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17 - 21 October 2011

Polymer-based organic solar cells: Tuning of active layer nanomorphology and enhancement of photovoltaic performance using alkoxy side groups

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Polymer-Based Organic Solar Cells: Tuning of Active Layer Nanomorphology and Enhancemenmt of Photovoltaic Performance using Alkoxy Side Groups

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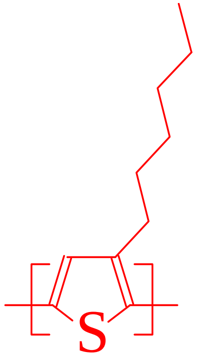
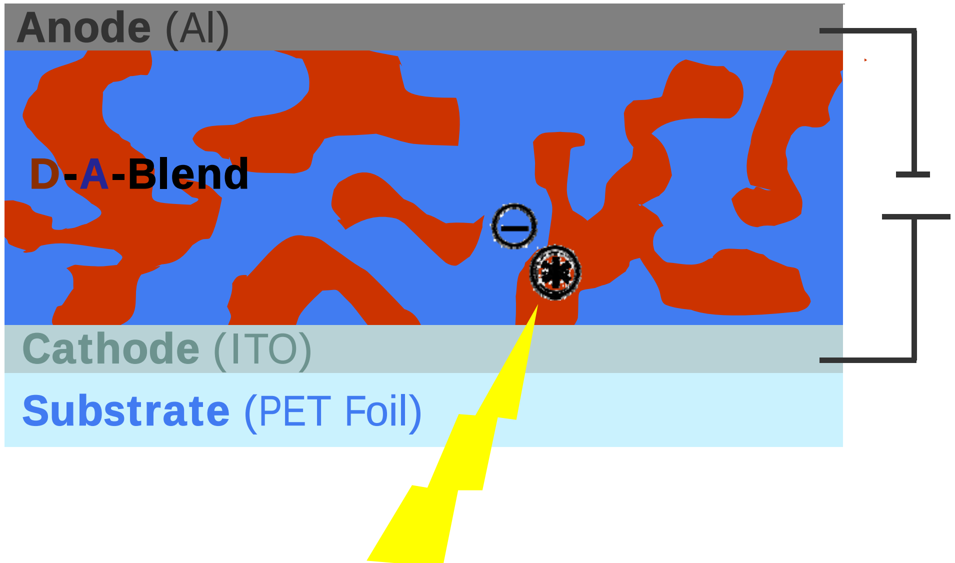
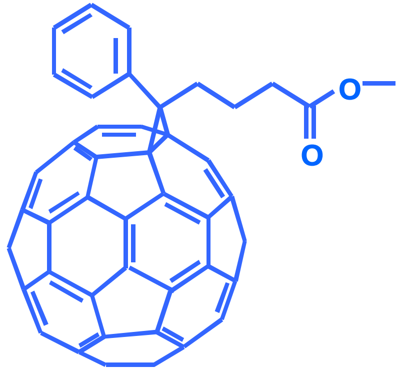
Trieste_20.10.2011

Working Principle





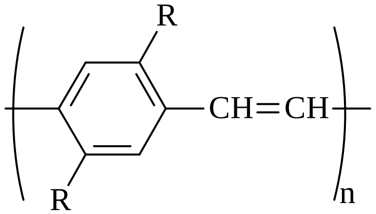


P3HT —excitation→ **P3HT*** → **$P3HT^{+}$**

P3HT* ↓ electron transfer

PCBM(0) → **PCBM(-I)**

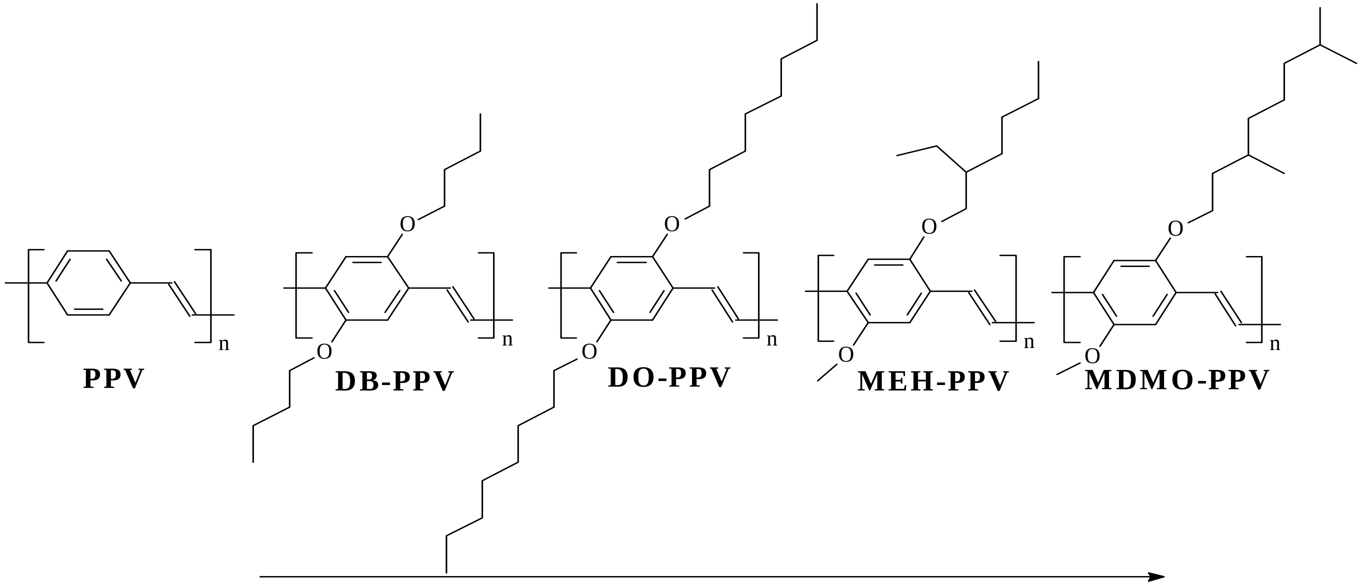
PCBM:[6,6]-phenyl-C_{61}-butyric acid methyl ester



I: R = H (gelb)
II: R = CH_3 (gelb)
III: R = CH_3O (rot)

insoluble

H.-H. Hörhold et al. *Makromol. Chem.* **1970**, *131*, 105.

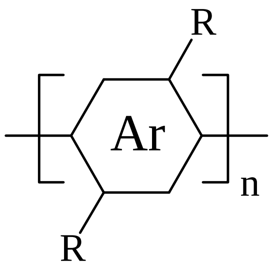


increase of solubility in common organic solvents

F. Wudl et al. *ACS Symp. Ser.* **1991**, *455*, 683

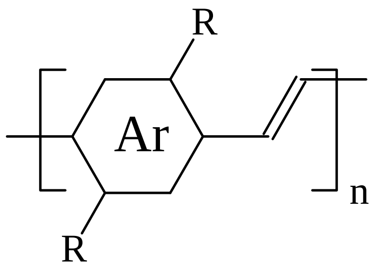
PPV in **OLED**: Burroughes, J. H. *et al. Nature* **1990**,*347*,539
PPV in **OPV**: Sariciftci, N. S. *et al. Science* **1992**, *258*, 1474.

Egbe et *al. J. Mater. Chem*. **2011**, *21*, 1338-1349



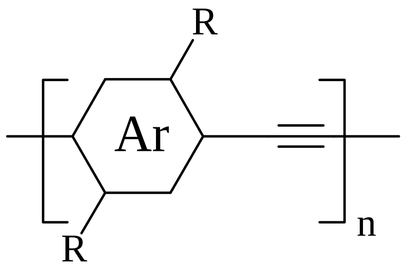
poly(arylene)s

PAs



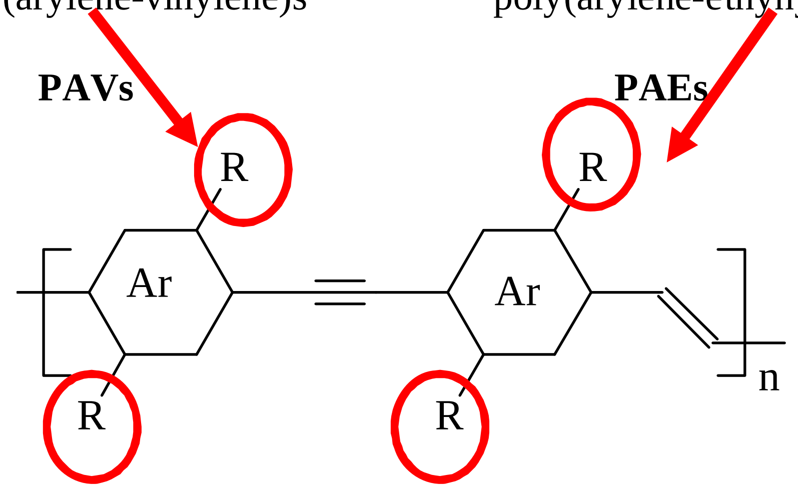
poly(arylene-vinylene)s

PAVs



poly(arylene-ethynylene)s

PAEs

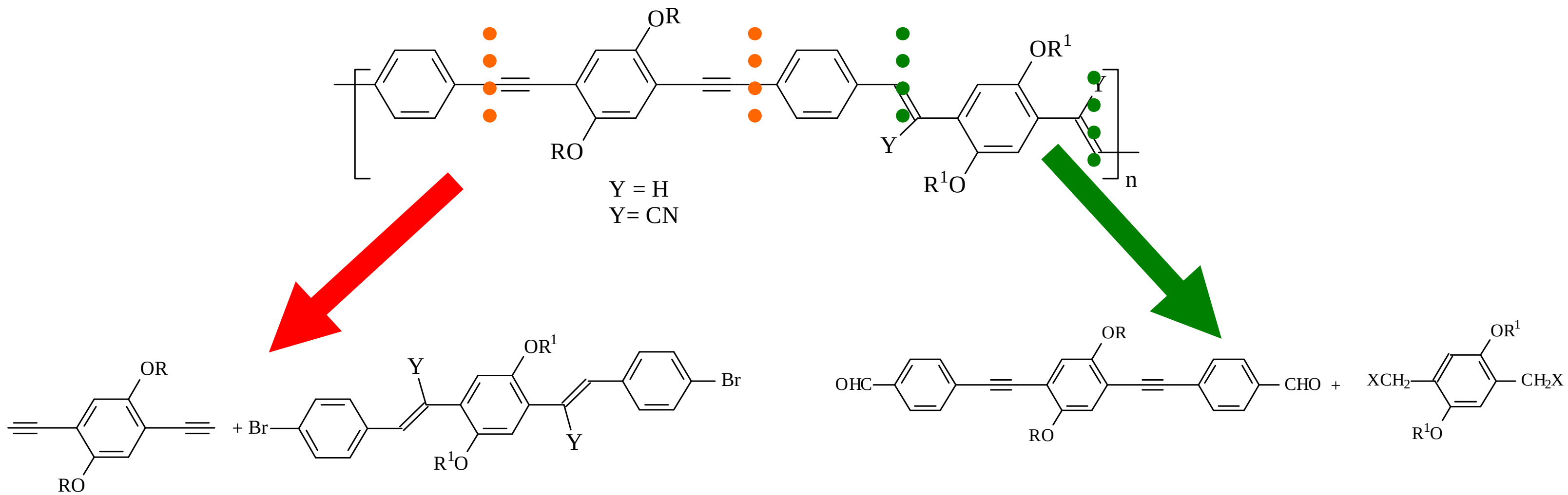


Poly(arylene-ethynylene)-*alt*-poly(arylene-vinylene)s

PAE-PAVs

Prog. Polym. Sci. 2009, *34*, 1023–1067

Retrosynthetic Approach



Sonogashira Reaction

Drawbacks:

- *Longer reaction time.*
- *Lower molecular weights.*
- *1 to 3% diyne defect structures.*
- *Difficulty to remove the catalyst from the end polymeric product.*

Advantage:

- *Polydispersity always around 2*

X =PO(OEt)$_2$ Horner-Wadsworth-Emmons Reaction

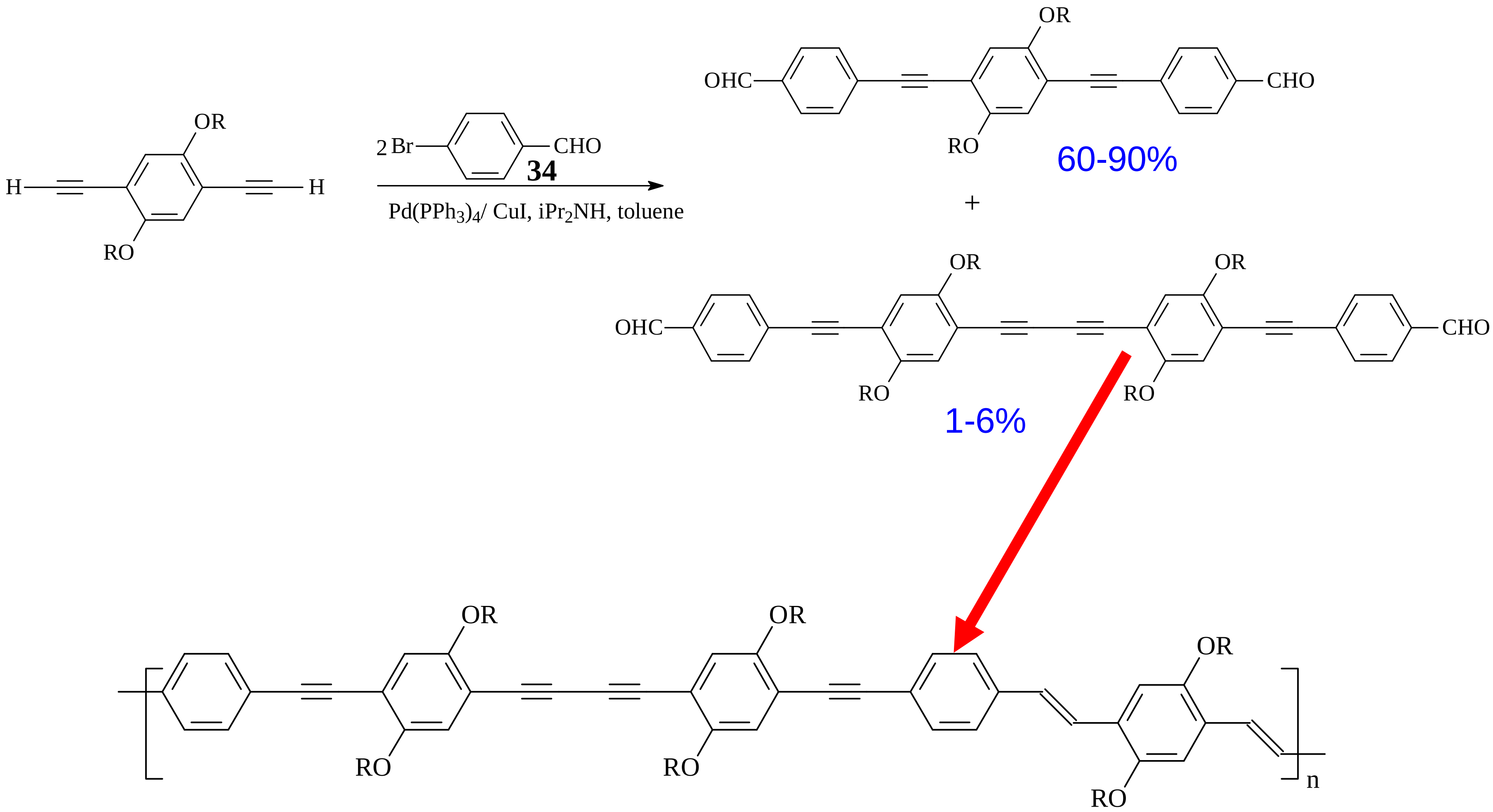
X = CN: Knoevenagel Reaction

Advantages:

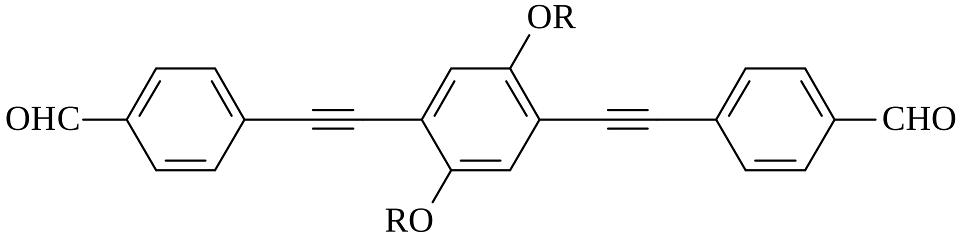
- Shorter reaction time.
- Higher molecular weight
- No defect structure
- Pure products after work up.

