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# Determination of Band Alignment in Hybrid Photovoltaics


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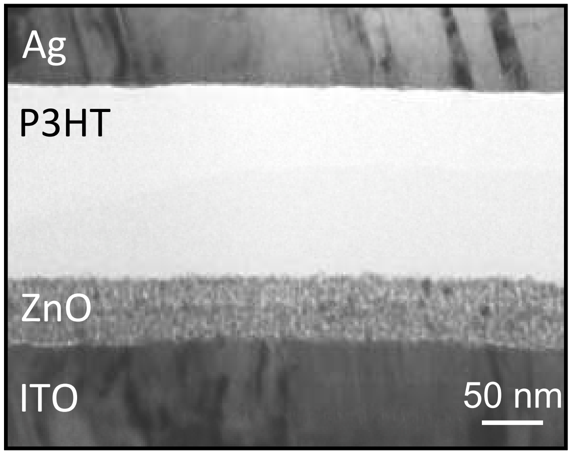
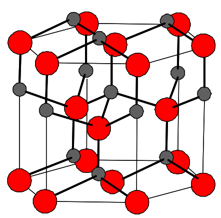
# An Introduction to ZnO Hybrid Solar Cells

- ZnO hybrid solar cells combine an organic electron donor material (P3HT) with an inorganic electron acceptor (ZnO)
- ZnO has high electron mobility, tunable band alignment, and the versatility of its structure
- Hybrid solar cells have greater stability in air than all-organic photovoltaic
- Hybrid solar cells suffer poor performance, in particular low photocurrent, compared to all-organic photovoltaics

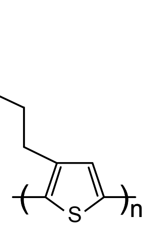
ZnO/P3HT Planar Solar Cell




TEM image collected by Ping Lu, Sandia National Labs



wurtzite ZnO




P3HT
Poly-(3-hexylthiophene)

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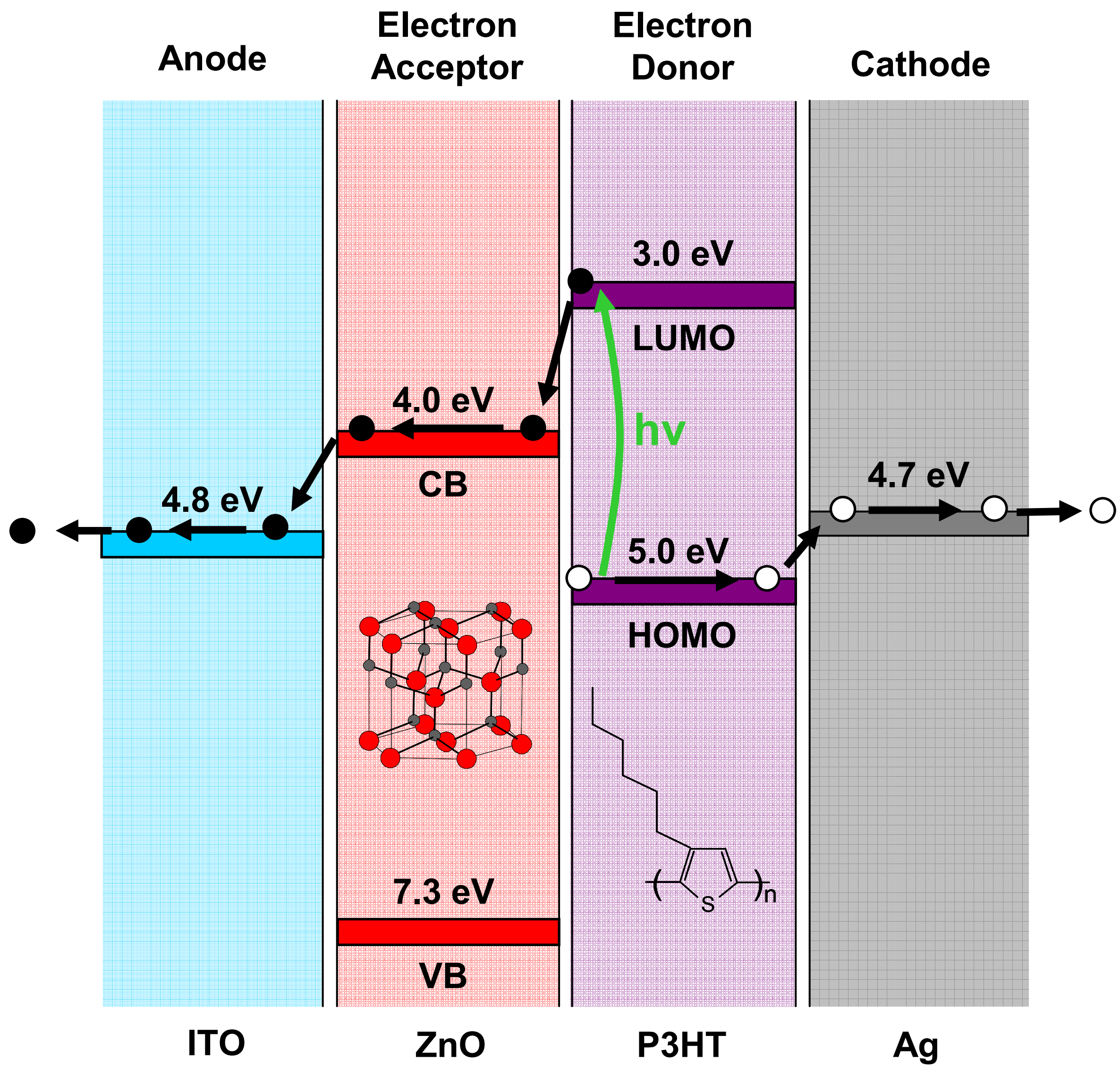
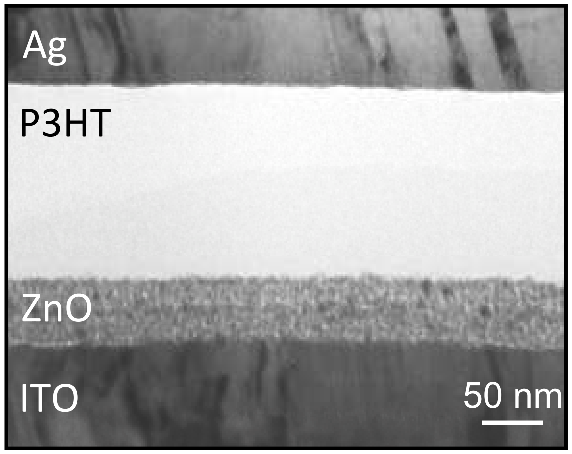
# Introduction to Inverted ZnO/P3HT Hybrid Photovoltaics

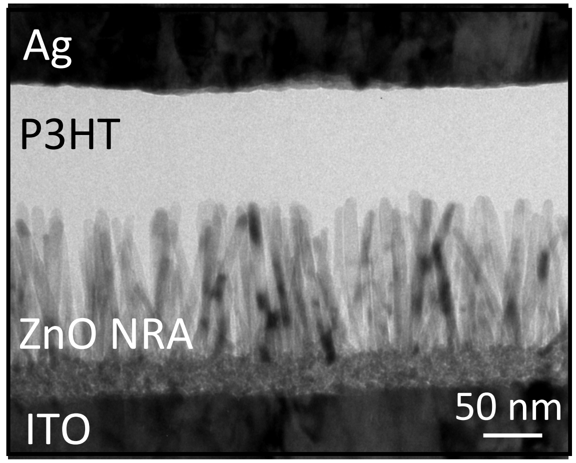


# Tuning Morphology in ZnO Hybrid Solar Cells

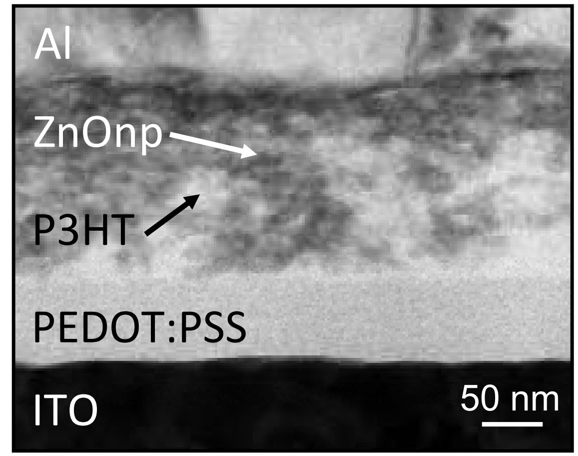
ZnO/P3HT Planar Solar Cell




ZnO Nanorod Array/P3HT BHJ Solar Cell




ZnOnp:P3HT BHJ Solar Cell




TEM images collected by Ping Lu, Sandia National Labs

ZnO Bilayer
$V_{oc}$ = 430 mV
$J_{sc}$ = 0.54 mA/cm$^2$
η = 0.13 %

ZnO Nanorod Array
$V_{oc}$ = 380 mV
$J_{sc}$ = 2.91 mA/cm$^2$
η = 0.55 %

ZnO Nanoparticles
$V_{oc}$ = 540 mV
$J_{sc}$ = 2.89 mA/cm$^2$
η = 0.70 %

$V_{oc}$ = Open circuit voltage
$J_{sc}$ = Short circuit current
η = Power conversion efficiency

