The Current-Voltage Trade-Off in Organic Solar Cells and How to Get Around It

Mark Thompson

Department of Chemistry
University of Southern California
The trade-off between $V_{OC}$ and $J_{SC}$

$J_{SC}$ is related to the absorption profile, minimum energy is related to the HOMO-LUMO gap.

$V_{OC}$ is related to the energy difference between the hole and the electron, $\Delta E_{DA}$.

HOMO-LUMO gap is smaller: collect a larger fraction of solar spectrum, increase $J_{SC}$, BUT $V_{OC}$ will suffer.
Device Performance of subPC acceptors

ITO/CuPc (400Å)/Acceptor (250Å)/BCP (100Å)/Al (1000Å)

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta_p ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-SubPc</td>
<td>1.8</td>
<td>0.13</td>
<td>0.34</td>
<td>0.08</td>
</tr>
<tr>
<td>NO(_2)-SubPc</td>
<td>2.5</td>
<td>0.22</td>
<td>0.43</td>
<td>0.2</td>
</tr>
<tr>
<td>C(_{60})</td>
<td>3.6</td>
<td>0.45</td>
<td>0.54</td>
<td>0.9</td>
</tr>
<tr>
<td>Cl-SubPc</td>
<td>1.6</td>
<td>0.59</td>
<td>0.55</td>
<td>0.5</td>
</tr>
<tr>
<td>SubPc/C(_{60})</td>
<td>4.0</td>
<td>0.97</td>
<td>0.57</td>
<td>2.1</td>
</tr>
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\( \Delta E_{DA} \) (eV) \( V_{oc} \) (V)

<table>
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<th>D/A</th>
<th>( \Delta E_{DA} ) (eV)</th>
<th>( V_{oc} ) (V)</th>
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Motivation for using Pt(TPBP) in photovoltaics

- High absorption coefficient
- Long exciton lifetime: high $L_D$

**Thin Film Spectra (20 nm)**

- $\alpha_{\text{Pt}} = 5.9 \times 10^5$ cm$^{-1}$
- $\alpha_{\text{Pd}} = 6.0 \times 10^5$ cm$^{-1}$
- $\alpha_{\text{CuPc}} = 2.1 \times 10^5$ cm$^{-1}$

- High absorption coefficient
- Long exciton lifetime: high $L_D$

$L_D = \sqrt{D \tau}$
Short Exciton Diffusion Length Drives Device Design

• Very large $L_D$ for single crystals, but need amorphous films

• Common OPV structure and materials
  – Buffer or blocking layer is commonly used
  – Donor: Phthalocyanines/porphyrins, oligo and polythiophenes, acenes (tetracene and pentacene)
  – Acceptor: perylene derivatives, $C_{60}$ and derivatives
  – Most have relatively short exciton diffusion lengths, and short measured exciton lifetimes

• Most OPV materials have high ISC efficiencies
  – CuPC: 0.55, $C_{60}$: > 0.9, acenes: > 0.9
  – Triplet excitons may be the active species in OPV

\[ L_D = \sqrt{D\tau} \]

<table>
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<th>Cpd.</th>
<th>$L_D$ (Å)</th>
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<tbody>
<tr>
<td>CuPC</td>
<td>150</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>400</td>
</tr>
<tr>
<td>tetracene</td>
<td>700</td>
</tr>
<tr>
<td>PPV</td>
<td>120</td>
</tr>
<tr>
<td>P3HT</td>
<td>70</td>
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Singlet vs. Triplet Exciton

1. \( D + h\nu \rightarrow D^* S_1/T_1 \)  
   absorption + ISC

2. \( D^* + D \rightarrow D + D^* \)  
   exciton migration

3. \( D^* + A \rightarrow [D^+A^-] \)  
   charge transfer

4. \( [D^+A^-] \rightarrow D^+ + A^- \)  
   charge separation

5. \( D^+ + A^- \rightarrow \text{current} \)  
   conduction
Motivation for using Pt(TPBP) in photovoltaics

Exciton energies
\( S_1 = 1.9 \text{ eV} \)
\( T_1 = 1.6 \text{ eV} \)

Driving force for exciton separation:
\( S_1 = 0.5 \text{ eV}, T_1 = 0.2 \text{ eV} \)

Net: \( \text{Por}^* + \text{C}_{60} \rightarrow \text{Por}^+ + \text{C}_{60}^- \)
## Pt(TPBP) OPV performance

![Graph showing J(V) relationship for Pt(TPBP) and CuPc](image)

