



Recent progress in organic solar cells: From a lab curiosity to a serious photovoltaic technology

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EASAC Workshop, Stockholm, 19.-20. September 2013



Acknowledgments



- Chris Elschner
- Christian Körner
- Wolfgang Tress
- Martin Hermenau
- Toni Müller
- Moritz Riede



Martin Pfeiffer Christian Uhrich Karsten Walzer



Peter Bäuerle Roland Fitzner Egon Reinold



- Christian May
- Stefan Mogck
- Tomas Wanski
- Claudia Lehmann
- Konrad Crämer



🗾 Fraunhofer



Motivation? Not needed...









- Large area & flexible substrates possible
- Large variety of carbon-based materials
- Low cost: approx. 1g/m² active material





Progression of Organic Products





4th wave: Organic electronics



2nd wave: OLED lighting











Potential of Organic Photovoltaics





- Flexible plastic substrates and thin organic layers
 - Low material and energy consumption
 - Short energy payback time
- Potentially transparent, color adjustable
- Compatible with low-cost large-area production technologies



NREL record chart



Best Research-Cell Efficiencies









- Often heard opinions about organic PV:
 - "Whatever efficiency, if OPV is cheap enough, it will be competitive....
 - "Five years lifetime is OK, we can exchange the modules"
- We need high efficiency (>15%), long lifetime (>20yrs) and low cost (<<50C/Wp)
- Main arguments for higher efficiency:
 - Electricity generation cost
 - Energy payback time
 - Limited areas available







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Kalowekamo&Baker, Solar Energy 83, 1224 (2009)

Available online at www.sciencedirect.com



Solar Energy 83 (2009) 1224-1231



www.elsevier.com/locate/solener

Estimating the manufacturing cost of purely organic solar cells Joseph Kalowekamo¹, Erin Baker*

In this paper we estimate the manufacturing cost of purely organic solar cells. We find a very large range since the technology is still very young. We estimate that the manufacturing cost for purely organic solar cells will range between \$50 and $140/m^2$. Under the assumption of 5% efficiency, this leads to a module cost of between \$1.00 and \$2.83/W_p. Under the assumption of a 5-year lifetime, this leads to a levelized cost of electricity (LEC) of between 49¢ and 85¢/kWh. In order to achieve a more competitive COE of about 7¢/kWh, we would need to increase efficiency to 15% and lifetime to between 15–20 years.

... In order to achieve a more competitive cost of electricity...we would need to increase efficiency to 15% and lifetime to between 15–20 years....





Cost calculations have large degree of uncertainty

Materials cost alone are significant

Cost Component	OSC			
	Type used	Cost estimate (\$/m ²)		
		Low	High	
Semiconductor	C ₆₀ , CuPc & SnPc	3.30	5.00	
Electrical contacts and interconnects	Aluminum, silver paint	3.40	5.00	
Substrate ^a	Flexible Plastic, ITO	7.90	13.68	
Protective cover	Flexible encapsulant	2.90	4.40	
Sealant	Surlyn	2.90	4.40	
Packaging material	_	2.00	3.00	
Specialty chemicals	4 TBP	1.00	2.00	
Other (absorbing dye; catalyst; electrolyte	N/A	N/A	N/A	
Total	(23.40	37.48	

Kalowekamo&Baker, Solar Energy 83, 1224 (2009)





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Total		23.40	37.48	

Kalowekamo&Baker, Solar Energy 83, 1224 (2009)





- Energy payback time:
- Organics clearly ahead
- Payback times <1 year possible with organics
- Go for high-efficiency !