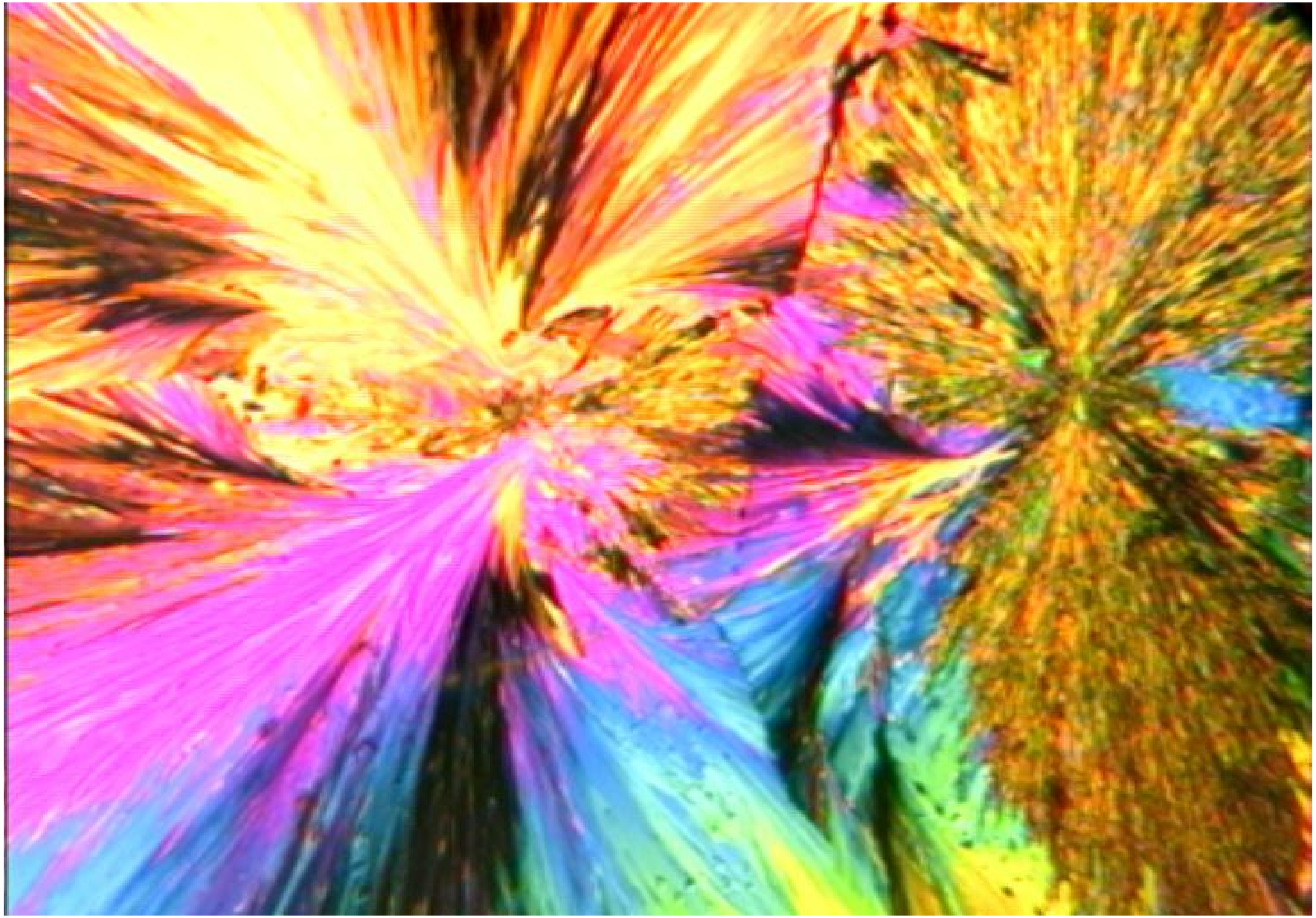
Macromol. Chem. Phys. **2001**, *202*, 2712-2726

Synthesis of Dialdehydes



Egbe *et al. J. Polymer Sci. Part. A: Polymer Chemistry* **2002** , *40*, 2670-2679.


OR
OHC
CHO
RO



Role of side chains

1. Solubilising agents

2. **The donating effect contribute in lowering the band gap of polymers**

3. **Influence the thin film supramolecular ordering**

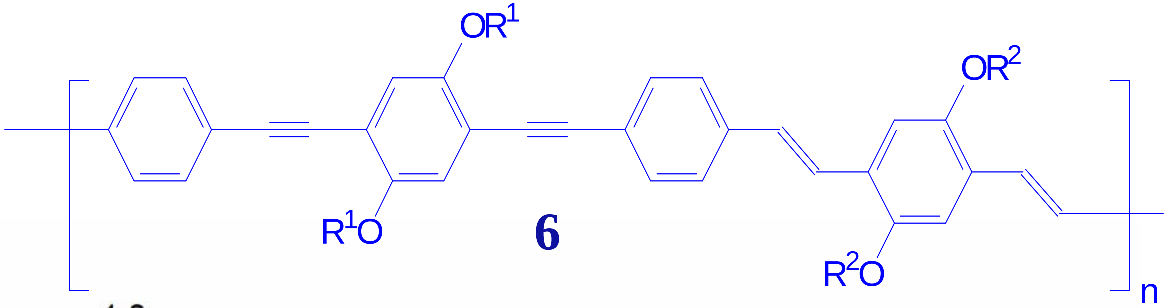
4. Dilute the amount of photoactive species

5. Can lead to discrepancy between optical and electrochemical $\boldsymbol{E}_{g}$

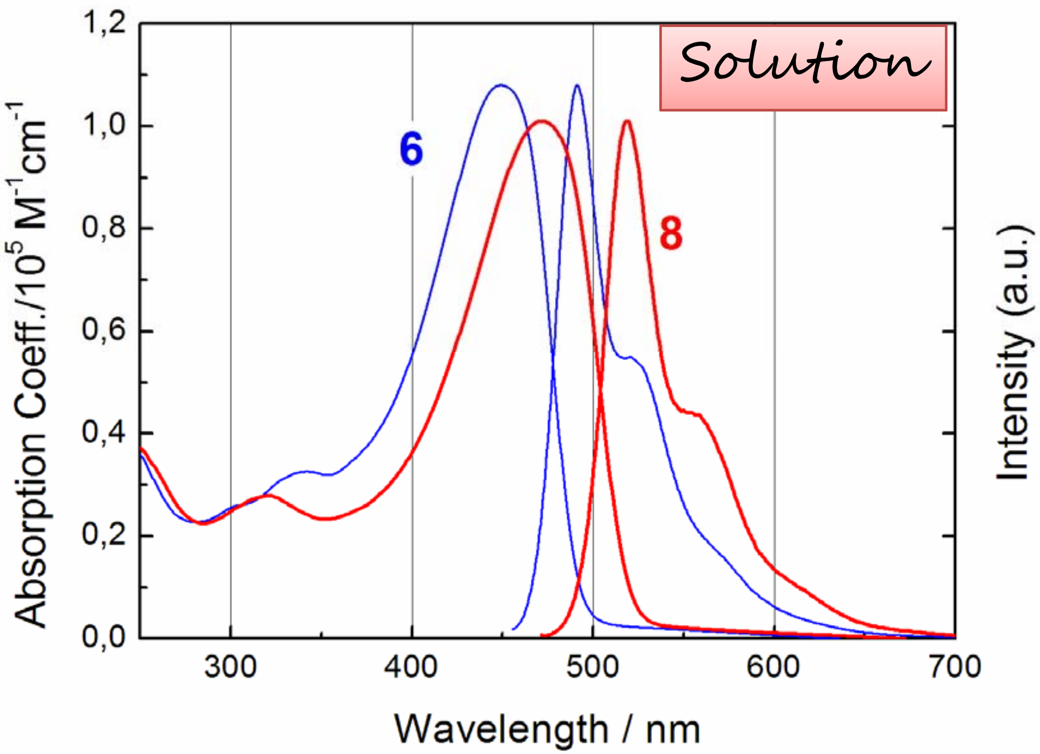
6. Insulating nature is good for electroluminescence

7. **Can be used to tune the (nano)morphology of solar cell active layers**

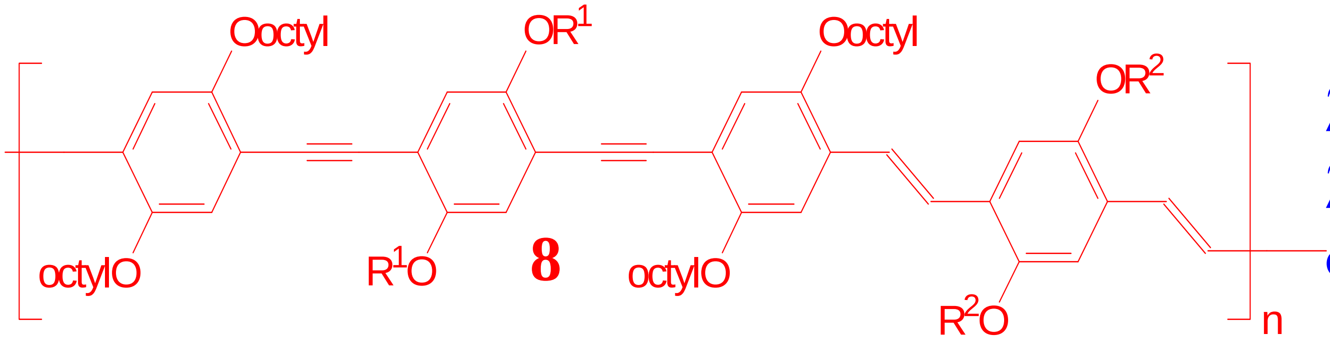
Macromolecules 2004*, 37, 6124. Macromol. Rapid. Commun*. 2005, *26,* 1389.
J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 1631.
Prog. Polym. Sci. 2009, *34*, 1023 (review article)
Macromolecules 2010*, 43*, 1261.*J. Mater. Chem*. 2010, *20*, 9726.
J. Mater. Chem. 2011, *21*, 1338 (feature article)



λ_a =450 nm
λ_f = 490nm
Φ_f =60-70%

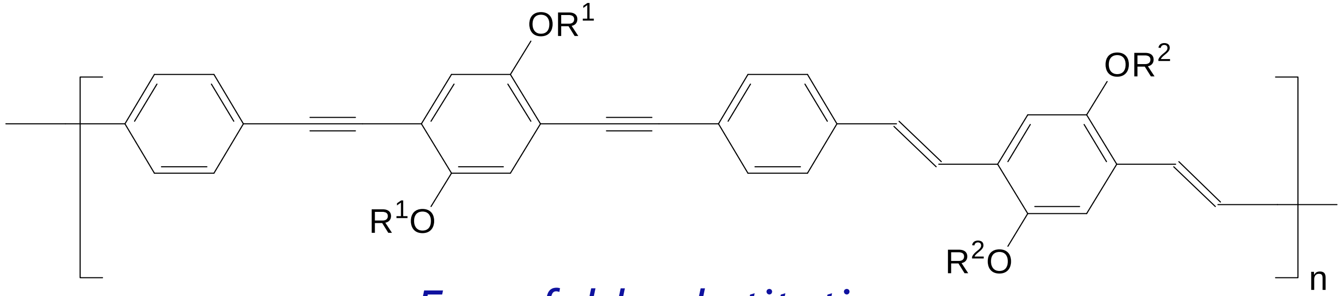


Increasing the number of side chains

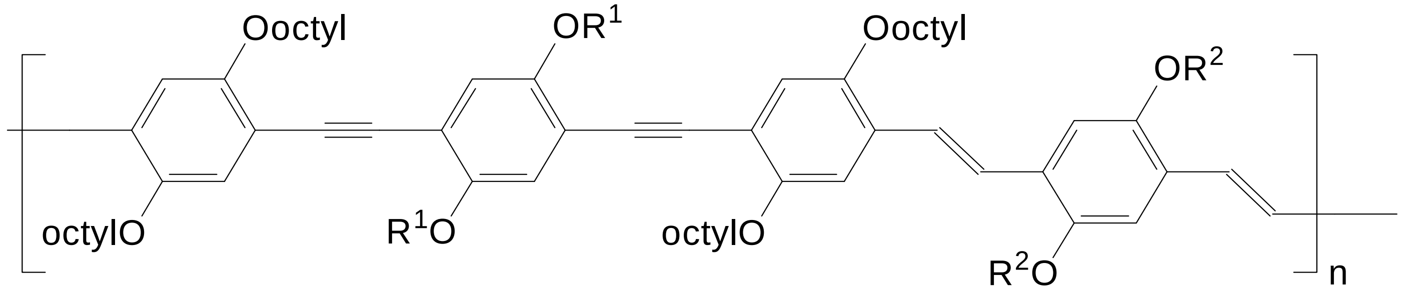


λ_a =470 nm,
λ_f = 520nm,
Φ_f =60-80%

Photophysics in Solid State



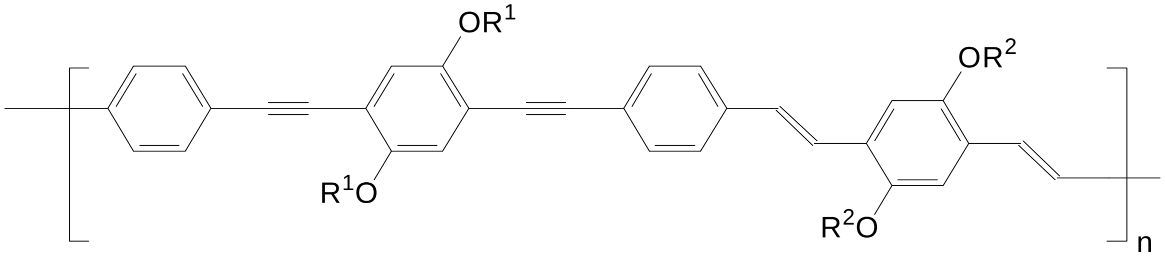
Four-fold substitution

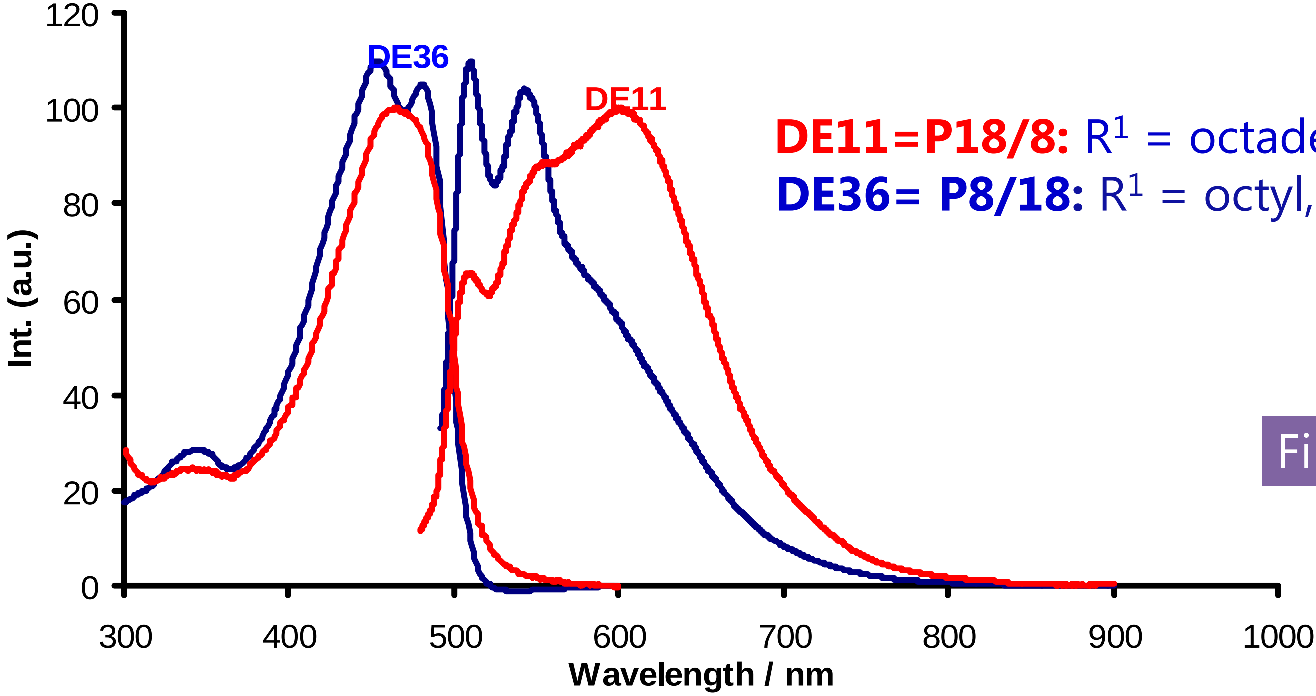


Eight-fold substitution

Solid state properties depend on the **number**, **position**, **length** and **geometry** of the grafted alkoxy side chains