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<tr>
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<th>Voc (V)</th>
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<th>η (%)</th>
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**QE%**

![Absorbance spectrum for Pt(TPBP) and C₆₀](image)

**Wavelength (nm)**

- 400
- 500
- 600
- 700

**Absorbance (a.u.)**

- Abs., PtTPBP
- Abs., C₆₀
Exciton diffusion length limitation

- **PtTPBP** is a good hole conductor
  - FF is not significantly affected by the thickness
- **Optimal thickness** = 150 Å
  - Measured exciton diffusion length = 57 Å
Exiton trapping in PtTPBP films

- Film of PtTPBP emits from an excimer or aggregate
  - OLED = doped film: no excimer present
  - Thin film exciton trapped 0.34 eV below molecular exciton, disordered solid may lead to deeper traps
  - Exciton/aggregate lifetimes are short

**Plots**

- Crystalline Pt(tBu)$_8$TPBP
- PL $\lambda_{\text{max}} = 754$ nm
  - $\tau = 18$ µsec
  - $\tau(77K) = 68$ µsec
  - $L_D = 30$ nm

M.D. Perez, et. al., Adv. Mat., 2009
Pt(TPBP) OPV performance

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**Kinetic Control of $V_{OC}$**

At $V_{OC}$ the photocurrent is cancelled out by the injected current: steady state

\[ D^* + A \xrightarrow{k_{ct}} D^+ + A^- \quad \text{Light} \]

\[ D^+ + A^- \xrightarrow{k_{rec}} D + A \quad \text{Dark} \]

\[ \Delta E_{DA}^\text{limit} = V_{OC} \]

**Diagram:**
- Light and dark states represented by red and black circles.
- $V_{OC}$ as the boundary between light and dark.
- Photocurrent graph showing increase in current with voltage.
Pt(TPBP) OPV performance


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$J_S \Rightarrow$ recombination rate

$300$ mV

$J_S$ (µA/cm²)
Chemical annealing of porphyrin films

Film A + Vapor B → Film AB

py
pyCN
dmap
pyz
triazine
Himi
Meimi
Phimi
UV vis spectra of 150Å ZnTPP film treated with ligands

• Film treated with ligand vapor only
• Reaction complete in mins.
• Film composition: ZnTPP:Ligand = 1:1
  – Based on NMR spectra of dissolved thin films
• Not clear isosbestic behavior
• Peak sharpening - film reorganization

Thin film structure – XRD measurement

ZnTPP film
ZnTPP•pz film
ZnTPP•pyz
Single crystal

ZnTPP•triazine film
ZnTPP•triazine film (1,-1,3)

Single crystal

Grazing Incidence XRD – relative orientation

• Orientation of the molecules is parallel to the substrate!
• Intensity spread for the (1,-1,3) as a function of polar angle $\chi$ shows that the crystallites are $+/- \ 8.2^\circ$ to the surface

ZnTPP-pz, 50 nm

Device performance

- High leakage, low $V_{OC}$
- Crystalline $\Rightarrow$ high conductivity
  - High conductivity = high FF
AFM images of 100Å films on glass substrates

ZnTPP
Section analysis

ZnTPP•pyz
Section analysis

ZnTPP•triazine
Section analysis

Aggregates are formed on chemical annealing

Device performance

- Using NPD to prevent leakage
  - Recovers $\frac{1}{2}$ of the $V_{OC}$
  - NPD $\lambda_{\text{max}} < 400$ nm
- Structure at the D/A interface affects rate of recombination
Kinetic Control of $V_{OC}$

At $V_{OC}$ the photocurrent is cancelled out by the injected current: steady state

\[ D^* + A \xrightarrow{k_{ct}} D^+ + A^- \quad \text{Light} \]

\[ D^+ + A^- \xrightarrow{k_{rec}} D + A \quad \text{Dark} \]

\[ \begin{array}{c}
D^* + A \\
\text{Light}
\end{array} \]

\[ \begin{array}{c}
D^+ + A^- \\
\text{Dark}
\end{array} \]

\[ V_{OC} \]

\[ h^+ \]

\[ \text{DONOR} \]

\[ \text{ACCEPTOR} \]

\[ V_{OC} \text{ upper} = \Delta E_{DA} \text{ limit} \]

\[ \text{Photocurrent} \]

\[ \text{Current, a.u.} \]

\[ \begin{array}{c}
-15 \\
-10 \\
0 \\
10 \\
15
\end{array} \]

\[ \begin{array}{c}
-0.5 \\
0.0 \\
0.5 \\
1.0 \\
1.5
\end{array} \]

\[ \text{Voltage, V} \]
Electron transfer rates for Pentacene/C$_{60}$

- Rates of forward and back electron transfer depend on orientation
- Parallel orientation gives rise to a high recombination rate

