanged

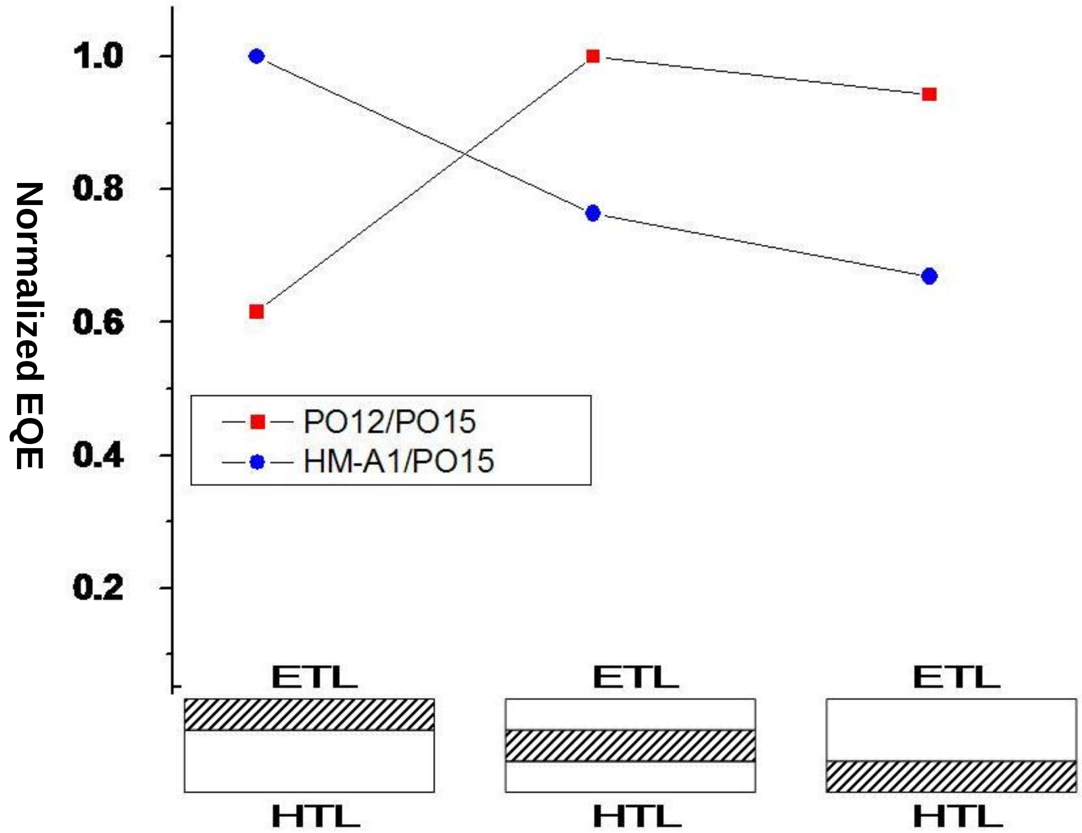


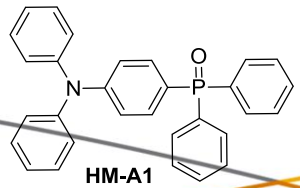
HOMO on the HTm

- E_{HOMO} different

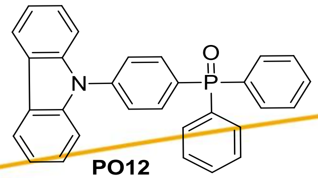
Tuning mobility: CBz vs. TPA

- HM-A1 devices are hole-rich
- Most of the emission occurs far away from the HTL interface
- Hole transport by TPA is more efficient than by CBz – higher mobility