A. Anctil et al., Progr. in Photovoltaics 2012, DOI: 10.1002/pip.2226



Outline



Motivation

Basics of organic solar cells

- Materials requirements for organic solar cells
- Exploring the thiophene zoo
- Tandem organic cells
- Lifetime&Manufacturing







Polymer/small-molecule heterojunction

Dye-sensitized solar cell





Hybrid organic-inorganic



Anders Hagfeldt Today 14:20







Solution Processing

Polymers&small molecules



- Layers made by e.g. printing
- High production speeds
 possible
- Room temperature process

Rene Janssen, today 13:20

Vacuum Sublimation

Only small molecules



- Layers made by sublimation of material in vacuum
- Easy access to multi-layer systems
- High material purity



Elementary processes in organic solar cells













Exciton diffusion length $L_{D} = (10 \pm 1) \text{ nm}$

 Exciton diffusion lengths are rather small: ≈ 10 nm

 Much higher values have been reported for materials with higher order

• Possible workaround: use triplet diffusion: so far not successful





- Absorption leads to tightly bound (0.2 ... 0.5 eV) excitons
- Separation in electric field inefficient
- Usual solar cell structure does not work

S. E. Gledhill et al. J. Mat Res. 20, 3167 (2005) P. Würfel, CHIMIA 61, 770 (2007)





Flat heterojunction (FHJ)

bulk heterojunction (BHJ)



donor

acceptor

Energy loss is unavoidable!

C. W. Tang, Appl. Phys. Lett. 48, 183 (1986)
M. Hiramoto et al., Appl. Phys. Lett. 58, 1062 (1991)
J. J. Hall et al., Nature 376, 498 (1995)
G. Yu et al. Science 270, 1789 (1995)







e.g. donor

Which factors are promoting CT separation?







- Open circuit voltage is determined by quasi-Fermi level splitting
- Related to ${\rm E}_{\rm \scriptscriptstyle CT}$
- Ultimate limit not known

- K. Vandewal et al., Nat. Mater. 8, 904 (2009)
- K. Vandewal et al., Advanced Functional Materials 22, 3480–3490 (2012)
- D. Veldman et al., Advanced Functional Materials 19, 1939 (2009)



High-efficiency polymer cells





Table 1 | Best device performance/parameters from PTB7:PC₇₁BM solar cells with conventional and inverted device structures, measured under 1,000 W m⁻² AM 1.5G illumination.

Device type	PCE (%)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	$V_{\rm oc}$ (V)
Conventional	8.24	15.4	70.6	0.759
Inverted	9.15	17.2	72.0	0.740
Inverted, tested by CPVT	9.214	17.46	69.99	0.754

Z. He et al., Nature Photonics **6**, 591 (2012)







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- Donor and acceptor must form network with high and balanced mobilities in both phases
- Domain sizes must be adjusted to guarantee exciton separation and charge carrier transport
- Typically, mobilities of about 10⁻³ cm²/Vs are needed

M. Mandoc et al., Appl. Phys. Lett. 90, 133504 (2007); Y.-X. Wang et al., Appl. Phys. Lett. 93, 133501 (2008), J.-T. Shieh et al., J. Appl. Phys. 107, 084503 (2010); A. Wagenpfahl et al., IEEE J. Sel. Top. Quantum Electron. 16, 1759 (2010); T. Kirchartz et al., Phys. Rev. B 80, 035334 (2009)





- Multi-scale approach needed for materials development
- Connection between molecular structure and device performance very complex







- Drift-diffusion model set up by Wolfgang Tress
- Bulk Heterojunction between two contacts
- Different recombination models studied



Direct (bimolecular) recombination





Direct recombination, without Langevin mechanism

app



W. Tress et al., Phys. Rev. B 85, 155201 (2012)



Direct recombination, with Langevin mechanism





W. Tress et al., Phys. Rev. B 85, 155201 (2012)





- Benzoporphyrins: Y. Matsuo et al., J. Am. Chem. Soc. 131, 16048 (2009)
- Squaraines: F. Silvestri et al, J. Am. Chem. Soc. 130, 17640 (2008); G. Wei et al., ACS Nano 4, 1927 (2010)

- Merocyanines: N. Kronenberg et al., J. Photon. Energy 1, 011101 (2010)
- Bodipys: T. Rousseau et al., Chem. Comm. 1673 (2009), R. Gresser et al., Tetrahedron 67, 7148 (2011)
- Thiophenes: K. Schulze et al., Adv. Mat. 18, 2872 (2006); E. Ripaud et al., Adv. En. Mat. 1, 540 (2011), Y. Sun et al., Nature Mat. 11, 44 (2012), Z. Li et al., Adv. En. Mat. 2, 74 (2012), J. Zhou et al., JACS 134, 16345 (2012)