Dashed, solid = CT: pent/C$_{60}$ $\rightarrow$ pent$^+$/C$_{60}$

Dotted = Recom.: pent$^+$/C$_{60}$ $\rightarrow$ pent/C$_{60}$

CT state energy correlates with $V_{oc}$

Plot courtesy of Koen Vandewal
Device performance

- High recombination rate ⇒ high dark current ⇒ low $V_{OC}$
- Amorphous interface is better than the wrong one
• Using thicker amorphous ZnTPP to recover most of $V_{OC}$, improve FF/$J_{SC}$

Device performance

- Using thicker amorphous ZnTPP to recover most of $V_{OC}$, improve FF/$J_{SC}$

Achieving the “ideal” morphology

- MoO$_3$, 8 nm
- ITO, 150 nm
- DPSQ, 16 nm
- C$_{60}$, 40 nm
- PTCBI, 8 nm
- Ag, 100 nm

• DPSQ: $\alpha \sim 10^5$ cm$^{-1}$

• Solvent vapor annealing (SVA): film exposed to a saturated solvent vapor (CH$_2$Cl$_2$): improves molecular diffusivity (and formation of nanoXstals)

• Annealing done before and after C$_{60}$ deposition.
Morphological control through Solvent Vapor Annealing

• Device performance not monotonically related to crystallinity.
• DPSQ crystallization in post-C$_{60}$ evident from absorption spectrum, but not XRD.
• Crystallized DPSQ templates C$_{60}$.
• Improved bulk crystallinity $\uparrow L_D$.
• Highly crystalline interfaces $\uparrow k_{PPr}$.
Solvent Vapor Annealing pre- & post-C$_{60}$ deposition

- SVA in DCM pre-C$_{60}$:
  - 0.12 V $\downarrow$ in $V_{OC}$.
  - $EQE \uparrow$ DPSQ $\rightarrow$ improved exciton transport.
  - $EQE \downarrow$ for C$_{60}$

- SVA post-C$_{60}$:
  - DPSQ $EQE \uparrow$ by 80%, $J_{SC} \uparrow$ by 25%.
  - No loss in $V_{OC}$ $\rightarrow$ interface is the same

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<td>74</td>
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<td>6.0</td>
<td>0.84</td>
<td>71</td>
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Solvent Vapor Annealing pre- & post-\(C_{60}\) deposition

- **SVA in DCM pre-\(C_{60}\):**
  - 0.12 V ↓in \(V_{oc}\).
  - \(EQE\) ↑DPSQ ➞ improved exciton transport.
  - \(EQE\) ↓for \(C_{60}\)

- **SVA post-\(C_{60}\):**
  - DPSQ \(EQE\) ↑by 80%, \(J_{sc}\) ↑by 25%.
  - No loss in \(V_{oc}\) ➞ interface is the same

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**$V_{OC}$ summary**

- The structure at the D/A interface influences $V_{OC}$
  - Sterics can increase spacing and thus $V_{OC}$
  - Ordering can be good or bad
  - Chemical annealing ZnTPP orders to the wrong structure
  - Disordered is better than the wrong order

- Can we increase $J_{SC}$ without altering $V_{OC}$?
  - Doping as seen yesterday, broaden absorbance below $E_g$
  - Singlet fission
Singlet fission routes around the Shockley-Queisser limit

- Incomplete absorption and thermolysis to band gap energy limit $\eta < 31\%$
Singlet fission routes around the Shockley-Queisser limit

- Incomplete absorption and thermolysis to band gap energy limit $\eta < 31\%$
- Singlet Fission solution: 45%
- You MUST absorb ALL photons
- Efficient Singlet Fission materials are largely limited to crystalline/polycrystalline materials

Theoretical efficiency > 45%!
Singlet Fission Materials

• Several materials systems have $\Phi_{\text{SF}} = 200\%$ (triplet yield)
• High efficiencies only observed for crystalline materials
• Tetracene
• Pentacene
• Diphenyl-benzofuran
• Carotenoids
Absorption/Emission of Acenes

DPT 1000 Å

Tetracene 1000 Å

Absorbance [Norm]

400 450 500 550 600 650
Wavelength [nm]