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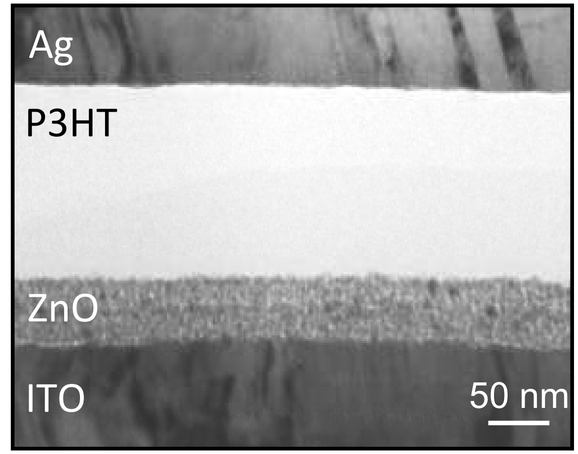
# Assessing New Electron Donor Materials for Hybrid Photovoltaics

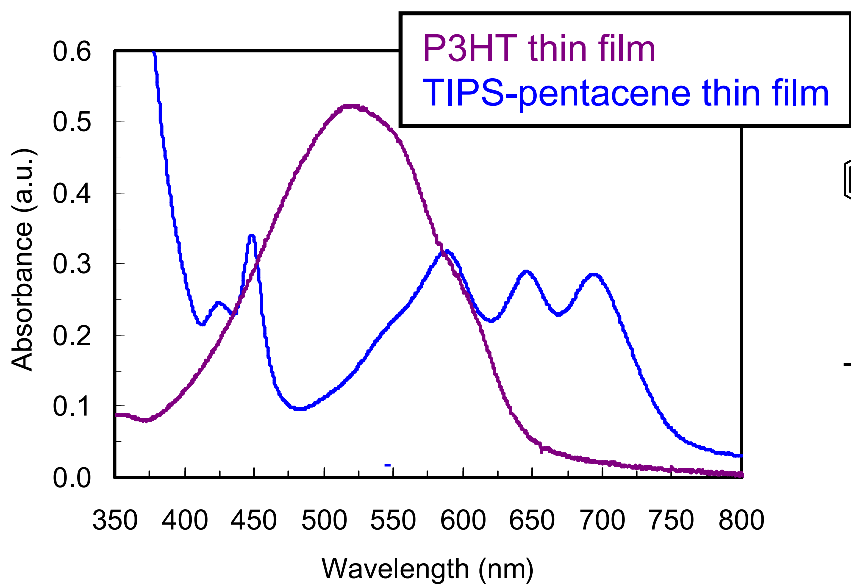
P3HT is the most common electron donor/absorber material used in hybrid photovoltaics

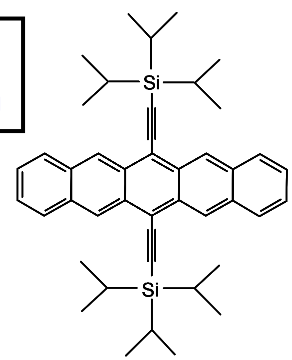
TIPS-pentacene is a promising alternative
- Solution processable
- Broad visible absorption
- High mobilities reported in field effect transistors
- CV estimates similar band alignment to P3HT

ZnO/P3HT Planar Solar Cell

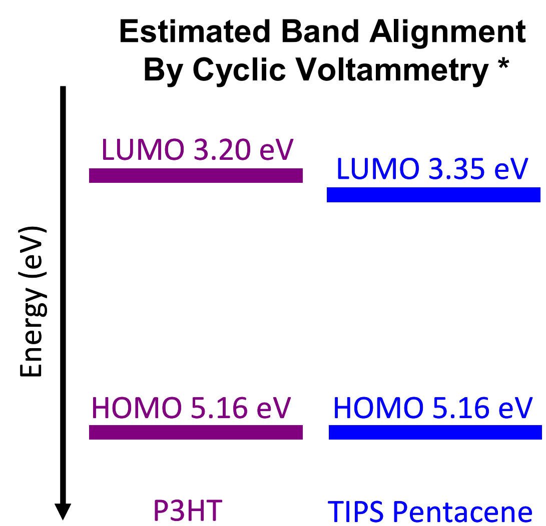



TEM image collected by Ping Lu, Sandia National Labs



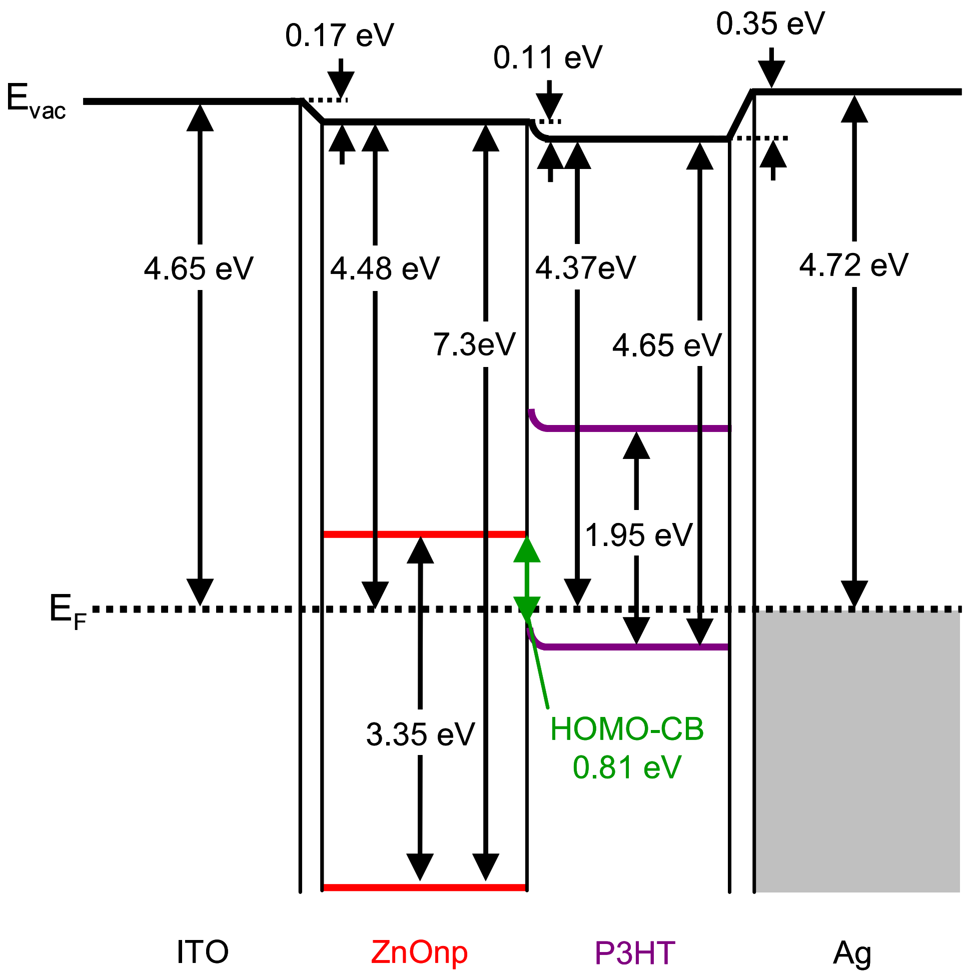



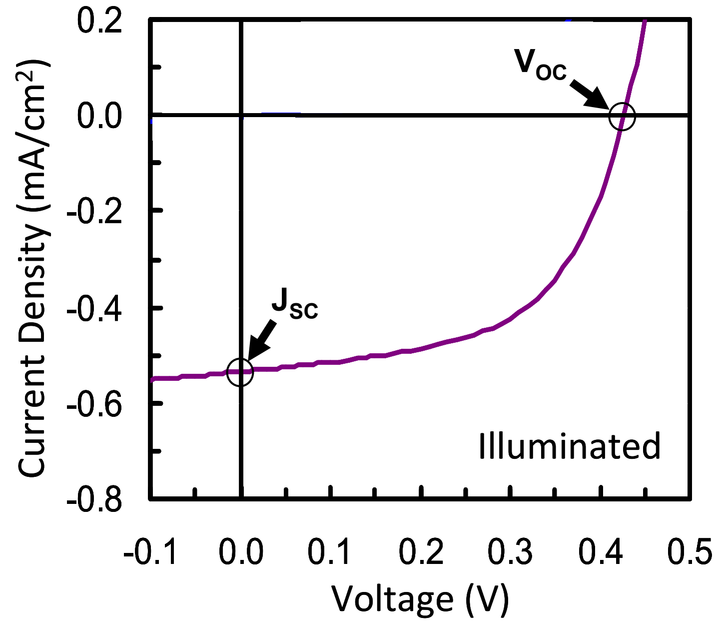

TIPS pentacene




* Lloyd, M.T.; Anthony, J. E.; Malliaras G.G. *Materials Today*, **2007**, *10*, 34-41.