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University of Ulm Department Organic Chemistry II









NC-

DCVnT-Bu: Schüppel et al., PRB 77, 085311 (2008)



Influence of side chains on energy levels





- Only weak effects of side chains in solution
- Stronger effects in thin films







en circuit voltage	Charge carrier separation efficiency fill factor FF saturation factor j _(-1V) /j _{sc}
V _{oc} = 1.13 V ↑	FF = 27.6% $j_{(-1V)}/j_{sc} = 1.32$
$V_{oc} = 1.00 V$	FF = 50.4% $j_{(-1V)}/j_{sc} = 1.10$
$V_{oc} = 0.93 V$	FF = 49.7% $j_{(-1V)}/j_{sc} = 1.15$
decreases	increases

with **increasing** chain length

ITO / Au(1) / pTNATA(30) / pNPD(10,4:1) / NPD(5) / DCVnT (8) / C₆₀ (40) / Bphen(6) / Al(100)

Minimum exciton separation loss is approx. 0.3eV









University of Ulm Department Organic Chemistry II

R. Fitzner et al., JACS 134, 11064 (2012)





- 4 molecules/unit cell
- Very close π - π stacking of 3.28Å



Singe crystals from gradient sublimation X-Ray analysis: M. Weil, Vienna


Dependence of Ordering on Substrate Temperature





Figure 4. GIXRD patterns of (a) 50 nm films of neat 1-3 deposited on glass substrates at room temperature and (b) 75 nm $1-3:C_{60}$ (2:1 v/v) blend layers fabricated by coevaporation on glass substrates at 90 °C, with the pattern for pristine C_{60} shown for comparison.



The p-i-n Concept for Organic Solar Cells





B. Maennig *et al.*, Appl. Phys. A 79, 1 (2004)M. Riede *et al.*, Nanotechnology 19, 424001 (2008)











GIWAXS single layers glass / DCV5Ts (30 nm)





GIWAXS blends glass / DCV5Ts : C60 (30 nm, 2:1)

TECHNISCHE





D33 (top): best OSC @80°C, crystallization @110°C D15 (bottom): best OSC @≈110°C (?), crystallization @140°C































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- Shockley-Queisser limit for single junction: 31%
- Major gains only for
 - Tandem junction: 42%
 - Triple junction: 49%
- Lower currents/higher voltages reduce electrical losses





Efficiency Outlook for Tandem Cells







Pin-tandem cells: doped layers are critical for optical optimization



P-i-n tandem cells:



- Pn-junction is ideal recombination contact
- optimizing interference pattern with conductive transparent layers

=>optical engineering
on nanometer layer
thickness scale

J. Drechsel et al., Appl.Phys.Lett. 86, 244102 (2005)



Pin-tandem cells: placing absorbers in different field maxima





Thickness of spacer layer:



74nm (1st min)

124nm (2nd max)

R. Schüppel et al., J. Appl. Phys. 107, 044503 (2010)



Pin-tandem cells: placing absorbers in different field maxima



R. Schüppel et al., J. Appl. Phys. 107, 044503 (2010)





 Stacking two D/A heterojunctions

 → reverse HJ
 → voltage loss

- Our Approach:
 - highly doped layers for energy level alignment at the interface
 - no quasi-Fermi level splitting
 - no loss of $V_{\rm oc}$



R. Timmreck et al., J. Appl. Phys. 108, 033108 (2010)





- Organic pin-diodes used to study the recombination contact
- Systematic study on the reverse behavior depending on:
 - i-layer thickness
 - dopant concentration



thickness

H.Kleemann et al., Nanoletters 10, 4929, 2010.
 H.Kleemann et al., Org. Electron. 14, 193, 2013.
 H.Kleemann et al., J. Appl. Phys. 111, 123722, 2012.



The physics of recombination contacts: Zener tunneling

Current density (mA/cm²)



- Organic Homo-diode (lr(piq)₃)[1,3]
- i-layer thickness from 1....12nm
- Reversible reverse breakdown obtained
- Breakdown controllable by i-layer thickness
- no effect on forward IV curve

H.Kleemann et al., Nanoletters 10, 4929, 2010.
 H.Kleemann et al., J. Appl. Phys. 111, 123722, 2012.