Dependence on the Position of Side Chains



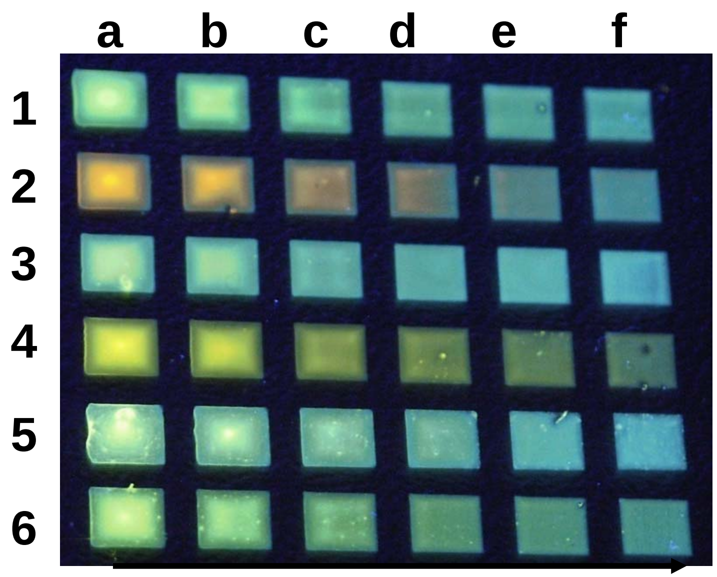


DE11=P18/8: R^1 = octadecyl, R^2 = octyl, orange
DE36= P8/18: R^1 = octyl, R^2 = octadecyl, yellow

Film thickness~150 nm

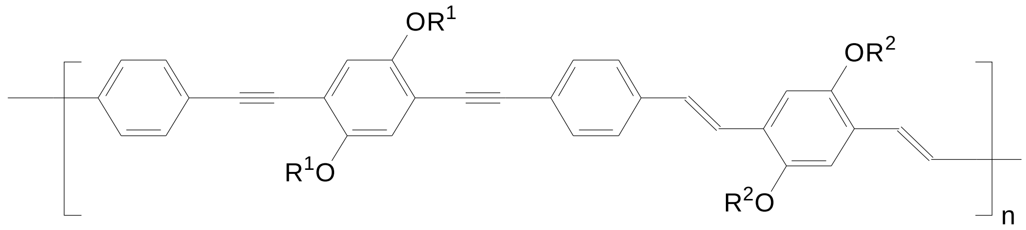
DE11: λ_a = 465 nm, E_g^{opt} = 2.39 eV, λ_e = 602 nm, Φ_f = 19%
DE36:, λ_a = 455, 482 nm, E_g^{opt} = 2.41 eV, λ_e = 510, 544 nm, Φ_f = 29%

Inkjet Printed Films: Combinatorial Effects of Side Chains and Film Thickness



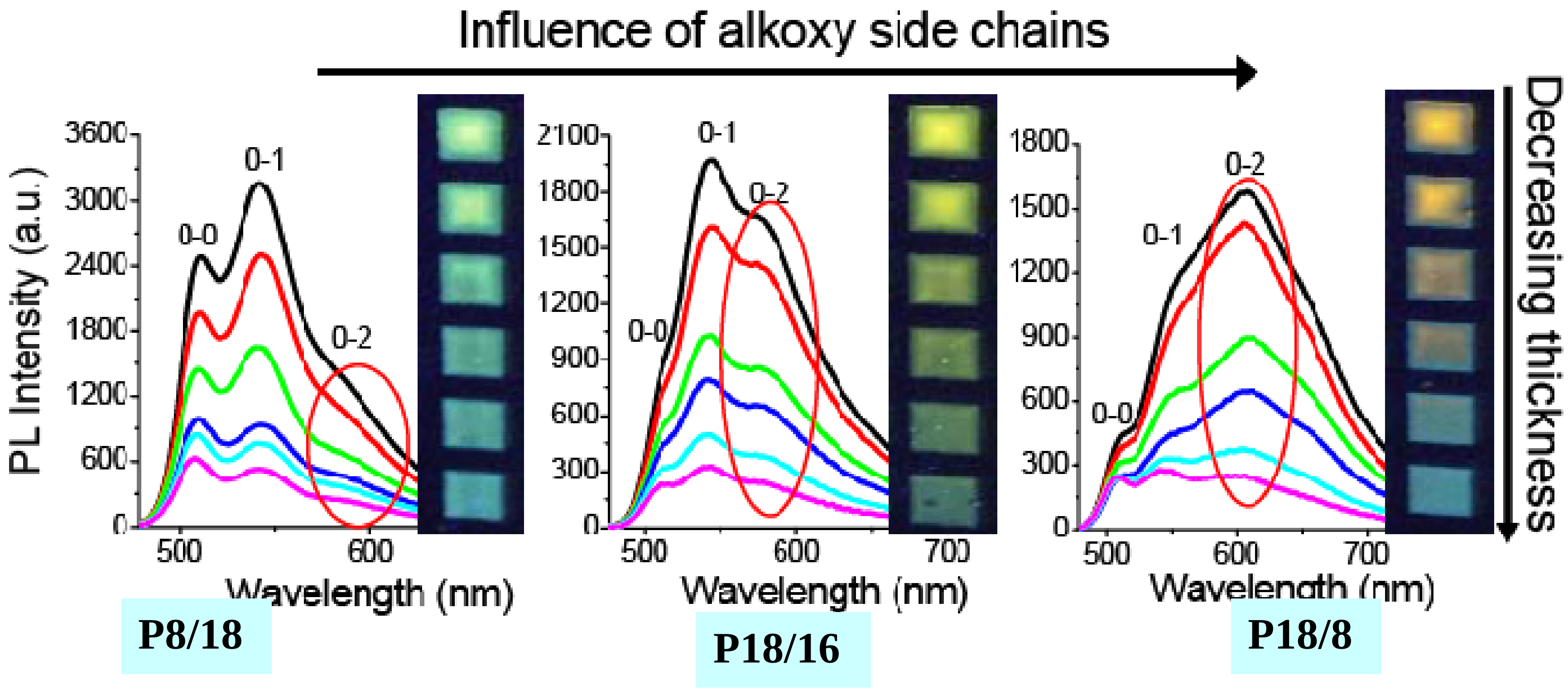
Decreasing film thickness

1. **P8/18**: R^1 = octyl, R^2 = octadecyl
2. **P18/8**: R^1 = octadecyl, R^2 = octyl
3. **P18/7**: R^1 = octadecyl, R^2=heptyl
4. **P18/16**: R^1 = octadecyl, R^2 = hexadecyl
5. **P18/12**: R^1 = octadecyl, R^2=dodecyl
6. **P12/12**: R^1 = R^2 = dodecyl



J. Mater. Chem. 2006, *16*, 4275-4280

Inkjet Printed Films: Combinatorial Effects of Side Chains and Film Thickness

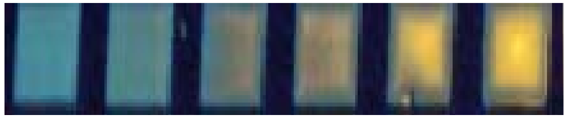


Intensity increase of the PL 0-2 transition (due to superposition with excimer-like emission)

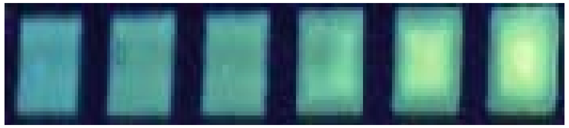
J. Mater. Chem. **2006**, *16*, 4275-4280

Effect of Blending

P18/8

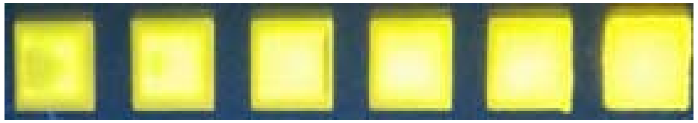


P8/18

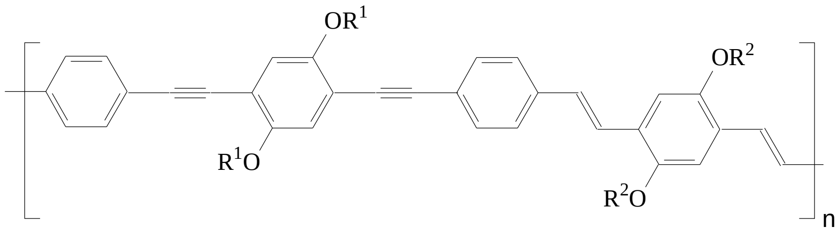


Increasing film thickness

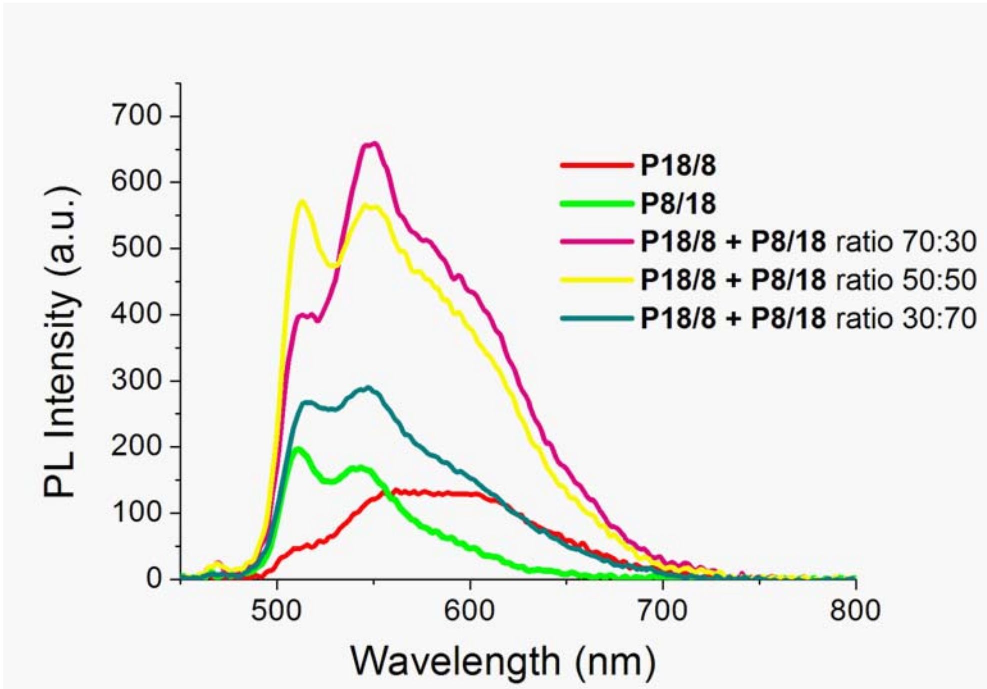
P18/8 + **P8/18** ratio 50:50



Increasing film thickness



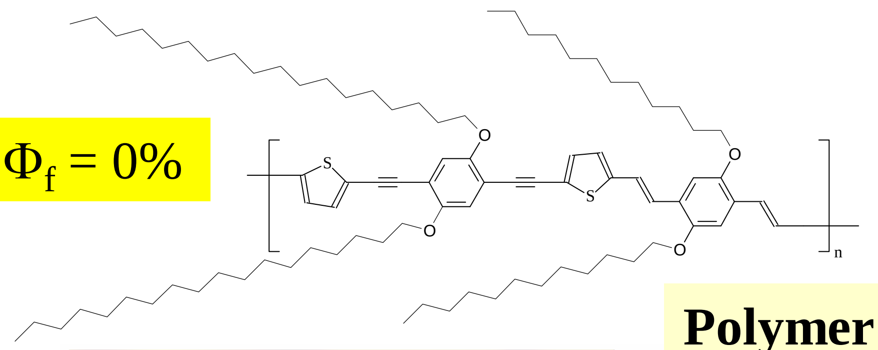
P18/8: R^1= octadecyl, R^2= octyl
P8/18: R^1 = octyl, R^2= octadecyl

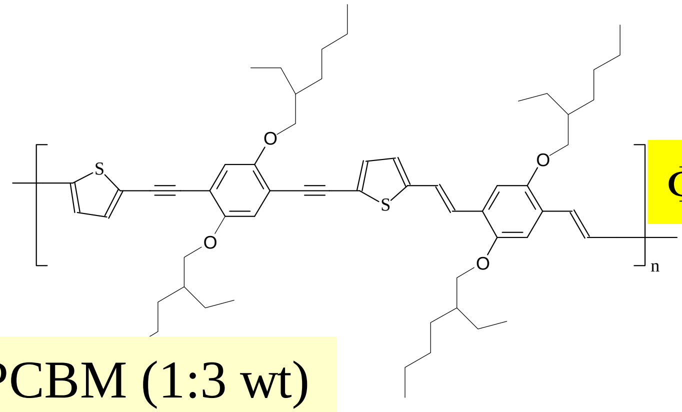


Tuning of solar cells active layer nanomorphology

Variation of side chain nature and length

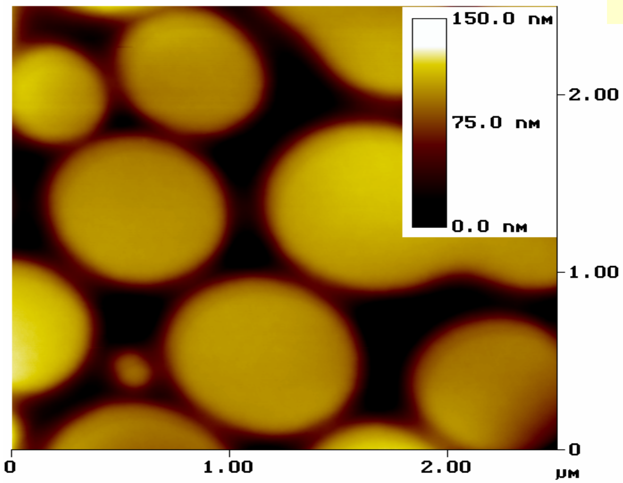
$\Phi_f = 0\%$



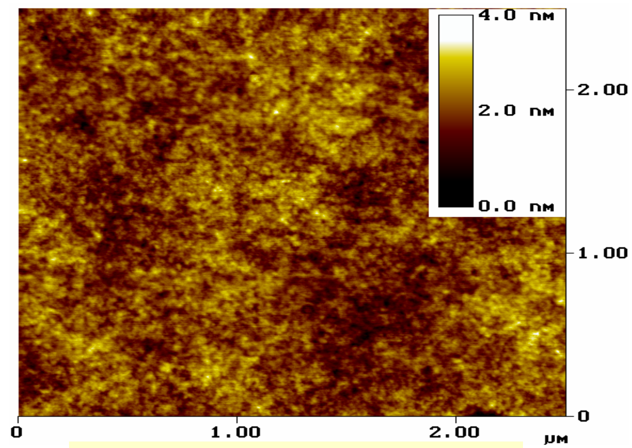


$\Phi_f = 3\%$

Polymer: PCBM (1:3 wt)