# The Goal: An Accurate Band Diagram for a Complete Photovoltaic Device




ZnO Bilayer
$V_{oc}$ = 430 mV
$J_{sc}$ = 0.54 mA/cm$^2$
$\eta$ = 0.13 %

$$* V_{OC} = (1/e)(E_{Donor}\ \text{HOMO} - E_{Acceptor}\ \text{LUMO}) - 0.3\ \text{V}$$

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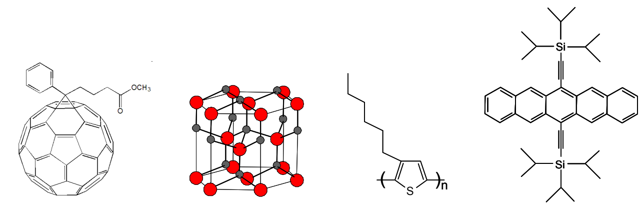
* Scharber et al., *Adv. Mater.* **2006**, *18*, 789.

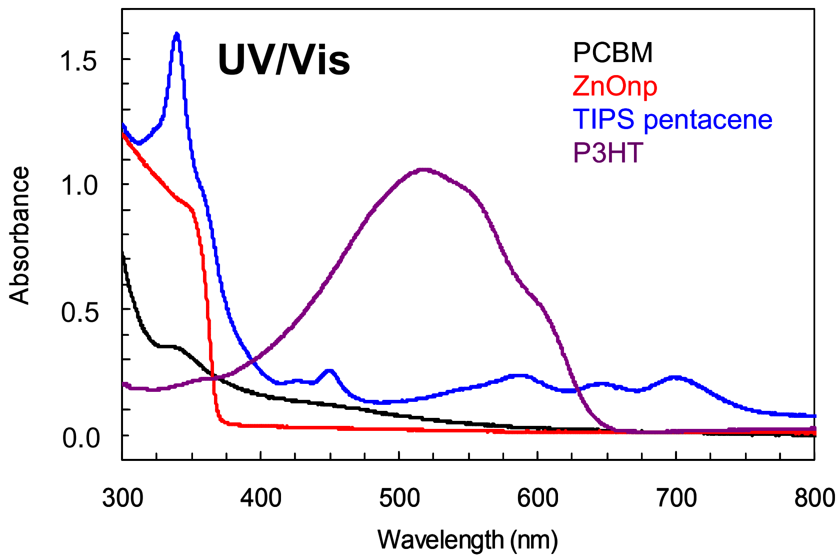
# Determination of Band Alignment for Organic and Hybrid Photovoltaic Materials

Typically UV Photoelectron Spectroscopy (UPS) in UHV or cyclic voltammetry are used to determine ionization potential

Neither of these techniques mimic the environment of thin films devices fabricated and tested under ambient conditions in the lab

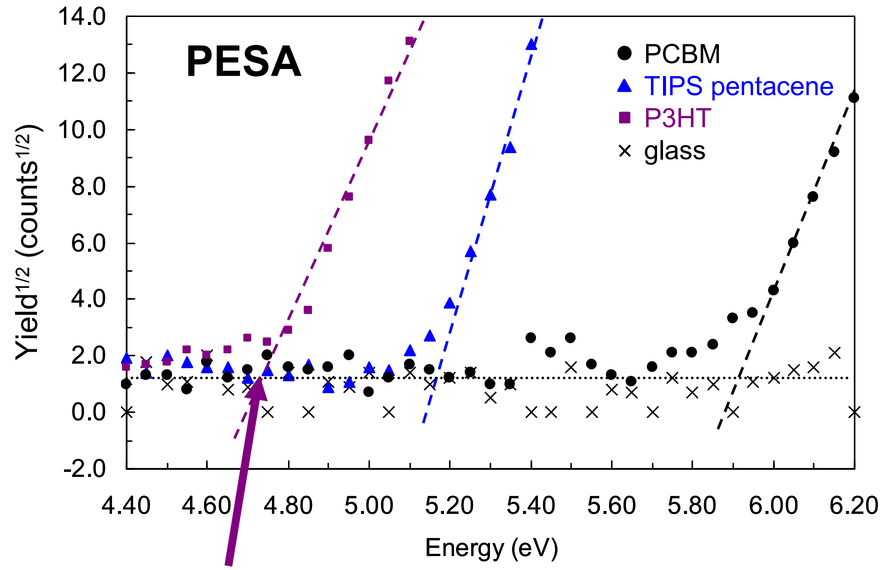



PCBM  ZnO  P3HT  TIPS pentacene




Optical band gap for these materials is determined using the absorption cut-off measured by UV/Vis

**Photoelectron Spectroscopy in Air (PESA)** allows for the determination of the ionization potential (IP) of semiconductors under ambient conditions




Intercept
P3HT IP = 4.7 eV

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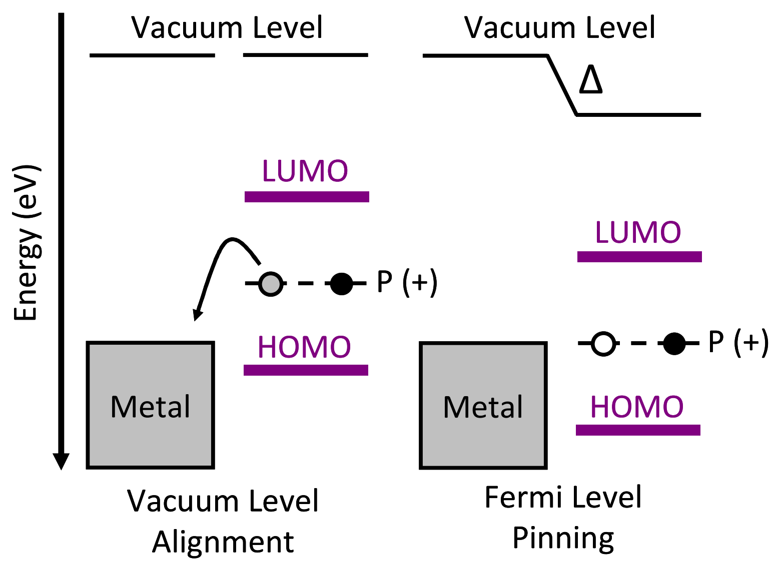
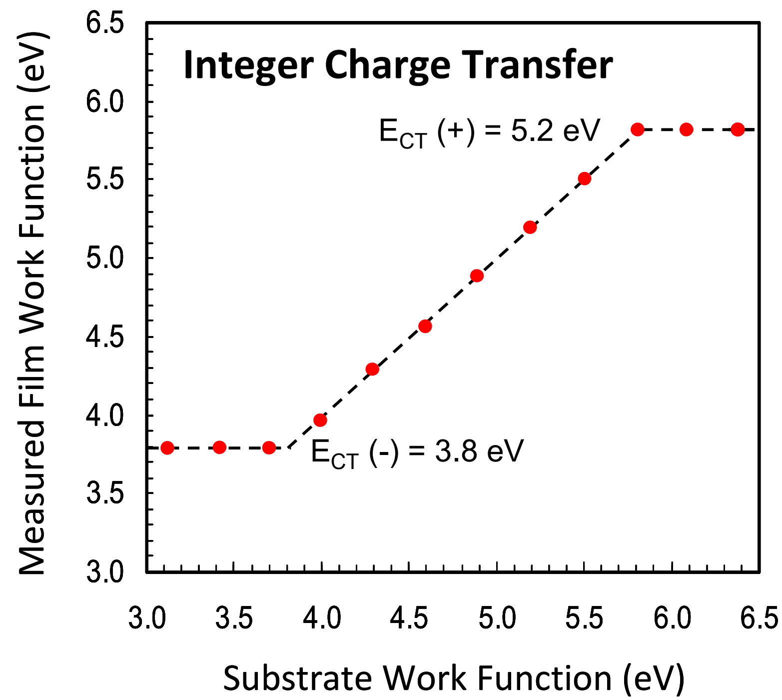
# Understanding Fermi Level Alignment at Interfaces in Solar Cells