- Strong exponential thickness vs. current relation
- Reverse current also controllable by doping in the p- and n-layer
- Thermal activation of current
 - 30meV in reverse
 - 170meV in forward
- Field and temperature dependence prove tunneling process

[1] H.Kleemann et al., Nanoletters 10, 4929, 2010.[3] H.Kleemann et al., J. Appl. Phys. 111, 123722, 2012.



TECHNISCHE UNIVERSITÄT DRESDEN Theoretical description of recombination contacts





- Modeling of the i-layer by a linear electronic ladder with N blocks and two energy levels for each block
- Slope of the ladder deduced from the built-in potential determined by impedance analysis

[1] H.Kleemann et al., Nanoletters 10, 4929, 2010.[2] H.Kleemann et al., Org. Electron. 14, 193, 2013.



Theoretical description of recombination contacts





- Breakdown can be better described using coherent transport (incoherent transport might be dominant on larger scales)
- Tunneling between HOMO and LUMO of nearest neighbors if levels are nearly aligned





- Combination of thiophene and phthalocyanine
- Absorption bands only reasonably separated



M. Riede et al., Adv. Funct. Mat. 21, 3019 (2011)





- Tandem is simply two stacked pin cells
- Optics controlled by transparent spacer layers











- Voltage almost perfectly doubled
- Significant loss in current
- Fill factor for tandem higher: 74%



	$V_{\rm oc}$	j _{sc}	FF	mismatch	Intensity	η
	[V]	[mA cm ⁻²]	[%]	[1	mW cm ⁻²]	%
F4-ZnPc-device	0.66	8.3	64	0.99	100	3.9
DCV6T-device	0.88	8.3	66	1.08	111	4.3
Tandem 60nm	1.53	3.2	74	_	98*	3.6*
Tandem 165nm	1.52	5.0	71	_	98*	5.6*



EQE of DCV6T:F4-ZnPc tandem cells



- Tandem system has significant overlap of absorption
- EQE spectra are nevertheless well separated
- EQE low due to thin absorber layers





V_{oc} I_{sc} FF η



Leerlaufspannung:	
Kurzschlussstrom:	
Füllfaktor:	
Wirkungsgrad:	

=	(1.6930	±	0.0085) V (
=	(9.08	±	0.23) mA
=	(68.27	±	0.68) %
=	(9.75	±	0.30)%

9.7 % on 1.1cm² certified by Fraunhofer ISE, Germany







Small-Molecule OPV Record > 1cm²



12 % Efficiency - new world Record for OPV

Measured by SGS at standard test conditions (December 2012)









9% Module Efficiency on Glass Record efficiencies thanks to minimum upscaling losses





7 Cells in Series	Active Area 122 cm ²	Total Area 142 cm²
VOC	11.8 V	11.8 V
VOC per cell	1.67 V	1.67 V
JSC mA/cm²	1.21	1.04
FF	63 %	63 %
Efficiency	9.0 %	7.7 %

Latest news: 9.8% on active area of 122 cm² module



Development of OPV Efficiencies



diagram available under www.orgworld.de





- Standard measurement: 1 sun, 25 °C, perpendicular incidence
- Reality: 40-60 °C, often less than 1 sun, diffuse light
- Organics:
 - Positive temperature coefficient
 - Higher efficiency for lower intensity
 - Special diffuse light responsivity
- Sums up in the O-Factor: up to 30% better harvesting!