HM-A1

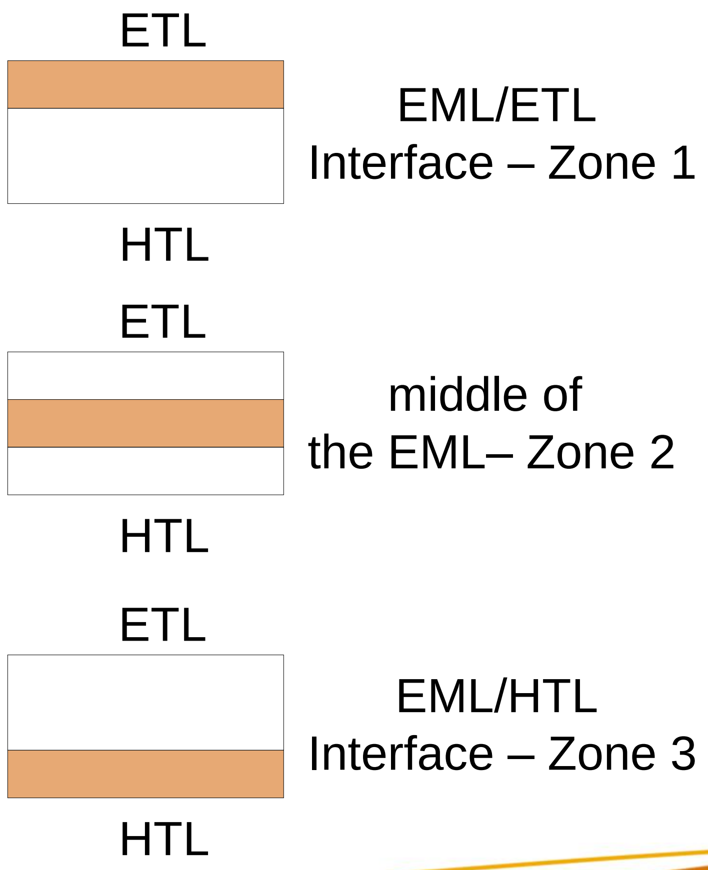


PO12

Probe charge balance by location of the recombination zone

- Emission zone location related to relative charge transport within the EML

- Host materials with:
  - holes > electrons = Zone 1
  - electrons > holes = Zone 3
  - holes ~ electrons = Zone 2



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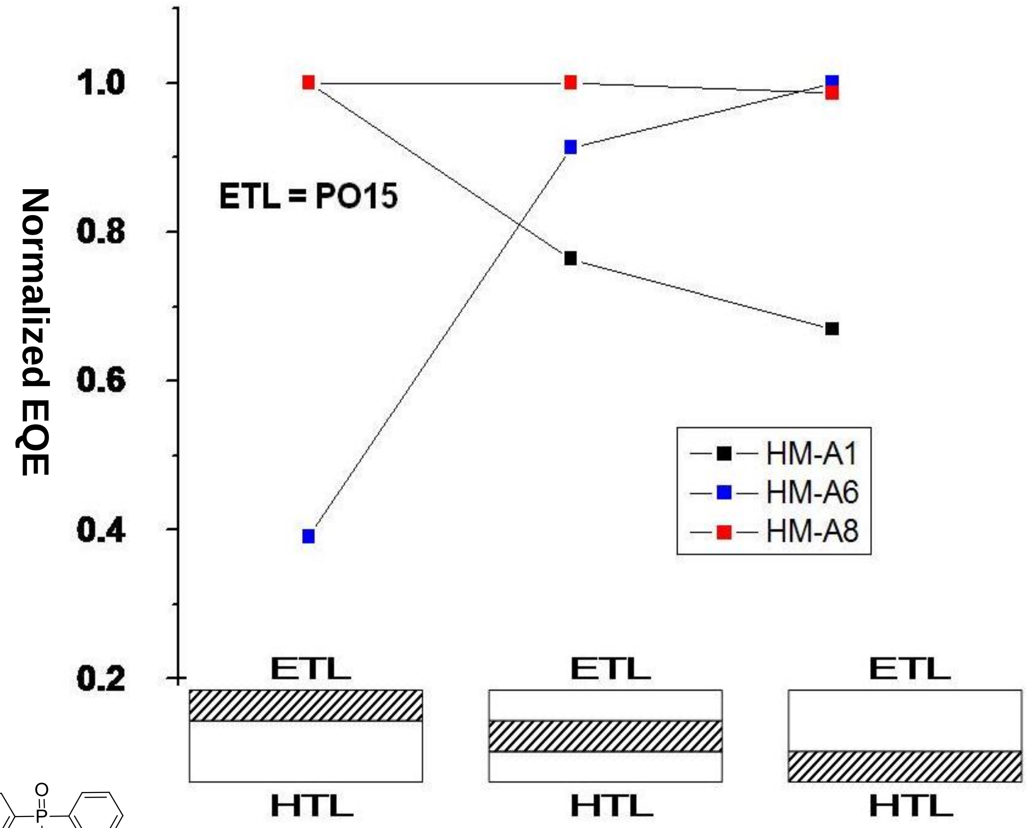
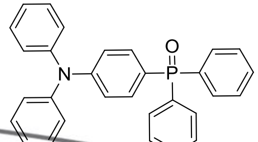
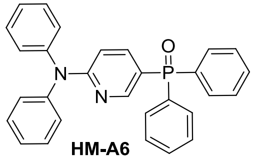
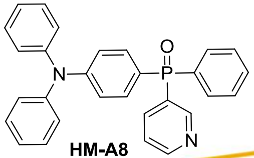
Effect of the position of the LUMO on the emission zone