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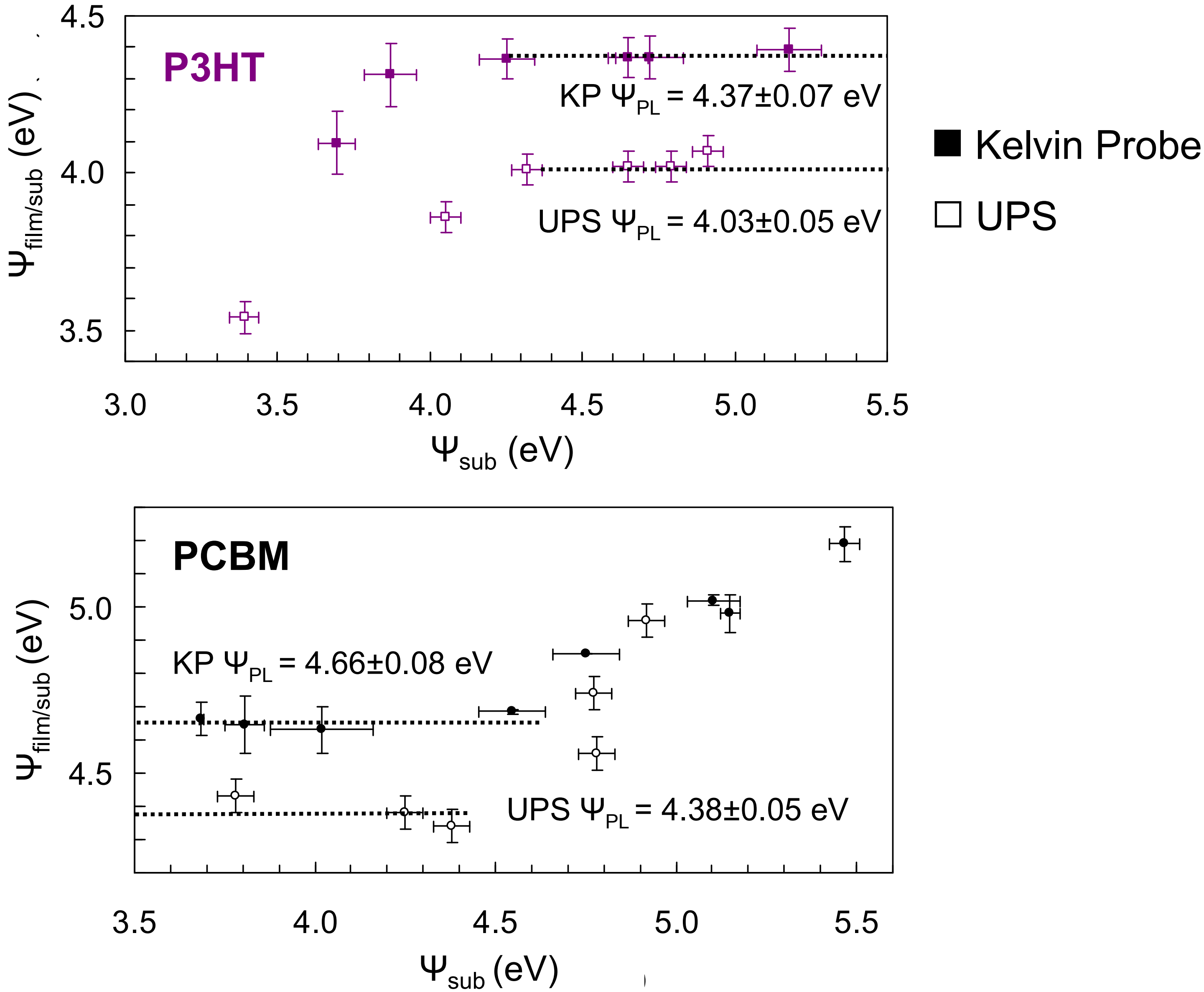
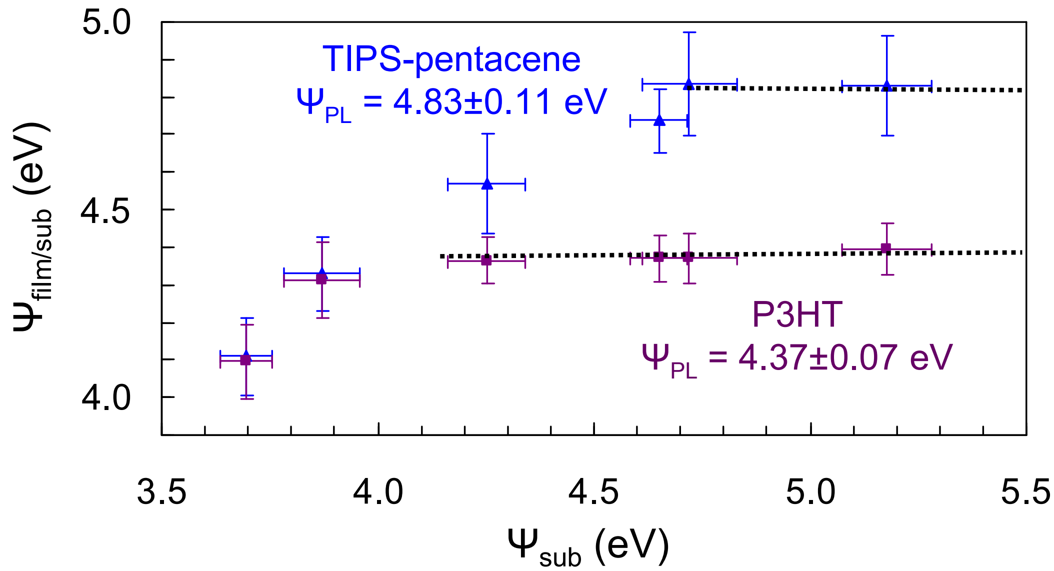
# Fermi level Alignment at Metal/Organic Interfaces Measured by UPS and Kelvin Probe

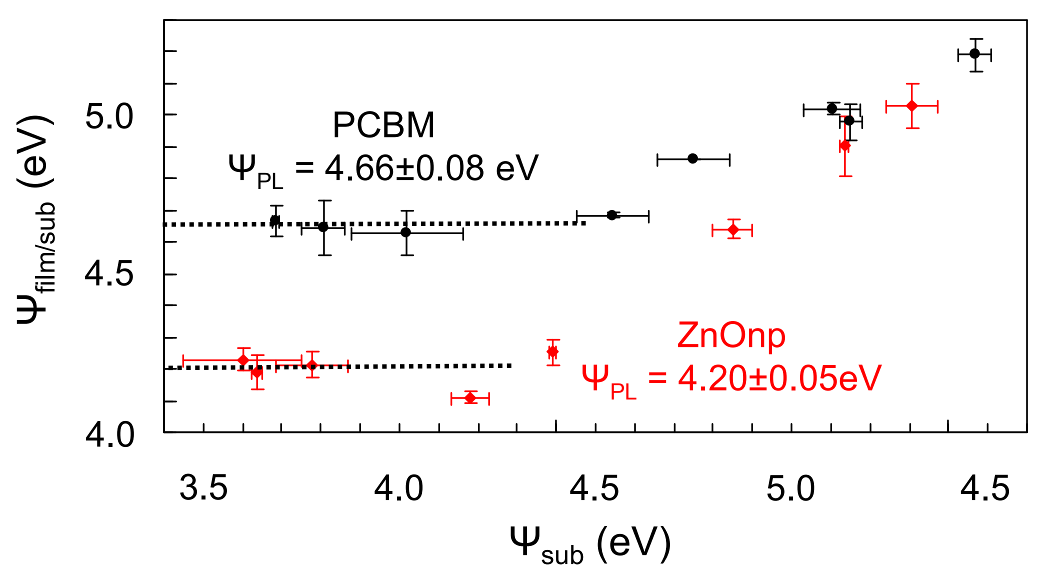


# Fermi level Alignment at Metal/Organic Interfaces Measured by Kelvin Probe

TIPS-pentacene and P3HT behave as electron donors, donating charge to high work function substrates




PCBM and ZnO behave as electron acceptors, accepting charge from low work function substrates