Positive temperature coefficient



Heliatek OPV: Efficiency has broad maximum between 30°C and 60°C

Say hello to solar. Wherever you are

c-Si and CIGS:

15 % lower efficiency at 60 °C

• µc-Si/a-Si:

10 % lower efficiency at 60 °C

3



Top Real Life Performance: Superior low-light performance







Measurement by SGS Fresenius

April 2012





- DCV6T:F4-ZnPc tandem cell
- Cells follow Lambertian behavior
- Result follow optical simulation



M. Riede et al., Adv. Funct. Mat. 21, 3019 (2011)







High independence on incident

angle:

- Efficiency development from 0 to 60° above the expected values of pure geometrical consideration
- Heliatek Absorber
- Certified Efficiency: 8.3 % (1 cm²)
- Collaboration of Heliatek und IAPP (TU Dresden)






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- Water and oxygen induced degradation of small molecule organic solar cells, M. Hermenau, M. Riede, K. Leo, S. Gevorgyan, F. Krebs, and K. Norrman, Solar Energy Materials & Solar Cells 95, 1268-1277 (2011)
- Total charge amount as indicator for the degradation of small molecule organic solar cells, M. Hermenau, S. Scholz, K. Leo, and M. Riede, Solar Energy Materials & Solar Cells 95, 1278-1283 (2011)









M. Hermenau et al., Solar EnergyMaterials&SolarCells 95, 1278 (2011)



• Degradation is directly proportional to photocurrent



M. Hermenau et al., Solar EnergyMaterials&SolarCells 95, 1278 (2011)





- ZnPc/C60 bulk heterojunction as model system
- Isotope techniques used to study oxygen and water diffusion
- Comparison of wet oxygen, dry oxygen, and dry nitrogen
- Analysis with TOF-SIMS and XPS

M. Hermenau et al. Solar En. Mat. & Solar Cells 95, 1268 (2011)





- Mainly current and FF degrade; V_{oc} is rather stable
- Water is much more relevant than oxygen
 - Water leads to oxidation of AI electrode
 - Water induced ZnPc degradation



M. Hermenau et al. Solar En. Mat. & Solar Cells **95**, 1268 (2011)





- State-of-the art Tandem device
- Collaboration between Heliatek & IAPP
- Absorber materials from BASF and Heliatek, dopants from Novaled
- Glass-glass encapsulation
- Halogen light at about
 1.5 suns









- Pin structures
- Glass-glass encapsulated
- Measured unter 2 suns



(Roughly) extrapolated lifetime: 37 years!



Christiane Falkenberg, PhD thesis, TU Dresden





• IEC standard damp heat test



Heliatek reliability lab measurement of BDR-based stack, 80 cm² active area

- Heliatek's foil-encapsulated solar films withstand lifetime tests well above industry standard PV limits
- Graph shows degradation of power generation after damp-heat stress (85°C, 85% RH) below 3%
- Based on commercially available barrier foils
- Heliatek propriety encapsulation and sealing process





Heliatek Roll coater





Roll-to-Roll Vacuum Coater









WHITE PIN OLED



Transparent OLED on Polymer web







- OPV has made major progress in the last few years
- Nanostructures and morphology control are key factors
- Tandem cells should allow lab efficiencies up to 20%
- Organic solar cells show superior harvesting properties
- Long lifetimes >20 years seem possible
- Low cost roll-to-roll processing demonstrated





- S. Reineke, S. Hofmann, S. Pfützner, H. Ziehlke, C. Körner, T. Menke, T. Müller, L. Burtone, D. Ray, C. Elschner, J. Meiss, M. Furno, C. Sachse, L. Müller-Meskamp, M.K. Riede, B. Lüssem, J. Widmer, M. Hummert, M. Gather (IAPP), T. Fritz
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- J. Amelung, M. Eritt (Ledon)
- D. Gronarz (OES)
- R. Fitzner, E. Brier, E. Reinold, A. Mishra, P. Bäuerle (Ulm)
- D. Alloway, P.A. Lee, N. Armstrong (Tucson)
- U. Zokhavets, H. Hoppe, G. Gobsch (Ilmenau)
- K. Schmidt-Zojer (Graz), J.-L. Bredas (Atlanta)
- R. Coehoorn, P. Bobbert (Eindhoven)
- T. Fritz (Jena)
- M. Felicetti, O. Gelsen (Sensient)
- A. Hinsch, A. Gombert (ISE)
- D. Wöhrle (Bremen), J. Salbeck (Kassel), H. Hartmann (Merseburg/Dresden)
- C.J. Bloom, M. K. Elliott (CSU)
- P. Erk (BASF) and others from OPEG
- BMBF, SMWA, SMWK, DFG, EC, FCI, NEDO





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