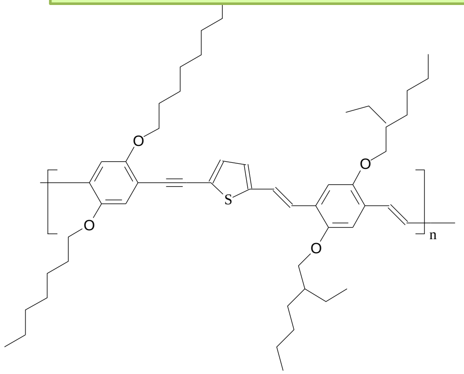
V_{OC} = 500 mV
FF= 37 %
I_{SC}= 1.44 mA/cm^2
η= 0.27%

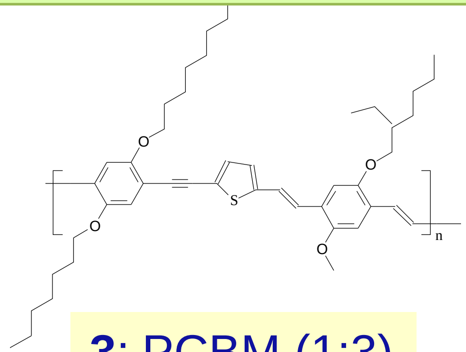


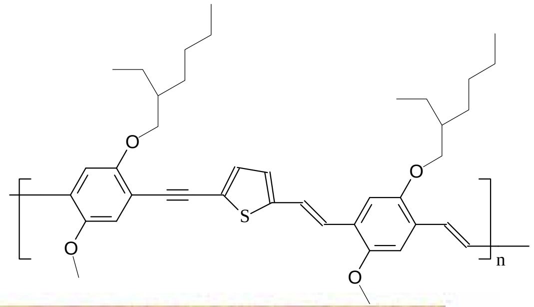
V_{OC} = 800 mV
FF= 46 %
I_{SC}= 4.20 mA/cm^2
η= 1.52%

J. Polym. Sci. Part A: Polym. Chem. **2007**, 45, 1631.

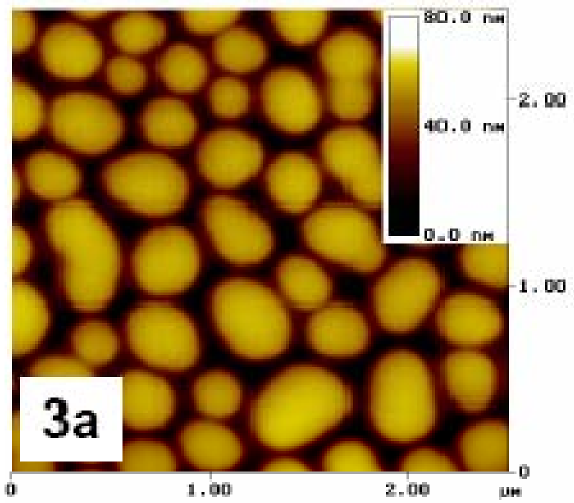
Variation of side chain volume fraction

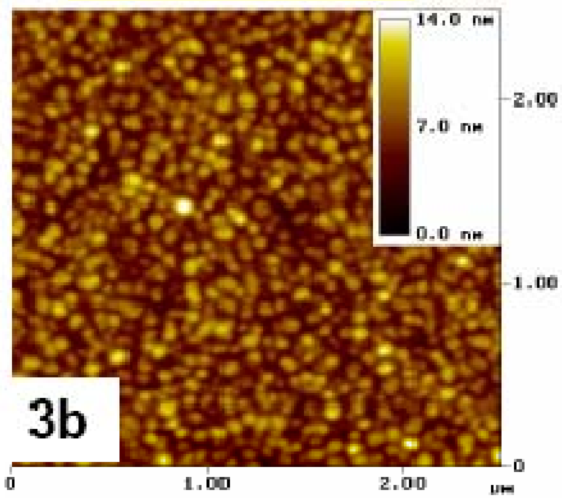


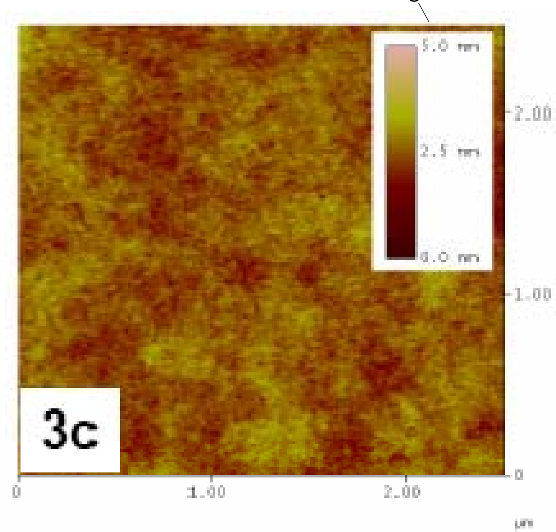




3: PCBM (1:3)







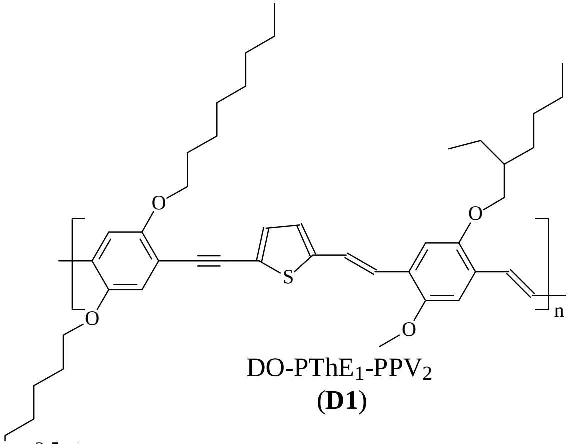
V_{OC} = 900 mV
FF= 54 %
J_{SC}= 2.50 mA/cm^2
η= 1.20%

V_{OC} = 900 mV
FF= 53 %
J_{SC}= 3.70 mA/cm^2
η= 1.74%

V_{OC} = 800 mV
FF= 44 %
J_{SC}= 5.15 mA/cm^2
η= 1.80%

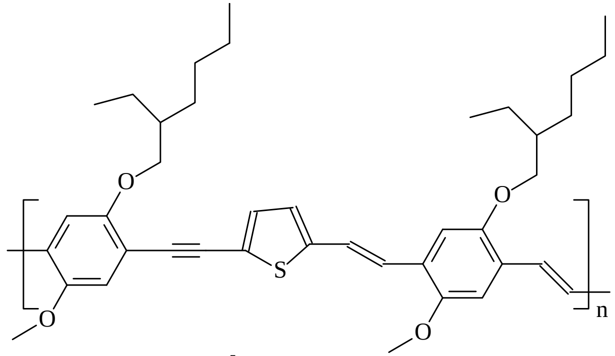
J. Polym. Sci. Part A: Polym. Chem. **2007**, 45, 1631. *Sol. Energy Mater. Sol. Cells* **2010**, 94, 484.

Ternary Blend

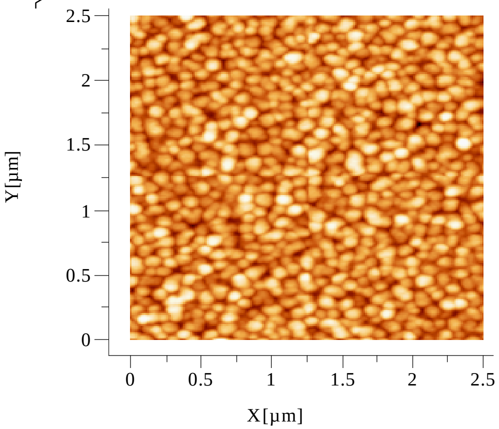


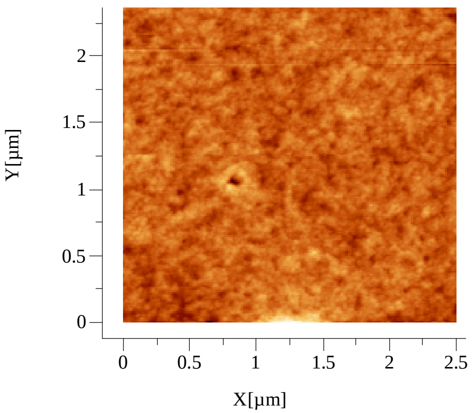
DO-PThE$_1$-PPV$_2$
(**D1**)

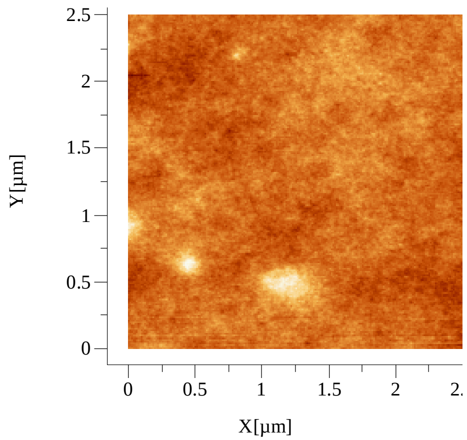
Material	μ ($cm^2.V^{-1}.s^{-1}$)
D1	1.8×10^{-5}
D2	2×10^{-6}
D1:D2	2.6×10^{-4}



MEH-PThE$_1$-PPV$_2$
(**D2**)





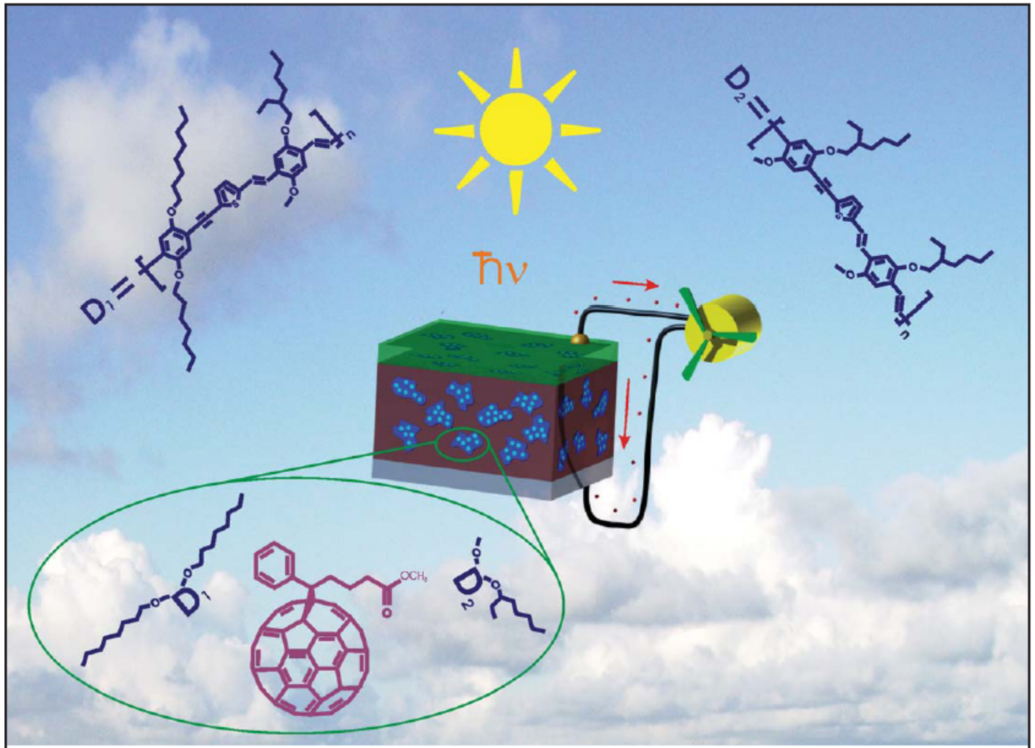


V_{OC} = 840 mV
FF= 41 %
J_{SC}= 4.5 mA/cm^2
η= 1.58%

V_{OC} = 860 mV
FF= 40 %
J_{SC}= 6.02 mA/cm^2
η= 2.0%

V_{OC} = 742 mV
FF= 36 %
J_{SC}= 4.95 mA/cm^2
η= 1.35%

J. Mater. Chem. **2011,** 21, 2594-2600



Highlighting joint research results from the labs of Linz Institute of Organic Solar Cells, Johannes Kepler University Linz Austria, and Department of Chemistry, Faculty of Science, Addis Ababa University, Ethiopia.

Title: Mobility and photovoltaic performance studies on polymer blends: effects of side chains volume fraction

Ternary blend of PCBM with two thiophene based poly(*p*-phenylene-ethynylene)-*alt*-poly(*p*-phenylene-vinylene)s (PPE-PPV) consisting of the same conjugated backbone but different types and volume fraction of alkoxy side chains on the phenylene-ethynylene unit, showed better photovoltaic performance as compared to binary blends of the single polymers mixed with PCBM.

As featured in:

See Getachew Adam *et al*, *J. Mater. Chem.*, 2011, **21**, 2594.

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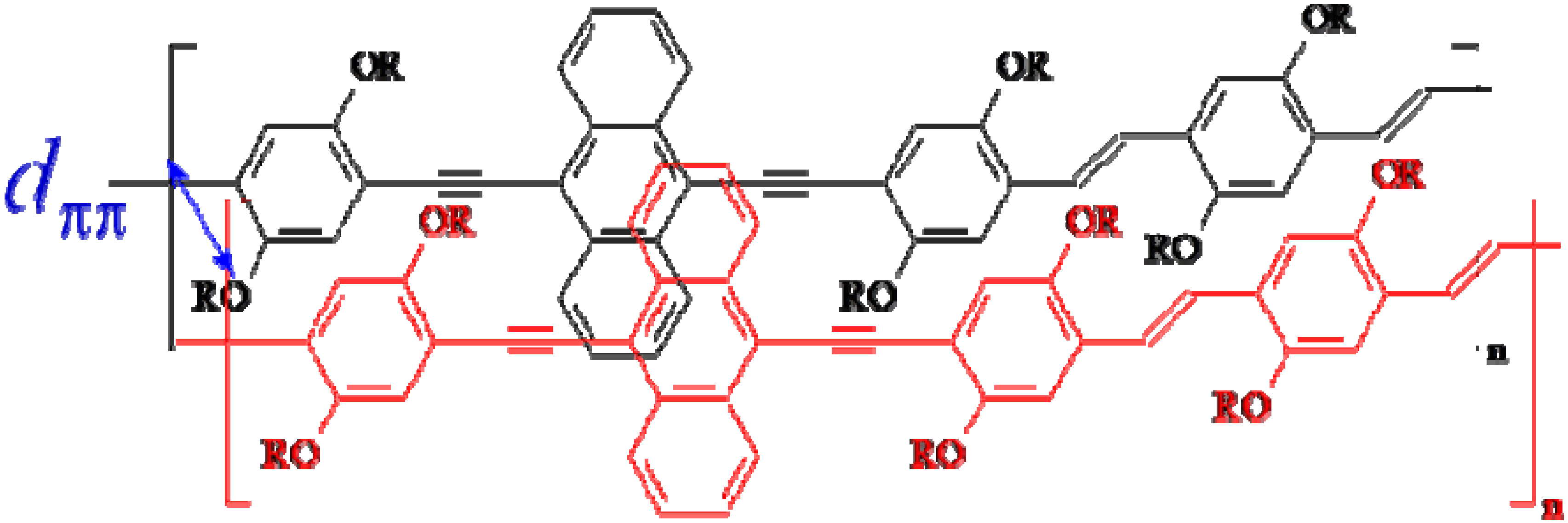
Getachew Adam