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# Critical Parameters for Construction of Device Band Diagram

| Film | HOMO (VB) (eV)[a] | $E_g$ (eV)[b] | LUMO (CB) (eV)[c] | Work Function (eV)[d] |
|---|---|---|---|---|
| P3HT | 4.65 ± 0.05 | 1.95 ± 0.05 | 2.70 ± 0.1 | 4.37 ± 0.07 |
| TIPS-pentacene | 5.20 ± 0.05 | 1.65 ± 0.05 | 3.55 ± 0.05 | 4.67 ± 0.13 |
| PCBM | 5.90 ± 0.05 | 2.20 ± 0.05 | 3.70 ± 0.05 | 4.66 ± 0.08 |
| ZnO nanoparticles | 7.3 ± 0.2 | 3.35 ± 0.05 | 4.0 ± 0.2 | 4.20 ± 0.05 |
| ITO | | | | 4.65 ± 0.06 |
| Ag | | | | 4.72 ± 0.11 |

[a] HOMO position determined by PESA, CB of ZnO determined by UPS
[b] Band gap determined by UV/Vis
[c] LUMO calculated from optical band gap and ionization potential
[d] Work function of thin films on appropriate substrate were measured by Kelvin probe

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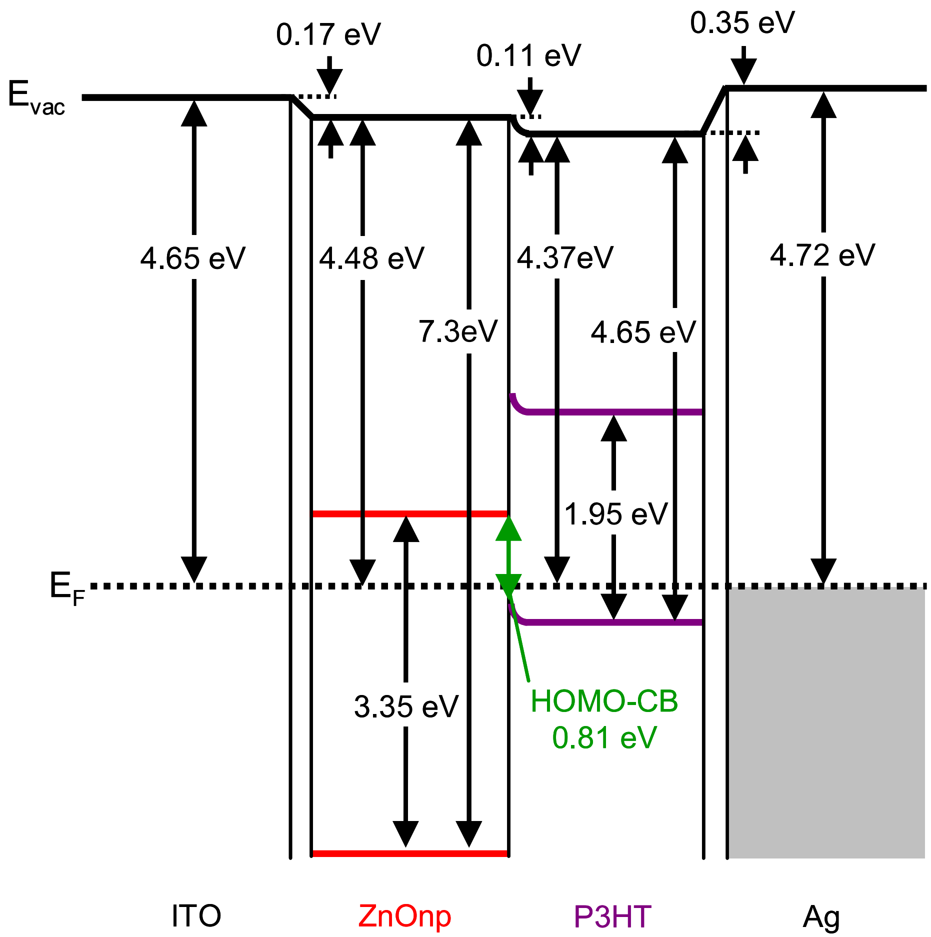
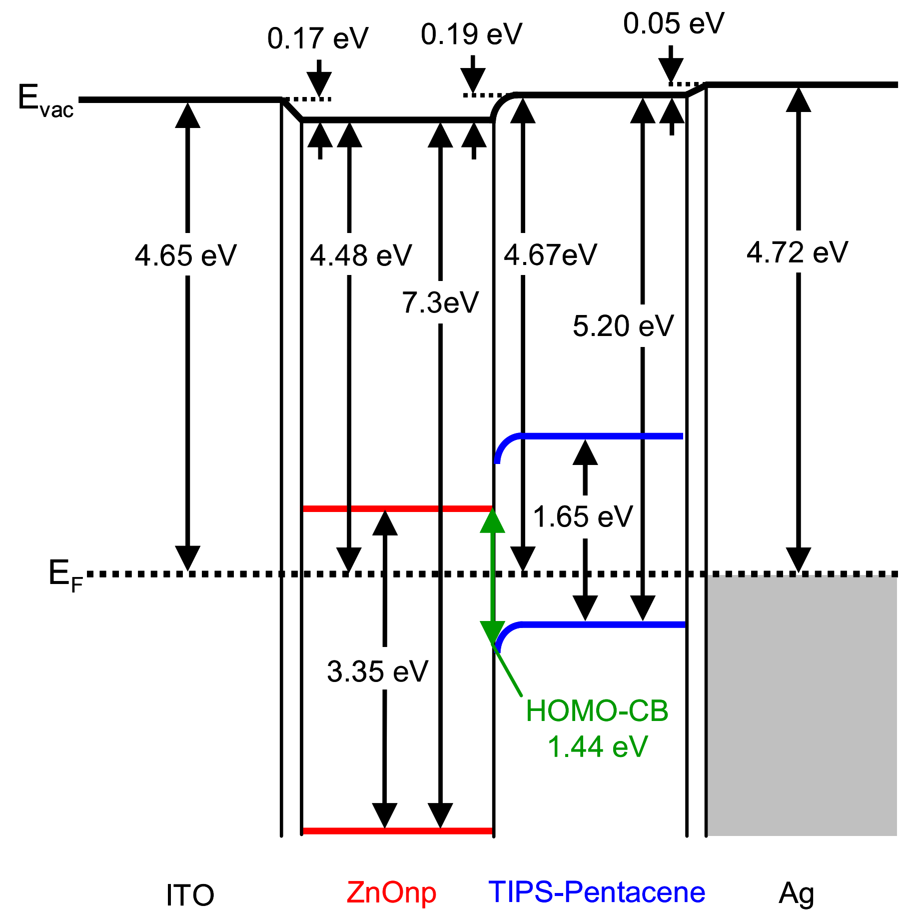
# Band Diagrams for P3HT and TIPS-Pentacene Hybrid Photovoltaics

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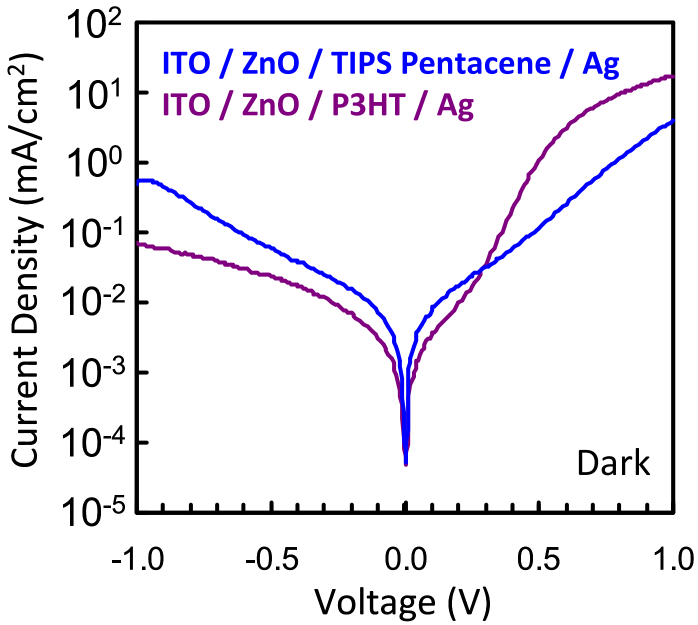
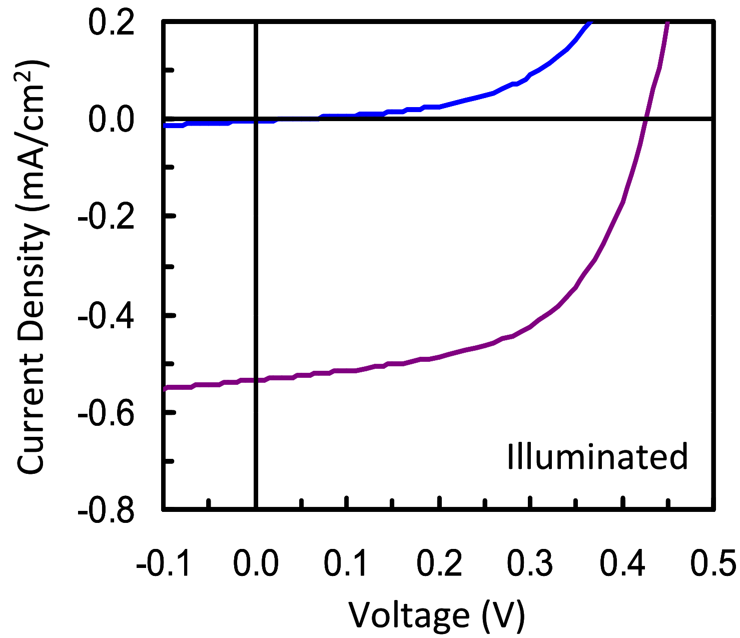
# Comparison of Hybrid Device Performance for P3HT and TIPS-Pentacene




| Sample | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm²) | FF (%) | $\eta$ (%) | Rs (Ωcm²) |
|---|---|---|---|---|---|
| ITO / ZnO / TIPS Pentacene / Ag | 47 | 0.00 | 24.5 | 0.00 | 21 |
| ITO / ZnO / P3HT / Ag | 427 | 0.54 | 55.8 | 0.13 | 20 |