- HM-A1 is hole rich
- HM-A6 is electron rich
- HM-A8 is closer to truly ambipolar



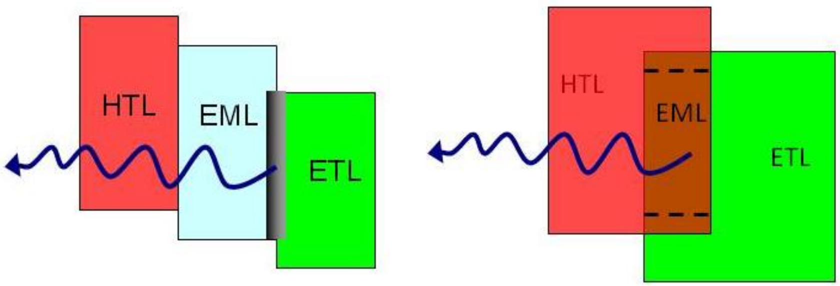

HM-A1


HM-A6

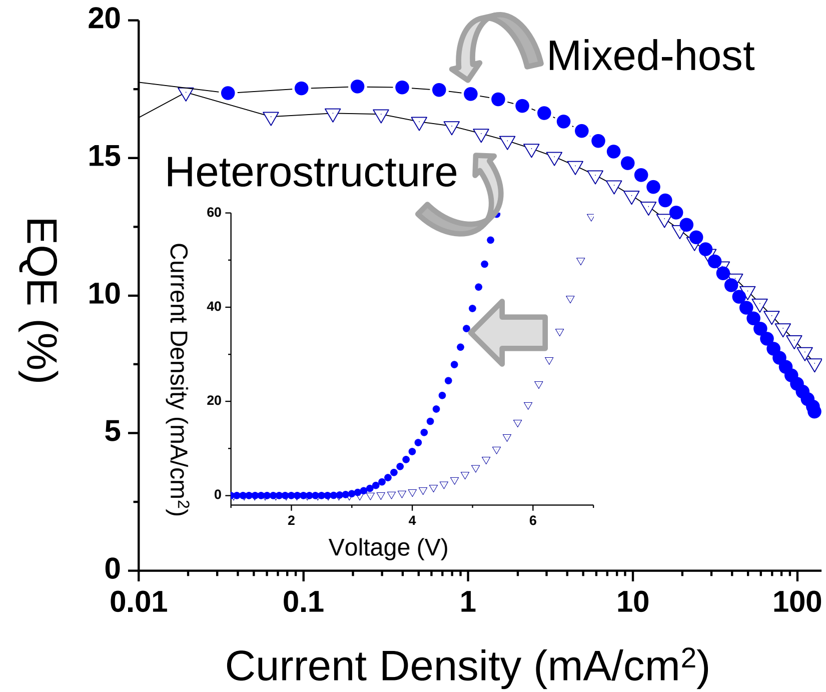

HM-A8

Polikarpov *Appl. Phys. Lett.*, **96**, 053306, 2010.

Blue OLEDs: baseline devices



Hetero-structure　　　Mixed-host



	Voltage (V)	EQE (%)	h_p(lm/W)
Hetero-structure	5% FIrpic:HMA1		
	4.1	16.4 %	38.3
Mixed host structure	TAPC(35%):PO15(60%):FIrpic(5%)		
	3.2	17.2 %	52.0
@ 1mAcm^{-2}	35nm HTL/15nm EML/50nm ETL/LiF-Al		

Chopra *Applied Physics letters*, 2010, *97*, 033304

Summary

- Conductivity dopants can reduce voltage, but…
  - Trade-off between efficiency and device complexity – implications for manufacturing?
- Interface doping is currently done ‘intrinsically’ – i.e., LiF or NaF EIL or H^+ for acidic HIL
  - Can do this more deliberately if necessary
- Designing host, ETL and HTL for high-efficiency blue (and white) devices requires understanding of the system
  - Device architecture directly impacts molecular design