J. Mater. Chem. **2011,** 21, 2594.

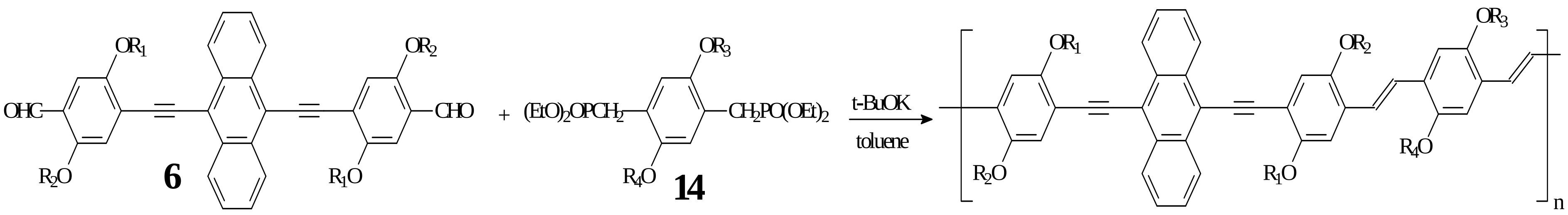
Effect of ππ-Stacking Distance



ππ-stacking distance, $d_{\pi\pi}$, tuned by
R = linear and or branched side chains

Phys. Status Solidi A. **2009,** *12*, 2695; *Macromolecules* **2010**, *43*, 1261; *Macromolecules* **2010**, *43*, 306, *J. Mater. Chem*. **2010**, *20*, 9726

Synthesis + X-Ray Data



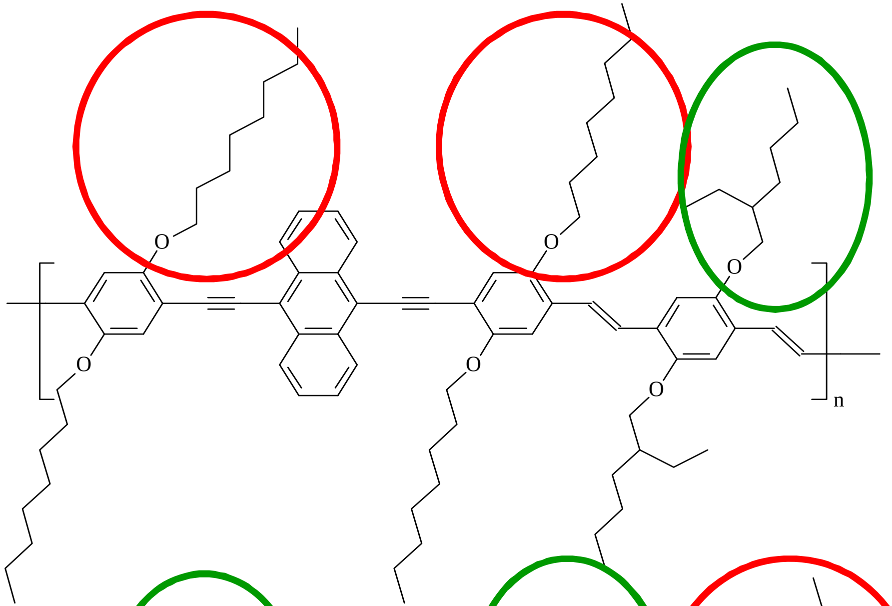
AnE-PV

Code	R_1	R_2	R_3	R_4	$d_{\pi\pi}$ / nm
AnE-PV*aa*	octyl	octyl	octyl	octyl	0.380± 0.002
AnE-PV*ab*	octyl	octyl	2-ethylhexyl	2-ethylhexyl	0.386± 0.002
AnE-PV*ac*	octyl	octyl	methyl	2-ethylhexyl	0.381± 0.002
AnE-PV*ad*	octyl	octyl	decyl	decyl	0.380± 0.002
AnE-PV*ae*	octyl	octyl	dodecyl	dodecyl	0.380± 0.002
AnE-PV*ba*	2-ethylhexyl	2-ethylhexyl	octyl	octyl	-
AnE-PV*bb*	2-ethylhexyl	2-ethylhexyl	2-ethylhexyl	2-ethylhexyl	-
AnE-PV*cc*	methyl	2-ethylhexyl	methyl	2-ethylhexyl	0.379±0.002

Macromolecules **2010**, *43*, 306. *Macromolecules* **2010**, *43*, 1261.

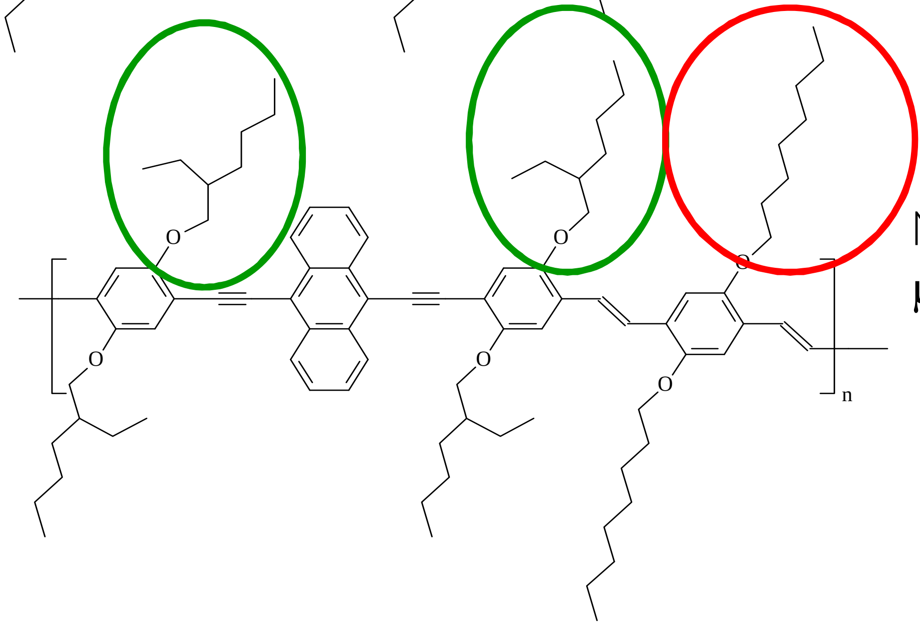
Comparison between AnE-PV*ab* and AnE-PV*ba*

AnE-PV*ab*



$d_{\pi\pi}$ =0.386 nm
μ_{hole} = 2.57 ×10^{-5} cm^2/V.sv

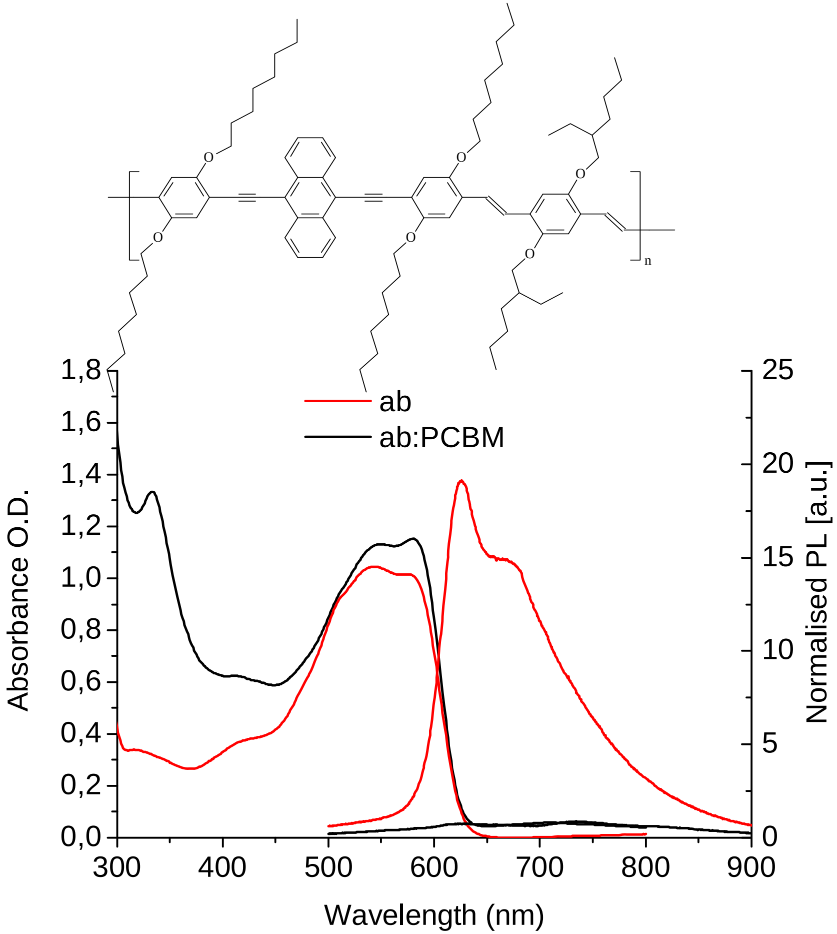
AnE-PV*ba*

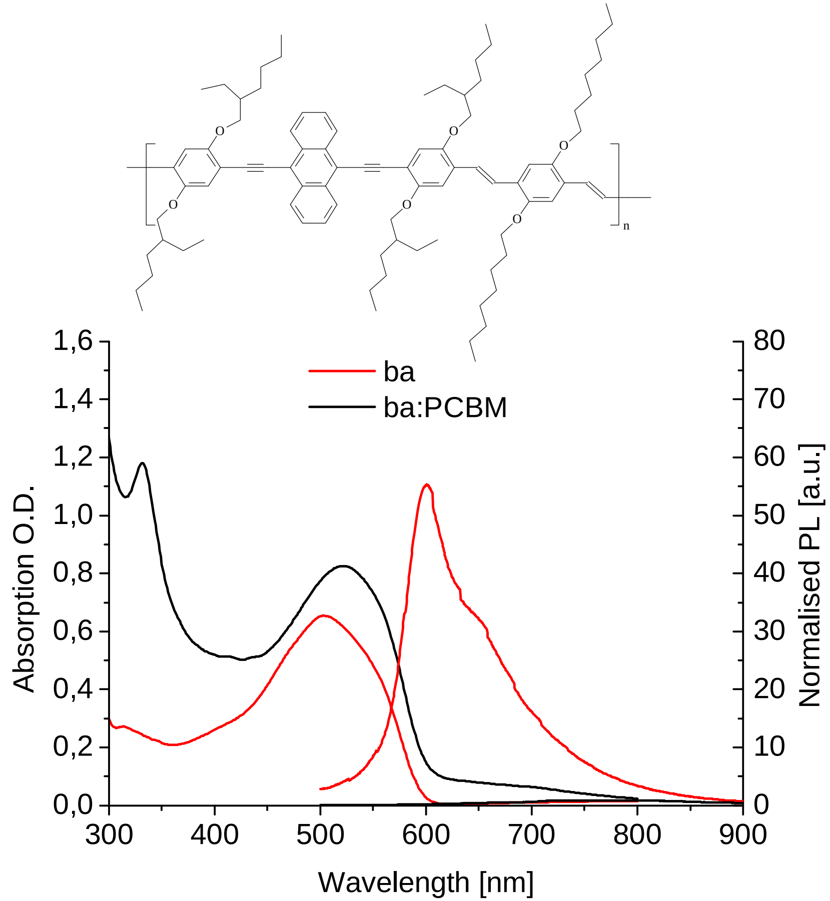


No stacking
μ_{hole} = 1.53 ×10^{-4} cm^2/V.sv

Macromolecules **2010**, *43*, 1261.

Comparison between **AnE-PV*ab*** and **AnE-PV*ba***

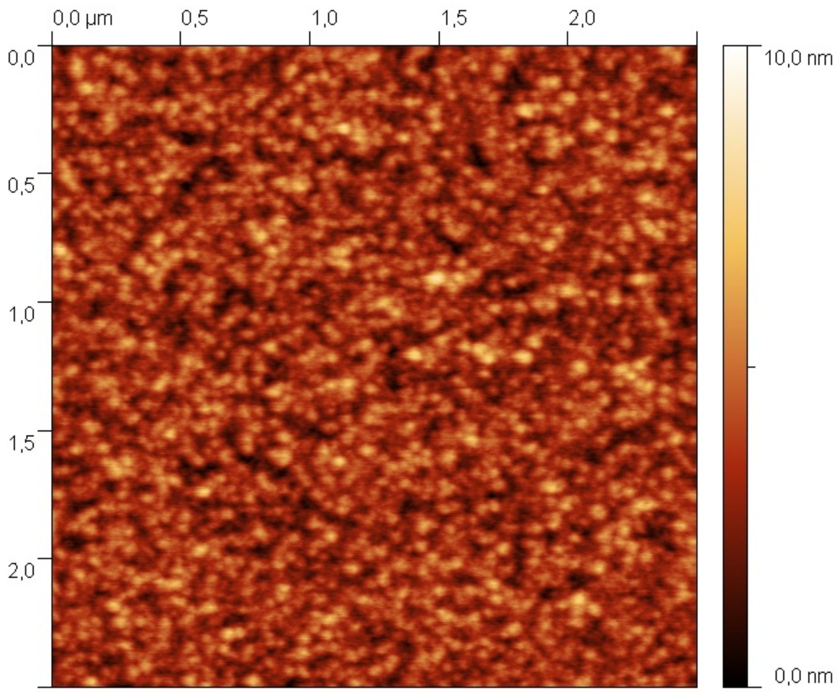




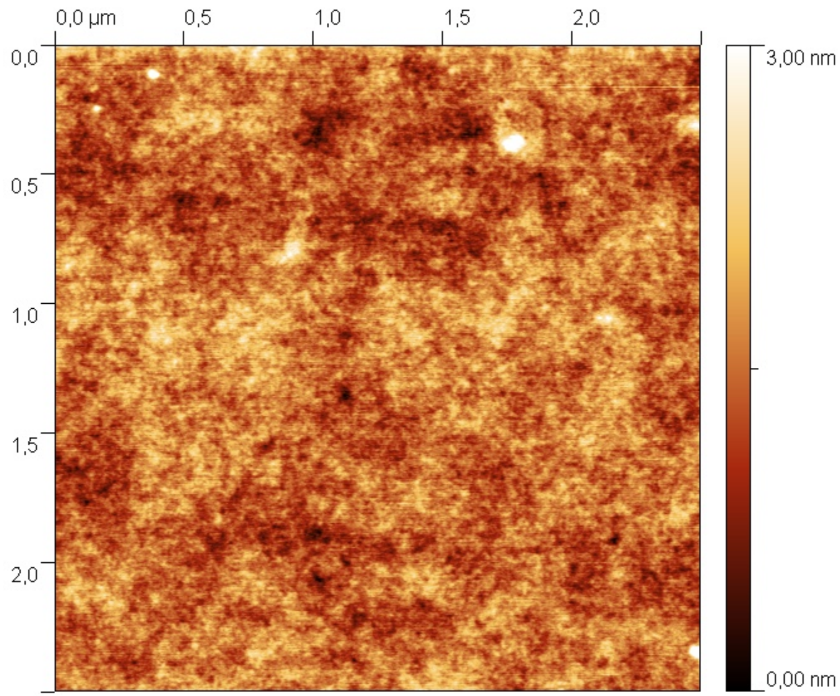
Macromolecules **2010**, *43*, 1261.