Despite favorable band alignment, the TIPS-pentacene device shows no photovoltaic response

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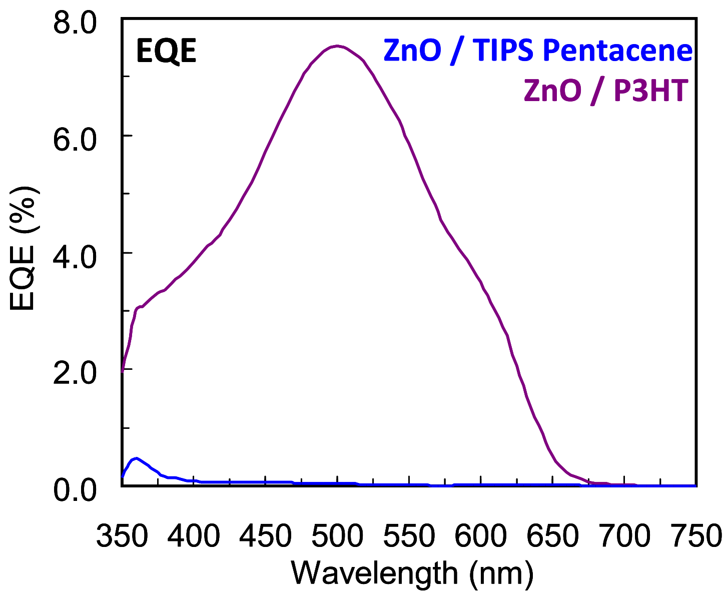
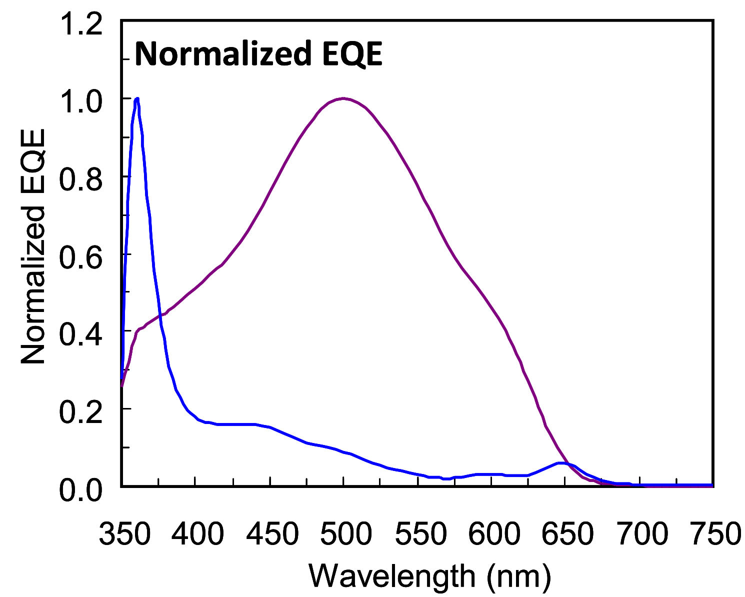
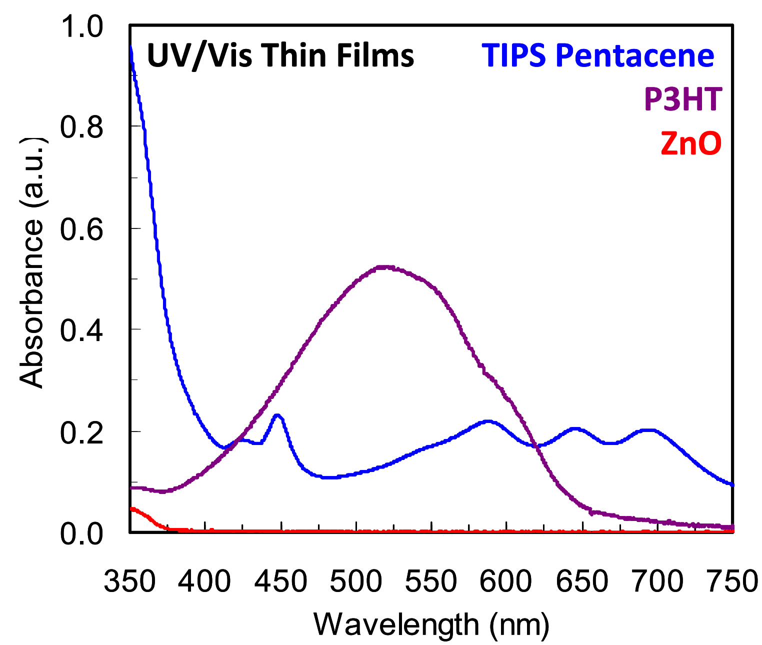
# Photocurrent Measurements for Hybrid Devices




External Quantum Efficiency (EQE) measurements of these devices show minimal current contribution from TIPS-pentacene absorption

Poor conversion rate from absorbed photons to electrons collected

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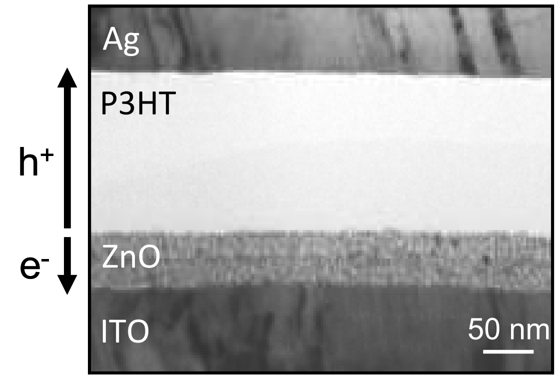
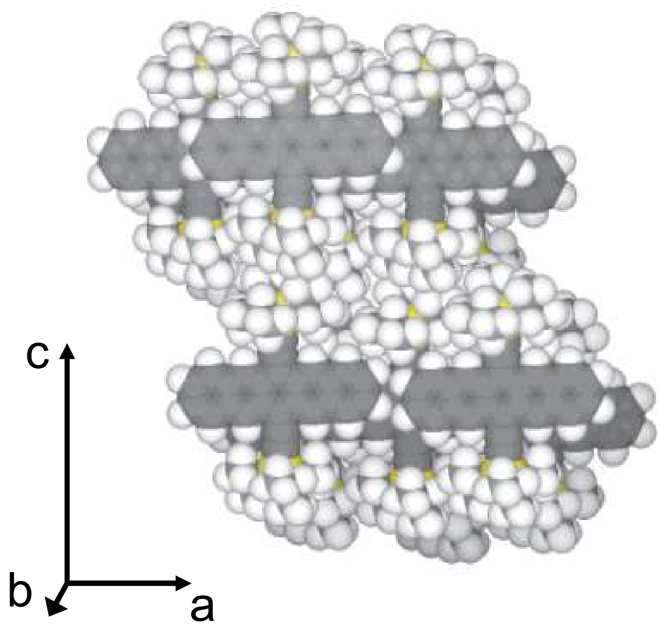
# Poor Vertical Charge Mobility in TIPS-Pentacene Thin Films