450 500 550 600 650 700 750
Wavelength [nm]

Amorphous thin film by X-ray and e·diffraction
Transient Absorption Spectroscopy

\[ \Delta \text{Abs} = \text{Abs}_{\text{ON}} - \text{Abs}_{\text{OFF}} \]
Singlet Fission in DPT

\[ S_n \leftrightarrow S_1 \]

**DPT**

**CHCl_3 Solution**

- 0.75 ps
- 10 ps
- 100 ps
- 400 ps
- 850 ps

**S_0**

**S_1**

**T_1**

Singlet Fission in amorphous DPT films

\[ Q_T = 122\% \]

- \( \tau_{\text{fast}} = 1.3 \text{ ps} \)
- \( \tau_{\text{slow}} = 105 \text{ ps} \)

Crystalline Tetracene: \( \tau_{\text{SF}} = 40-80 \text{ ps} \)

DPT Crystal Structure

3.68 Å Pair

4.00 Å Pair

4.00 Å Pair

3.68 Å Pair
NAQMD: Kinetic Monte Carlo Simulations

- Utilize Surface Hopping for State Transitions
- Wavefunctions from TD-DFT
- Fermi’s Golden Rule for Transition Probabilities
- 5000 individual trajectories

Simulations suggest 3.9% of molecules give 91% of fission events!
Simulations suggest 3.9% of molecules give 91% of fission events!
Singlet fission routes around the Shockley-Queisser limit

- Incomplete absorption and thermolysis to band gap energy limit $\eta < 31\%$
  

- You MUST absorb ALL photons

Theoretical efficiency $> 45\%$

Red Dye to Fill the SF Gap

Materials studied as co-deposited films

Spectra in THF solution

DPT

PtTPBP

PtTPBP phosphorescence

Wavelength (nm)

Absorbance (arb. units)

Emission (arb. units)

DPT

PtTPBP

S

T

DPT S

T

PtTPBP

S

T

DPT Triplet

Red Dye to Fill the SF Gap

Materials studied as co-deposited films

Spectra in THF solution

DPT

PtTPBP

PtTPBP phosphorescence

Wavelength (nm)

Absorbance (arb. units)

Emission (arb. units)
Sensitizing to the red in SF materials

S$^1$,Pt(TPBP)$\rightarrow$T$^1$,Pt(TPBP): 85% Efficient
S$^1$,DPT$\rightarrow$T$^1$,DPT: 80% Efficient
Singlet fission: 61%

τ$_{SS}$ = 4.6 ps
τ$_{ISC}$ = 400 fs
τ$_{TT}$ = 35 ps

Singlet Fission 1 + 105 ps
S$^1$ + S$^0$ $\rightarrow$ 2 T$^1$
< 50% SF comes from prompt

Need to eliminate delayed SF to make this structure work.

Combining SF with mid-band absorption

- Problems:
  - We did not shut off $S_{11} \to S_{12}$.
  - Low doping level for PtTPBP
- Spatially separating the SF material from all singlet traps will eliminate transfer (layered rather than mixed structure)
Singlet Fission Conclusions

- Singlet fission can be observed for both crystalline and amorphous materials
  - DPT shows SF in both thin films and NP
- SF takes place at specific dimer sites
  - Prompt and diffusive SF
- What is the preferred dimer structure?? Is efficient “unimolecular” singlet fission possible? Can we create systems with only prompt SF?
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CAMP

Center for Advanced Molecular Photovoltaics

King Abdullah University of Science and Technology
Solar Cell Efficiency

Cell Efficiency \( \eta_p \) = \( \frac{P_{\text{max}}}{P_o} \)

\( P_o \)
(1 sun, AM1.5)
Solar Cell Efficiency

\[ P_0 \text{ (1 sun, AM1.5)} \]

\[ P_{max} = V_m J_m \]

\[ \eta_p = \frac{P_{max}}{P_o} = \frac{J_{sc} \times V_{oc} \times FF}{P_o} \]
Solar Cell Efficiency

\[
P_0 \quad (1 \text{ sun, AM1.5})
\]

\[
\text{Accepted Donor}
\]

\[
\text{Current Density (mA/cm}^2\text{)}
\]

\[
\text{Applied Test Voltage (V)}
\]

\[
\text{Power Density (mW/cm}^2\text{)}
\]

\[
P_{max} = J_{sc} V_{oc} FF
\]

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\eta_p = \frac{P_{max}}{P_o} = \frac{J_{sc} \times V_{oc} \times FF}{P_o}
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