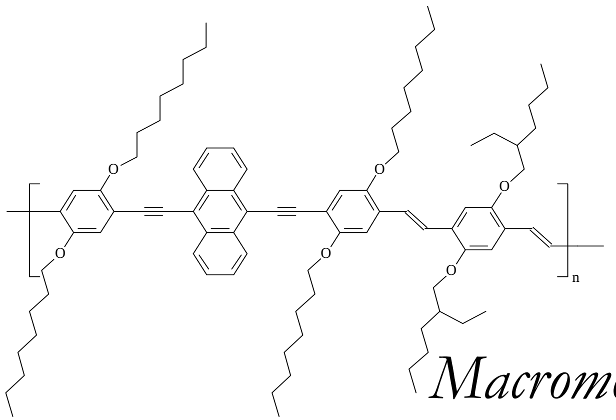
Comparison between AnE-PV*ab* and AnE-PV*ba*

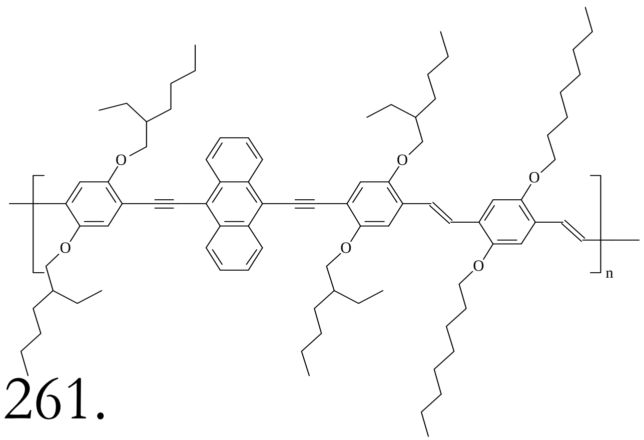
AnE-PV*ab*:PCBM (1:1)



AnE-PV*ba*:PCBM (1:1)

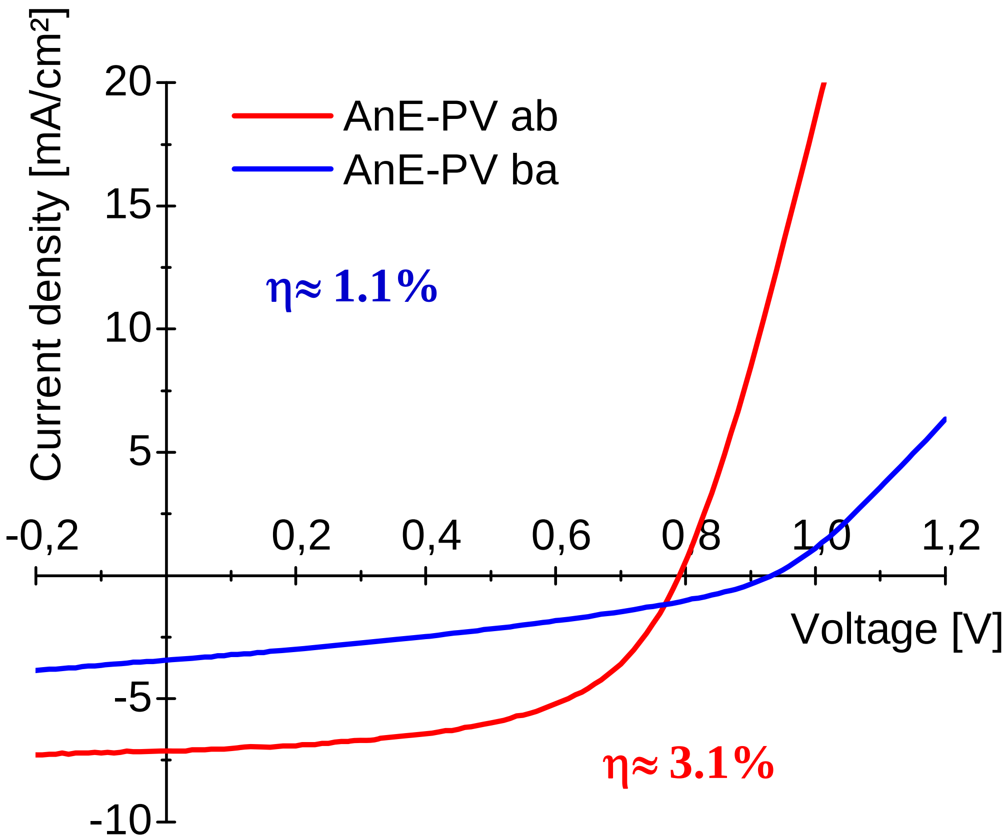






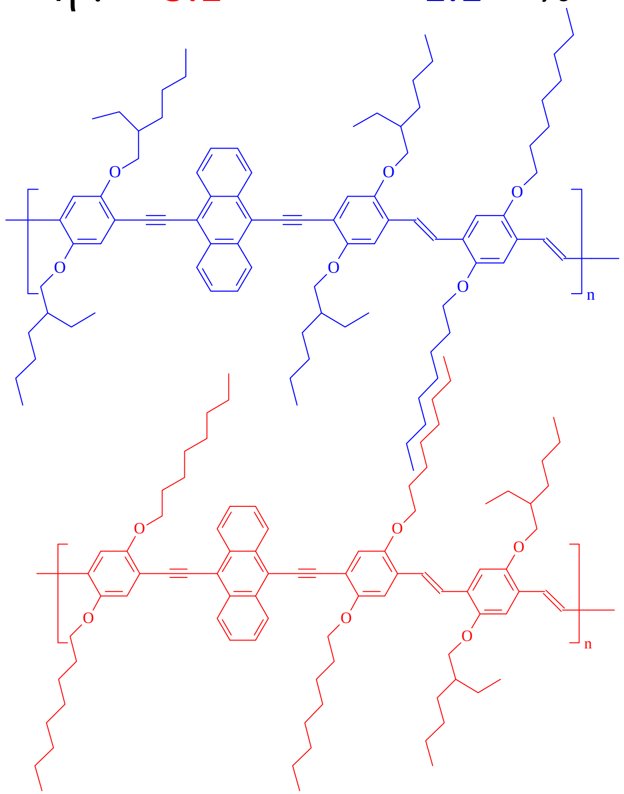
Macromolecules **2010**, *43*, 1261.

Comparison between AnE-PV*ab* and AnE-PV*ba*



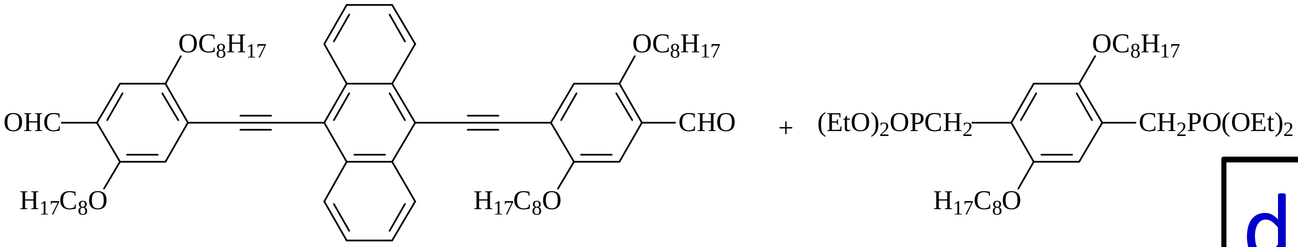
AnE-PV*ab* ⇔ AnE-PV*ba*

J_{SC} :	7.14	3.44	mA
V_{OC}:	0.79	0.93	V
FF:	55.65	34.67	%
η :	3.1	1.1	%



Macromolecules **2010**, *43*, 1261.

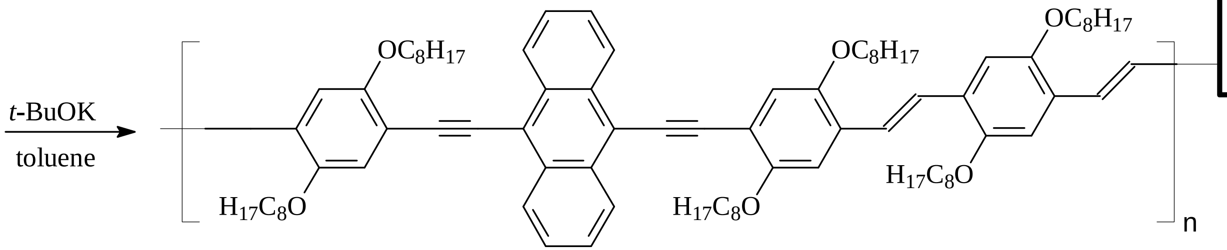
Side Chain Based Random Copolymer



1a: C_8H_{17} = octyl (1)
+
1b: C_8H_{17} = 2-ethylhexyl (1)

2a: C_8H_{17} = octyl (1)
+
2b: C_8H_{17} = 2-ethylhexyl (1)

$d_{\pi\pi}$ = 0.393 nm



M_n = 27,000 g/mol
M_w = 54,000 g/mol

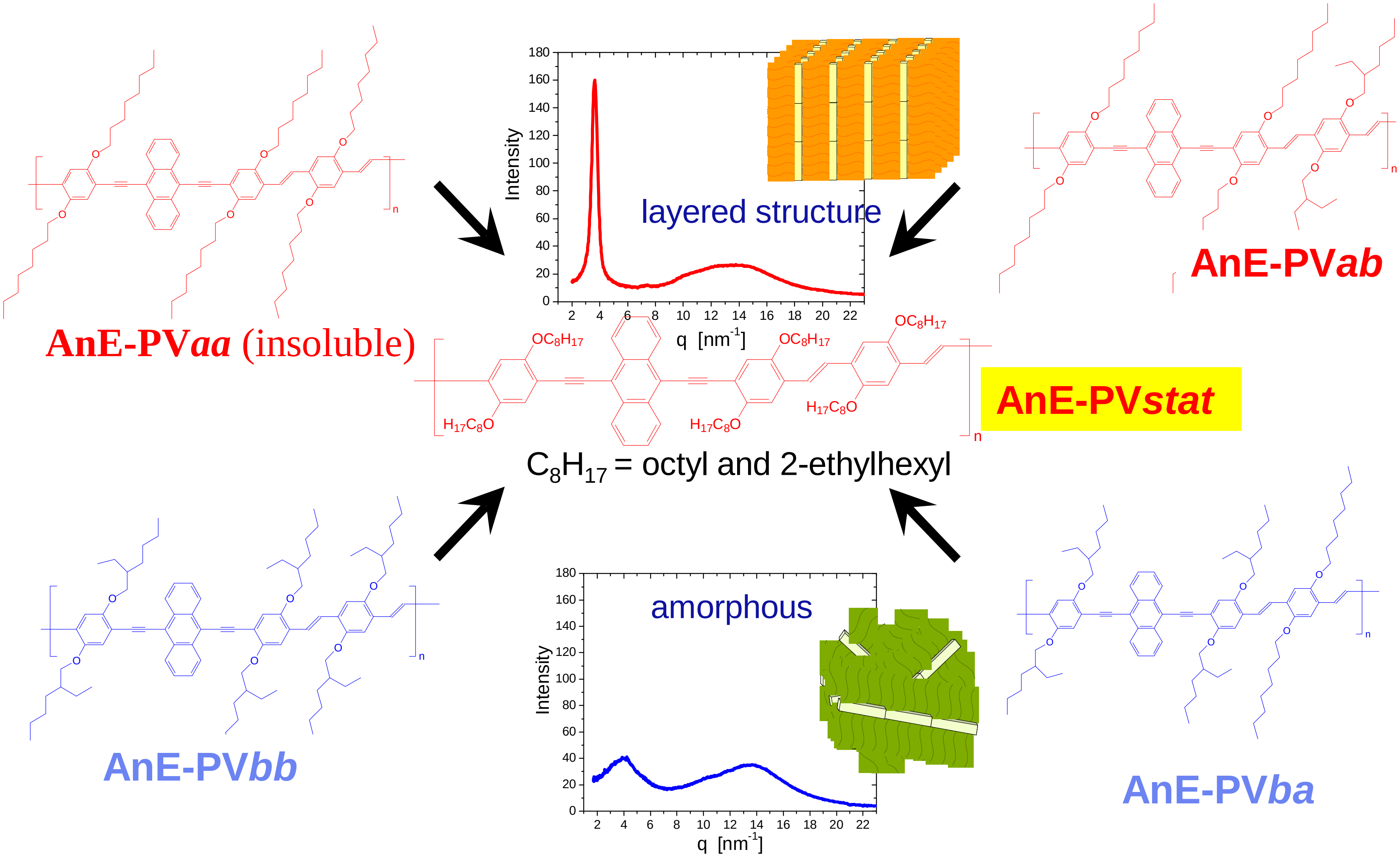
AnE-PV*stat*

Statistical distribution of sequences of
C_8H_{17} = octyl and of C_8H_{17} = 2-ethylhexyl