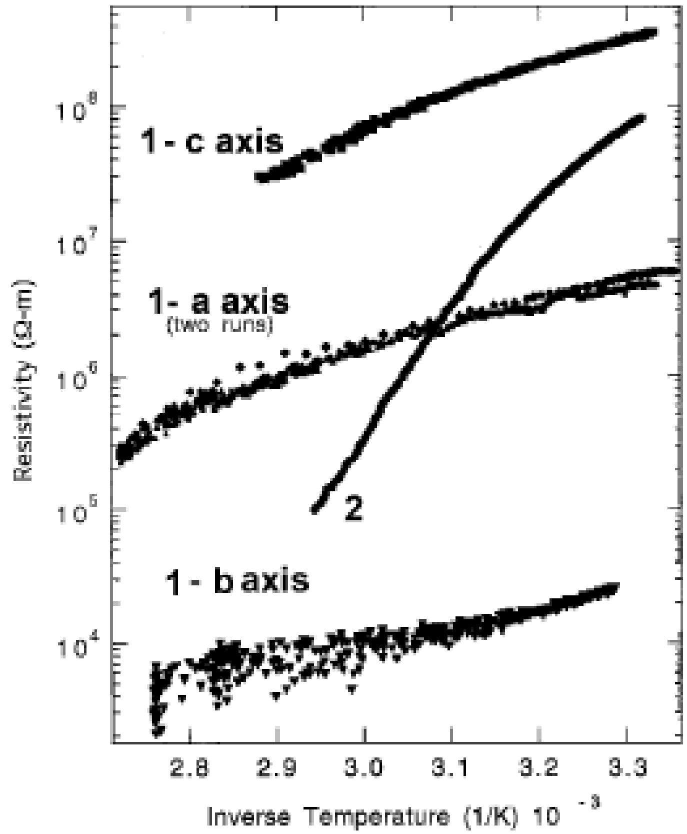
- Need good vertical charge transport in solar cells
- Films of TIPS-pentacene show higher resistivity in this direction
- Poor hole mobility in the TIPS-pentacene film may be limiting charge collection

ZnO/P3HT Planar Solar Cell



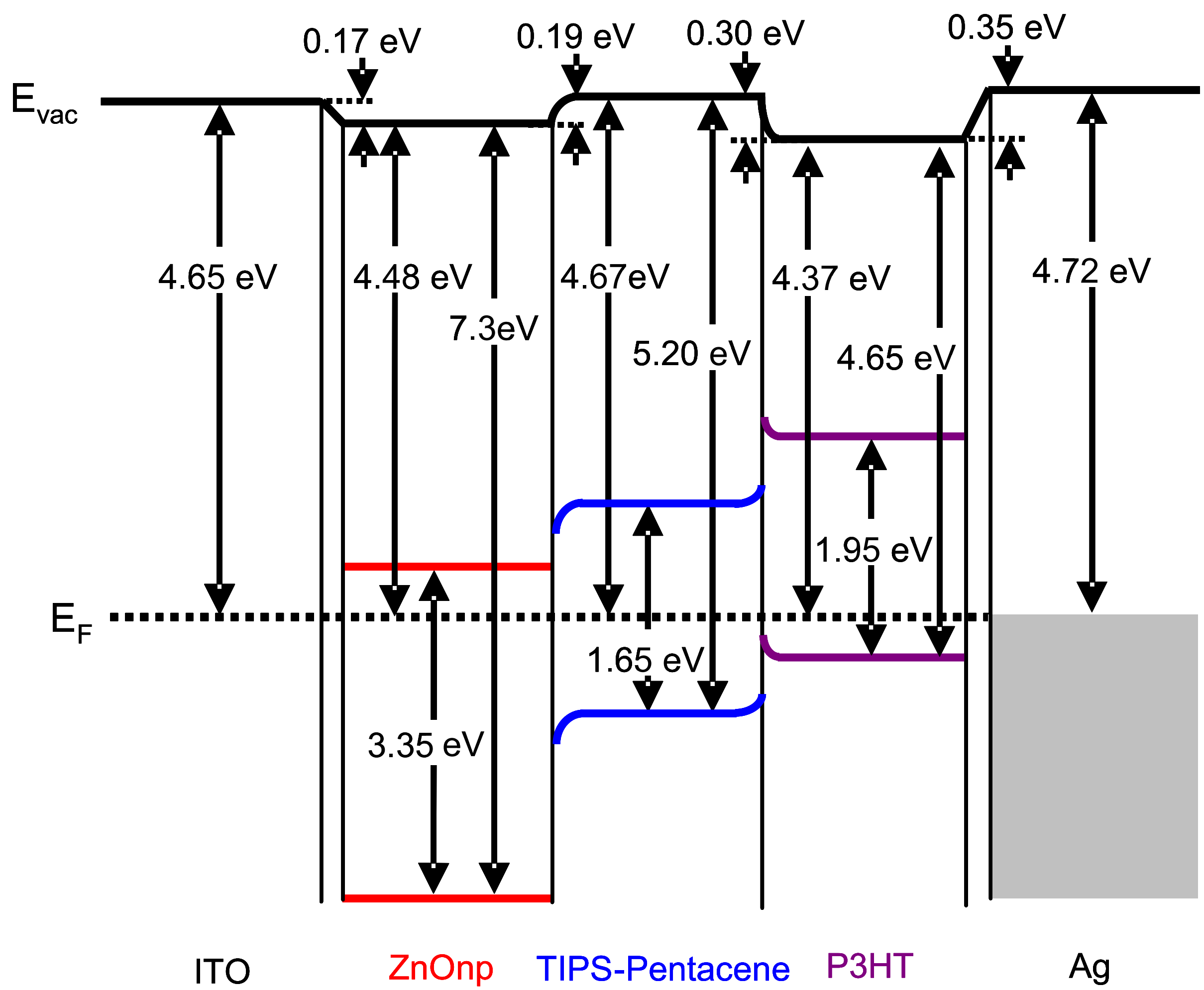

Solid-state ordering of TIPS-pentacene




Anthony et. al., *JACS*, **2001**, *123*, 9483.

# Addition of P3HT to the Electron Donor Layer to Aid in Hole Transport




**P3HT should be able to transport separated charge to the Ag electrode**

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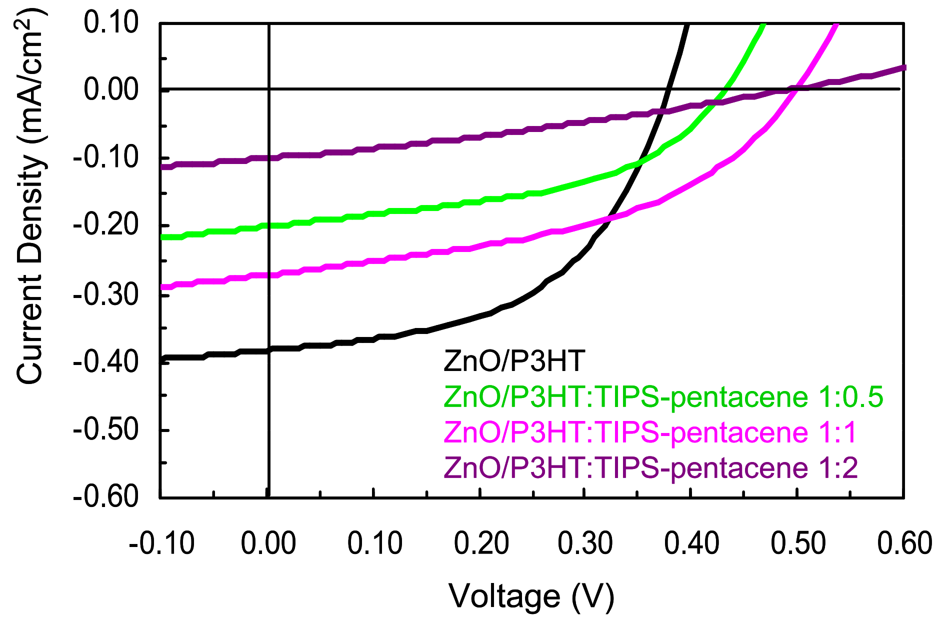
# Device Performance for Mixed P3HT:TIPS-Pentacene Hybrid Solar Cells

Addition of TIPS-pentacene film to P3HT films results in an increase in the $V_{OC}$ as predicted by the band diagrams