$\mu = 5.43 \times 10^{-4}$ cm^2/Vs

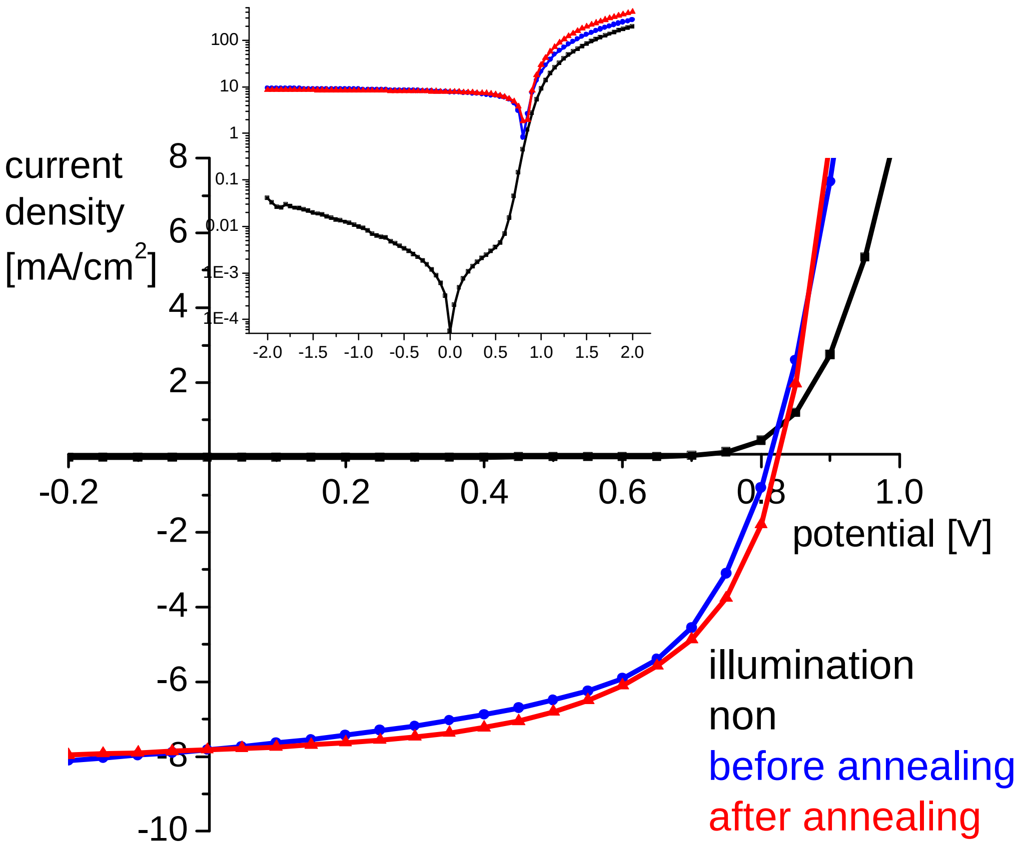
J. Mater. Chem. 2010, *20*, 9726

Side Chain Based Random Copolymer



-stat shows slightly higher bulk ordering than *-aa*

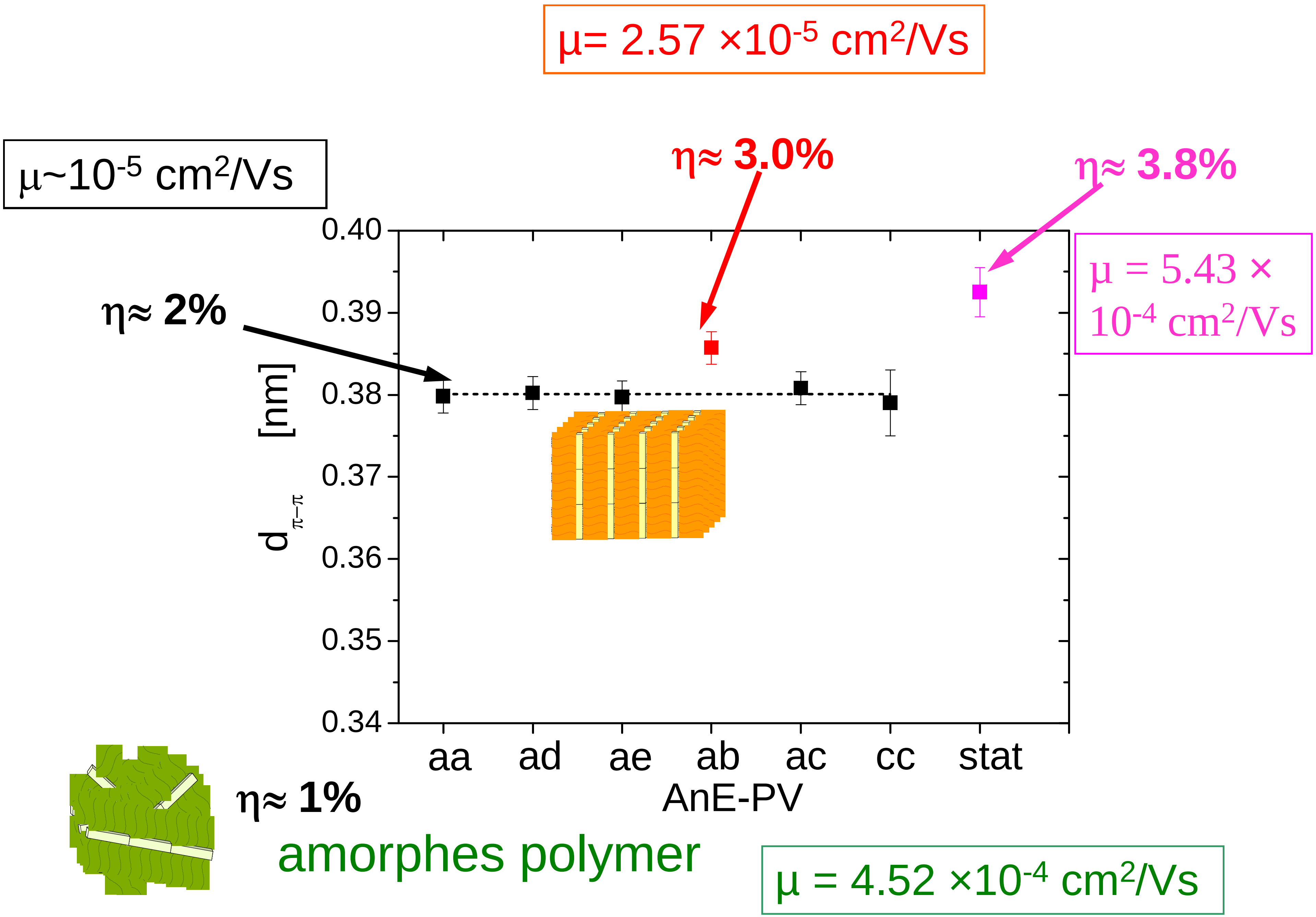
Photovoltaic Properties: *stat*



Stat:2PCBM	before	after
V_{oc} [mV]	810	830
J_{SC} [mA/cm^2]	7.82	7.83
FF [%]	56	58
η [%]	3.6	3.8

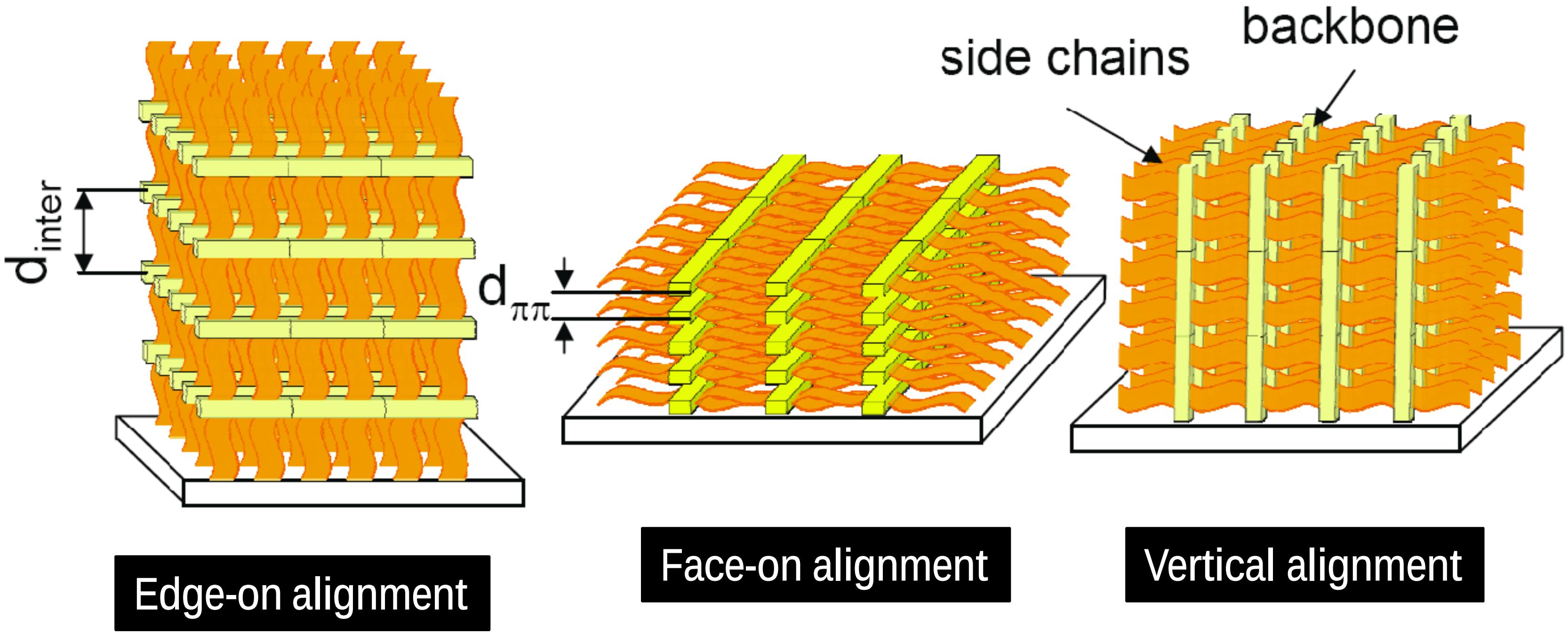
M_n = 27,000 g/mol
M_w = 54,000 g/mol

J. Mater. Chem. **2010**, *20*, 9726



μ= 2.57 ×10-5 cm2/Vs
μ~10-5 cm2/Vs
η≈ 3.0%
η≈ 3.8%
μ = 5.43 × 10-4 cm2/Vs
η≈ 2%
0.40
0.39
0.38
0.37
0.36
0.35
0.34
dπ−π [nm]
aa
ad
ae
ab
ac
cc
stat
AnE-PV
η≈ 1%
amorphes polymer
μ = 4.52 ×10-4 cm2/Vs

Possible Polymer Alignment on a Substrate (Electrode)

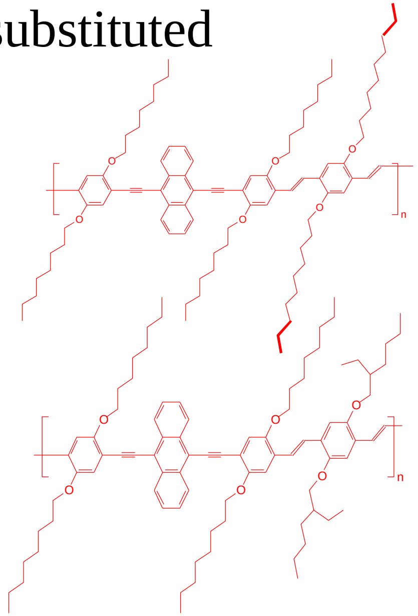


S. Rathgeber et *al*. *Polymer* **2011**, *52*,3819

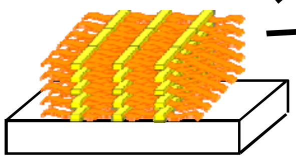
GIWAXS Studies of Solar Cells Active Layers

Polymer:PCBM (1:0) (1:1) (1:2)

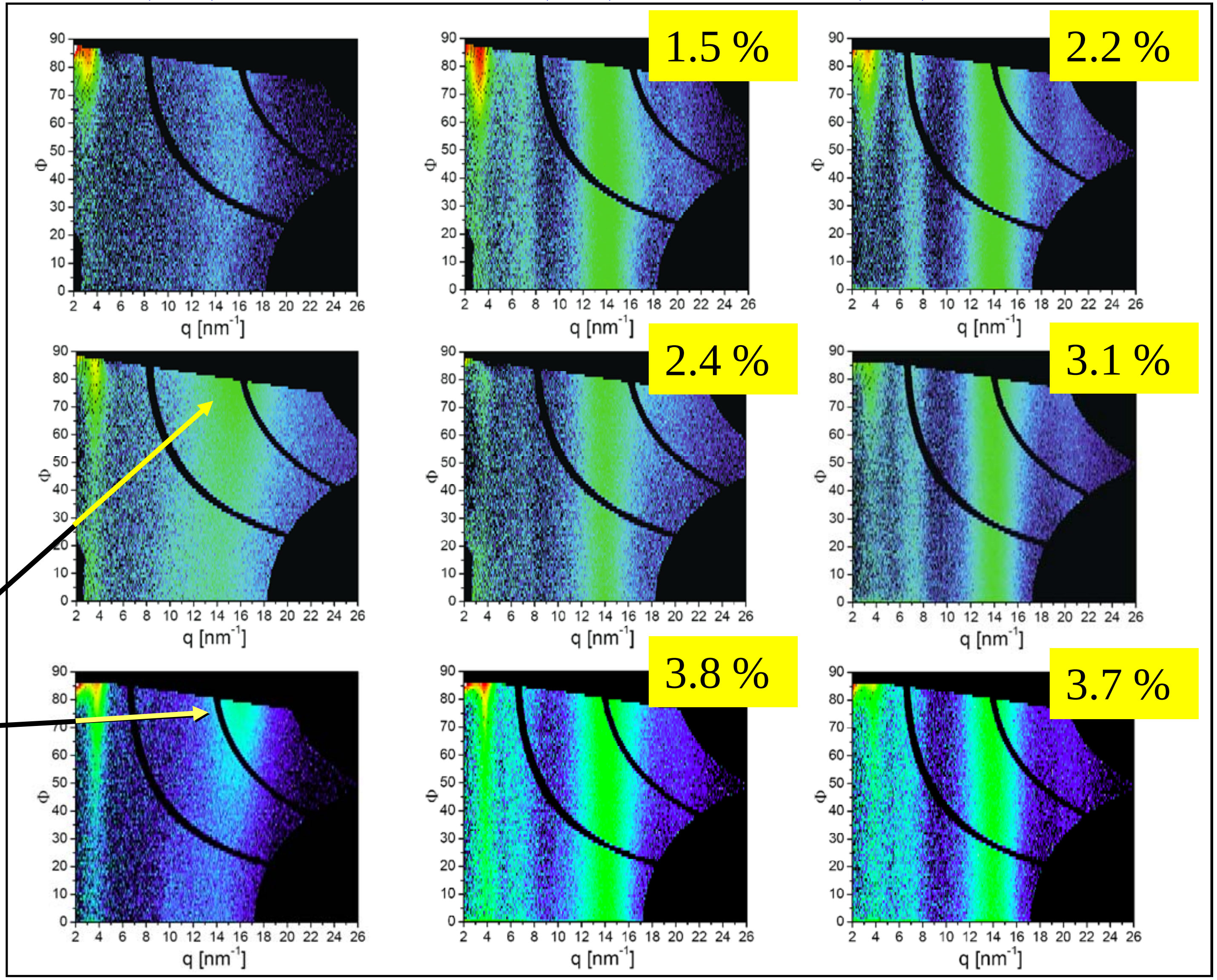
fully linear substituted



partly branched



statistical distribution of side chains



•Polymers with solely linear side chains align edge-on the substrate

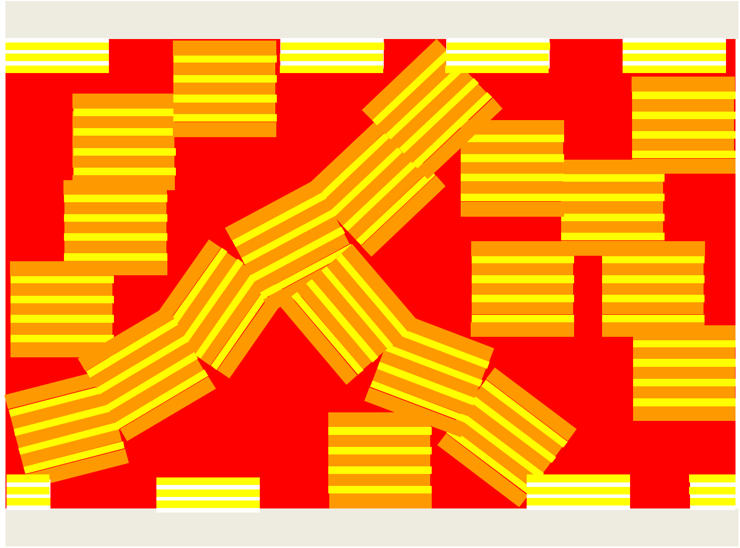
•Polymers bearing branched side chains align face-on on the substrate

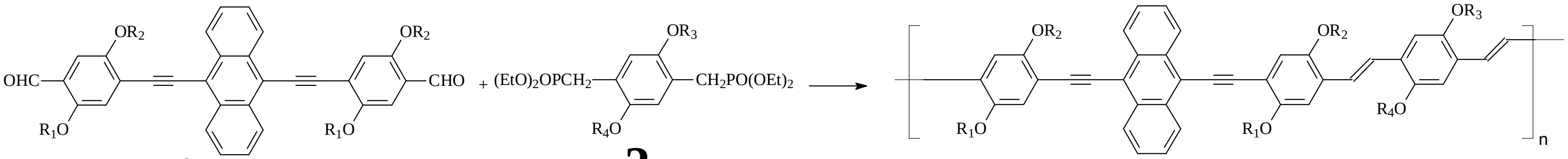
•Face-on alignment is favorable for better charge transport and consequently for better performance

AnE-PV*stat* leads to active layers with:

- well ordered lamellar domains, also in the presence of the fullerene,
- "face-on" domains close to the electrodes,
- enhanced isotropic domain orientation throughout the active layer.

This leads to the best solar cell performance!