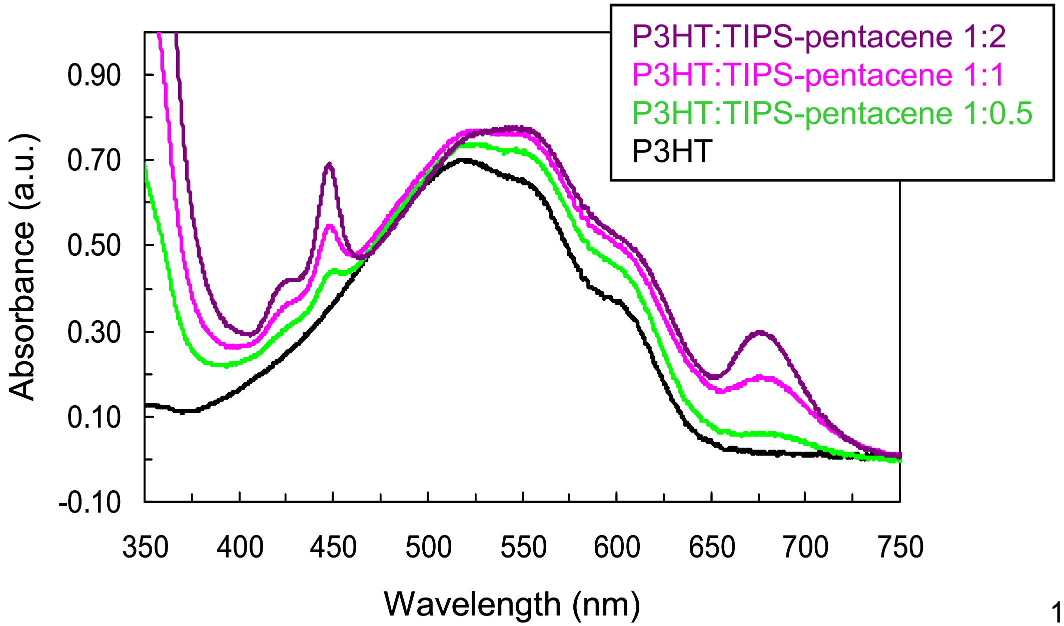
However, $J_{SC}$ suffers with increasing amounts of TIPS-pentacene, likely due to the lower mobility phase

These devices are not optimized



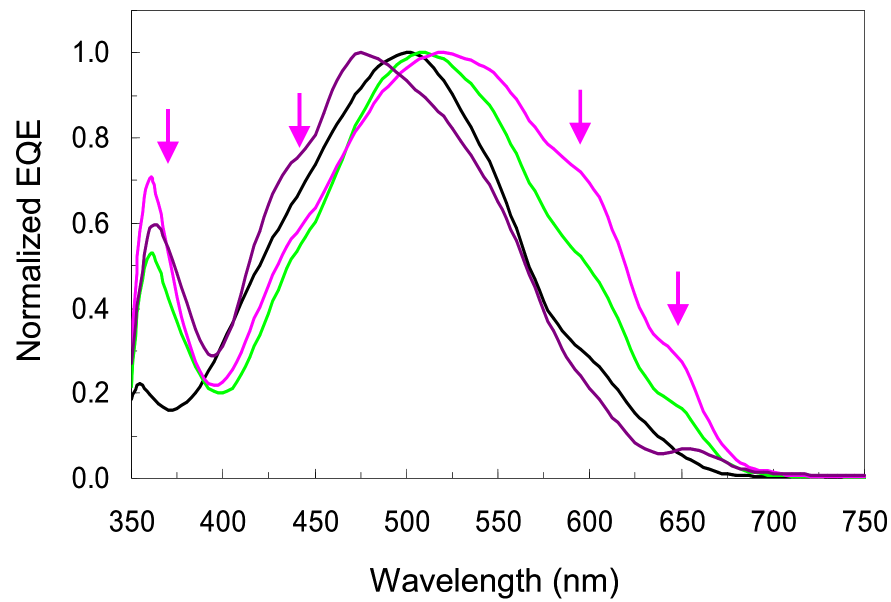

| Device | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) | $R_s$ ($\Omega$/cm$^2$) |
|---|---|---|---|---|---|
| ITO/ZnO/P3HT/Ag | 379 | 0.38 | 51.6 | 0.075 | 15 |
| ITO/ZnO/P3HT:TIPS-pentacene 1:0.5/Ag | 431 | 0.20 | 47.1 | 0.041 | 26 |
| ITO/ZnO/P3HT:TIPS-pentacene 1:1/Ag | 498 | 0.27 | 45.2 | 0.061 | 94 |
| ITO/ZnO/P3HT:TIPS-pentacene 1:2/Ag | 482 | 0.10 | 30.1 | 0.014 | 2318 |

# Photocurrent Measurement for Mixed P3HT:TIPS-Pentacene Hybrid Solar Cells




Combining TIPS-pentacene and P3HT broadens the absorption of the devices, allowing for capture of a greater proportion of the solar spectrum

EQE measurements show current contributions from absorption by both P3HT and TIPS-pentacene

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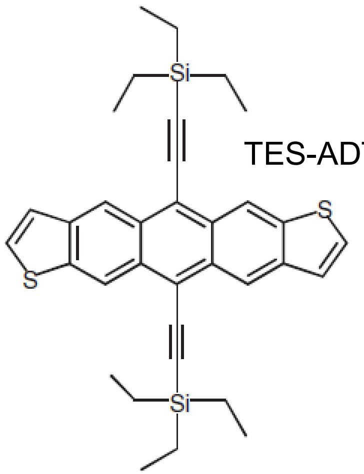
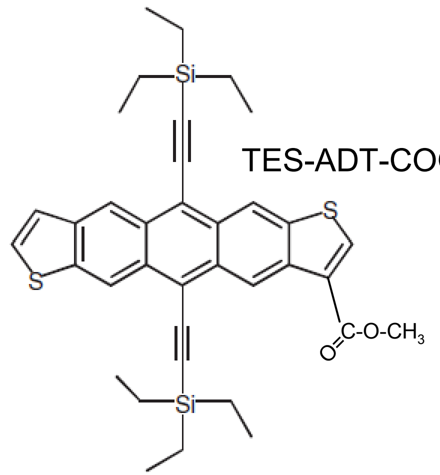
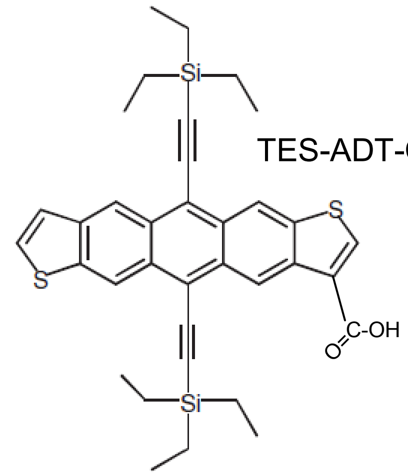
# New Pentacene Derivatives from John Anthony's Group



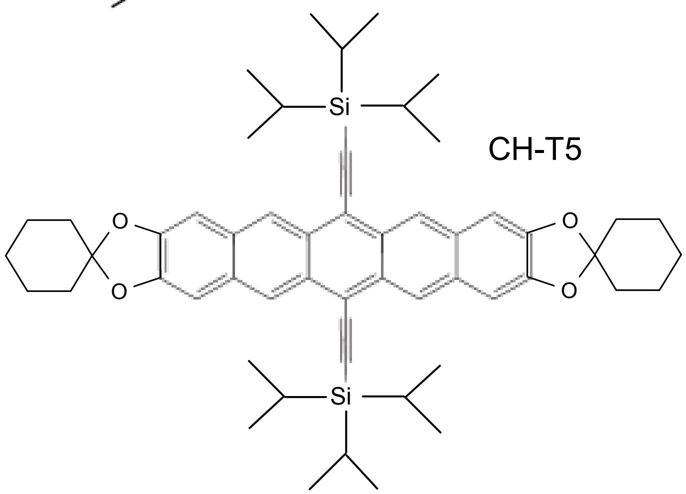
TES-ADT



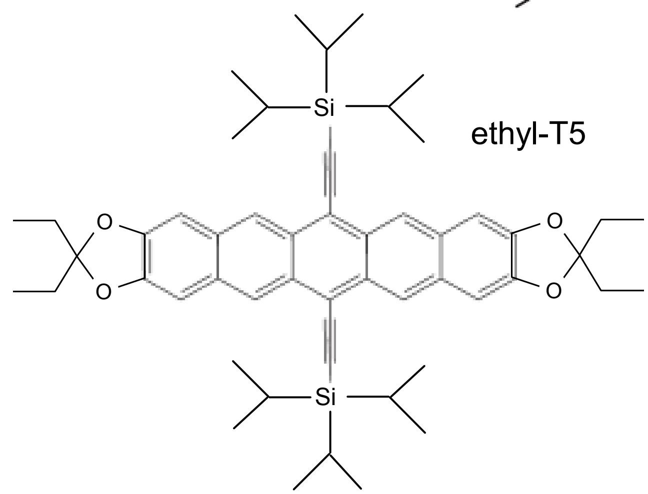
TES-ADT-$COOCH_3$



TES-ADT-COOH



CH-T5



ethyl-T5

Our collaborators are working on tuning electronic structure, absorption characteristics, and crystal packing structure to increase vertical charge mobility