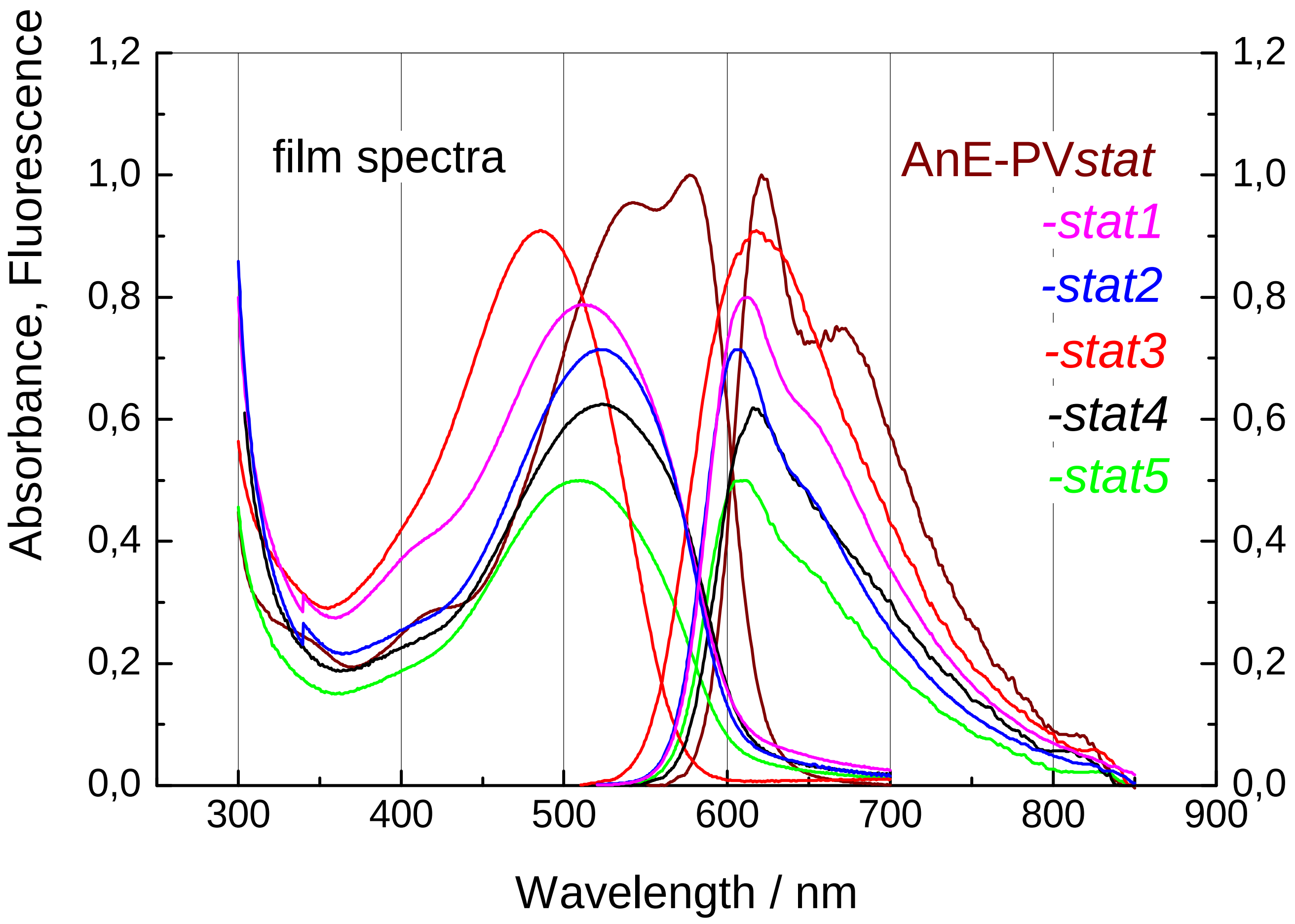




1a: $R_1 = R_2$ = octyl
1b: $R_1 = R_2$ = 2-ethylhexyl
1c: R_1 =methyl, R_2 = 2-ethylhexyl
1d: $R_1 = R_2$ = 3,7-dimethoxyoctyl

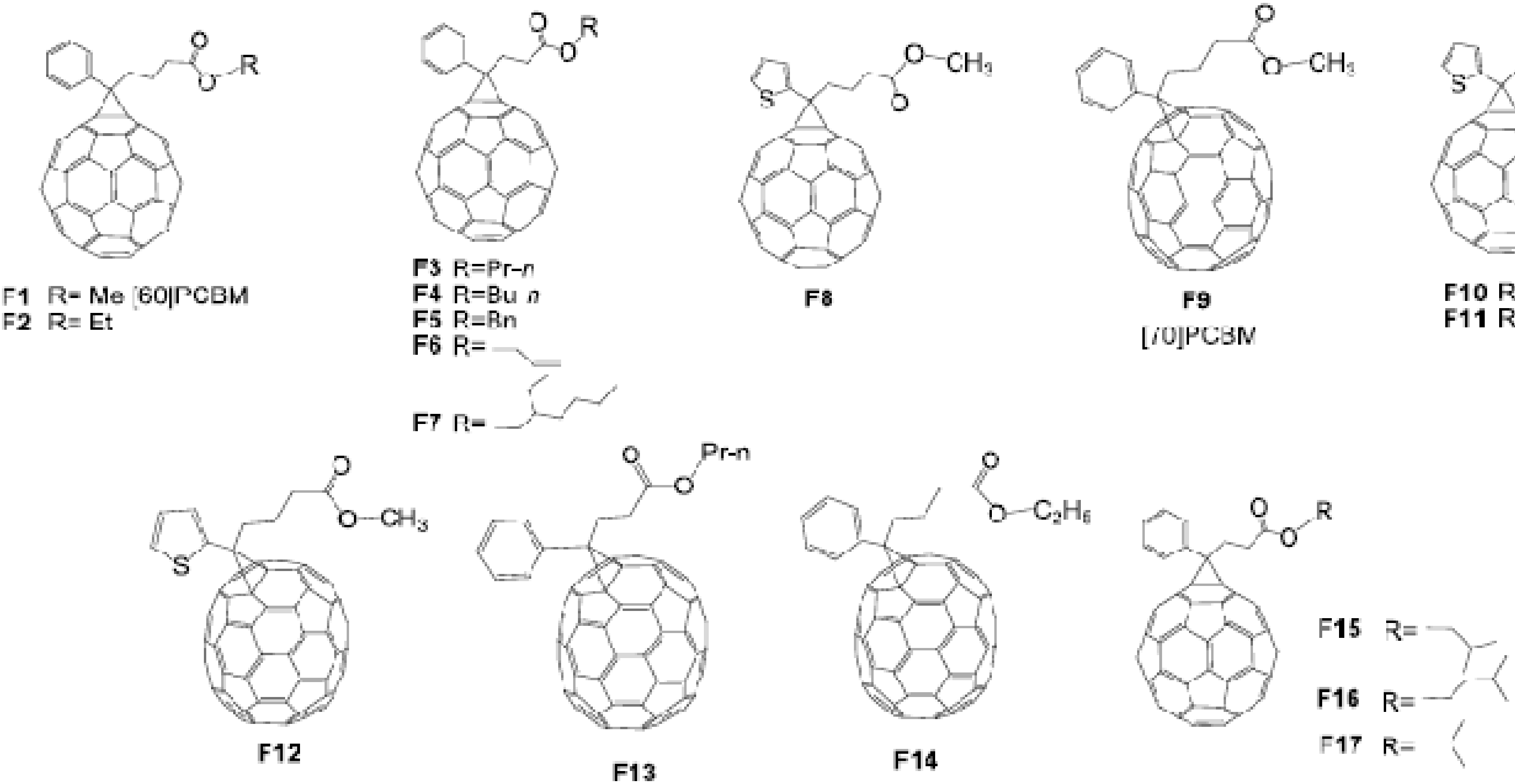
2a: $R_3 = R_4$ = octyl
2b: $R_3 = R_5$ = 2-ethylhexyl
2c: R_3=methyl, R_4 = 2-ethylhexyl
2d: $R_3 = R_4$ = 3,7-dimethoxyoctyl

Polymer	1-a	1-b	1-c	1-d	2a	2b	2c	2d	Yield[%]
AnE-PV*stat*	1	1	0	0	1	1	0	0	80-90[a)]
AnE-PV*stat1*	1	1	0	0	2	0	0	0	87
AnE-PV*stat2*	1	1	0	0	0	2	0	0	94
AnE-PV*stat3*	0	1	1	0	0	1	1	0	72
AnE-PV*stat4*	1	0	1	0	1	0	1	0	70
AnE-PV*stat5*	1	1	1	0	1	1	1	0	60
AnE-PV*stat6*	1	0	0	1	1	0	0	1	79
AnE-PV*stat7*	0	1	0	1	0	1	0	1	70
AnE-PV*gg*	0	0	0	1	0	0	0	1	73



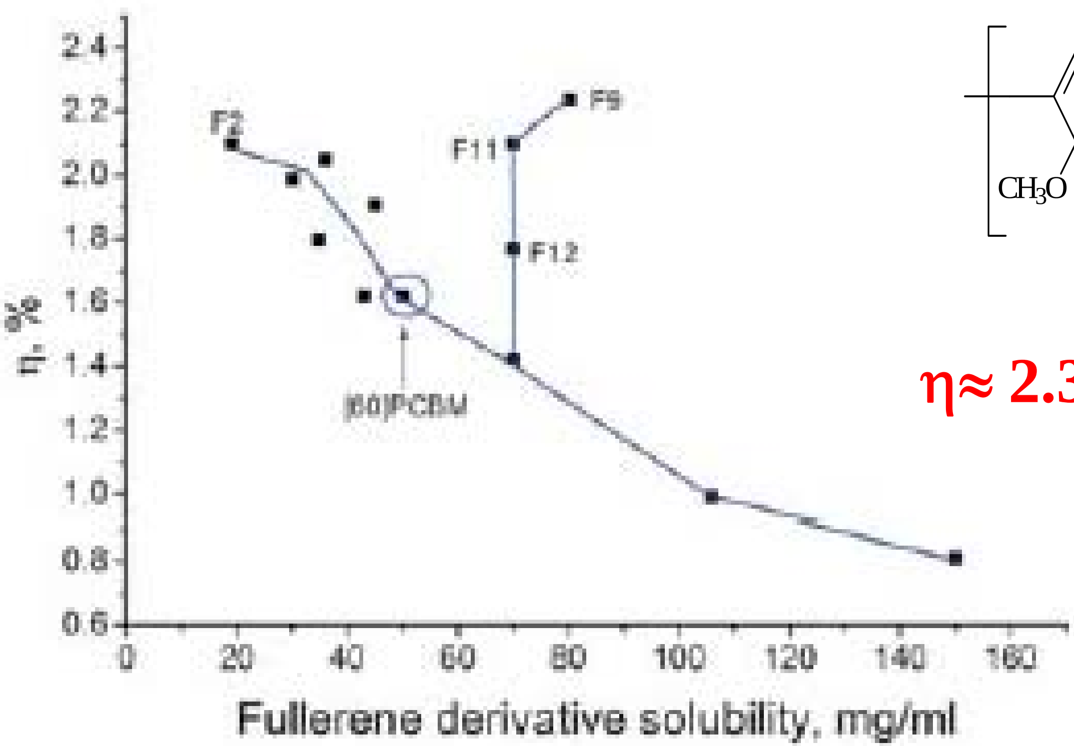
film spectra
AnE-PVstat
-stat1
-stat2
-stat3
-stat4
-stat5
Absorbance, Fluorescence
Wavelength / nm
0,0
0,2
0,4
0,6
0,8
1,0
1,2
300
400
500
600
700
800
900

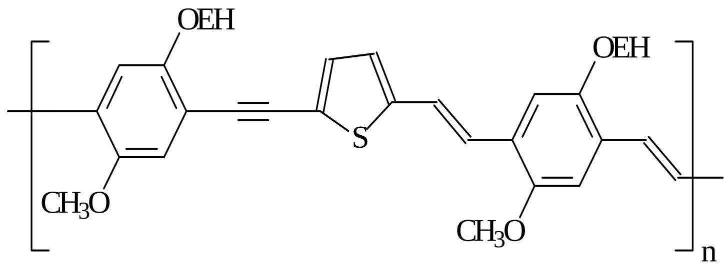
Effect of Fullerene Derivatives



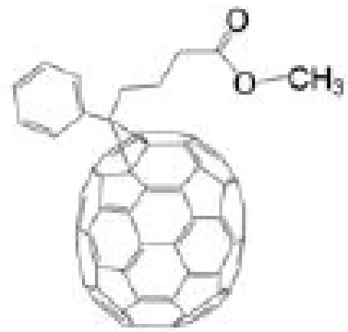
P. Troshin *et al*. *Adv. Funct. Mater*. **2009**, *19*, 779.

Effect of Fullerene Derivatives



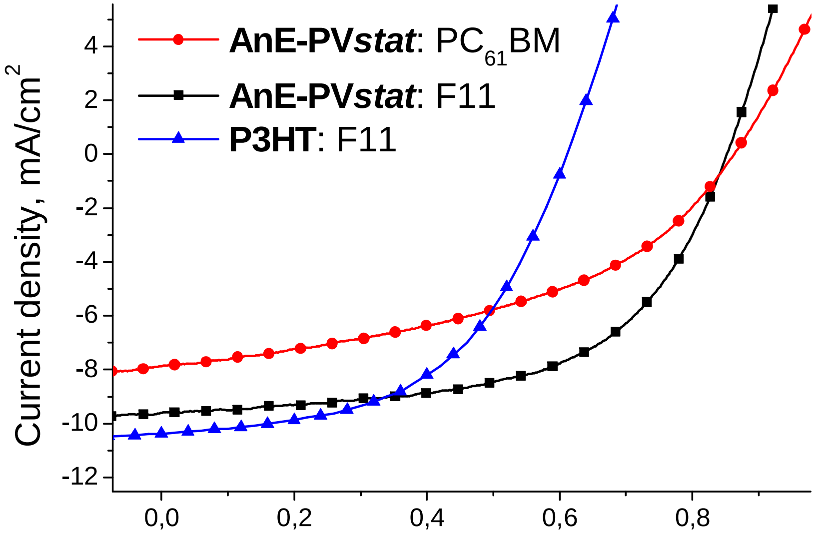


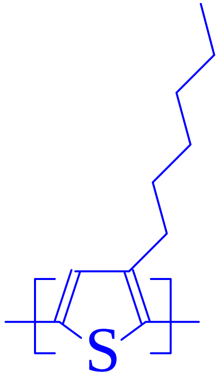
η≈ 2.3%



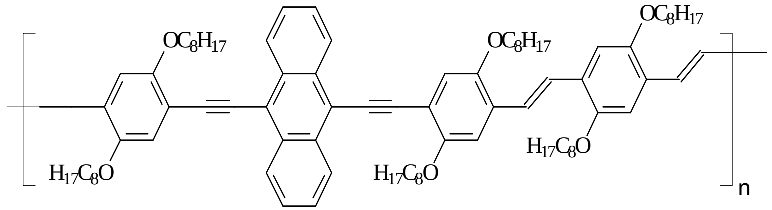
F9
[70]PCBM

J. Mater. Chem. **2011**, 21,2356-2361





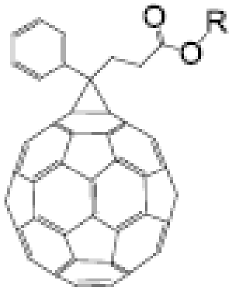
P3HT



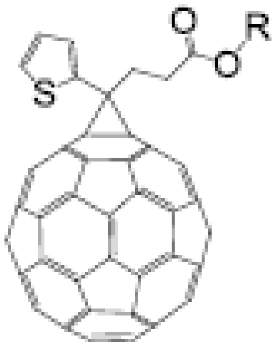
AnE-PV*stat*

M_n = 5000 g/mol

M_w = 18000 g/mol



F3 R=Pr-*n*



F10 R= Pr-*n*
F11 R= Bu-*n*

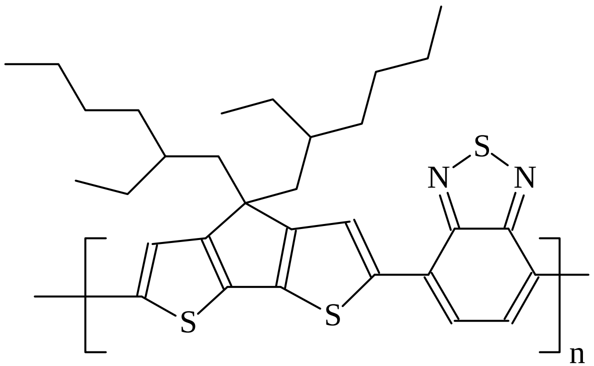
η= 4.8-5%

Active layer	V_{OC} [mV]	J_{SC} [mA/cm^2]	FF [%]	η [%]
P3HT:PCBM (1:1)	**640**	**10.6**	**55**	**3.7**
P3HT:F11 (1:1)[a)]	**605**	**10.1**	**53**	**3.3**
stat:PCBM (1:2)[a)]	870	8.0	49	3.4
stat:PCBM (1:3)	836	5.2	48	2.1
stat:F3 (1:2)	**822**	**9.2**	**65**	**4.9**
stat:F3 (1:2)	809	8.5	68	4.7
stat:F11 (1:3)[a)]	**852**	**9.9**	**58**	**4.9**
stat:F11 (1:3)	**860**	**9.7**	**59**	**5.0**
stat:F11 (1:3)	850	9.3	61	4.8
stat:F11 (1:3)	856	9.5	59	4.8

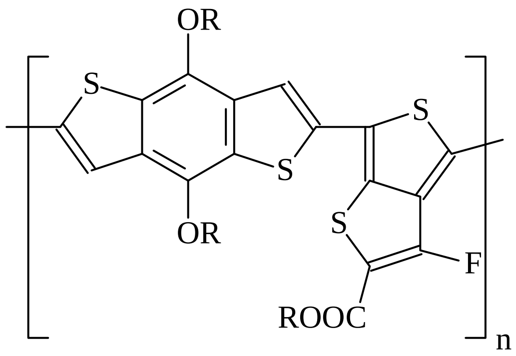
Some Conditions for High Performance Solar Cells Donor Materials

- Low band gap polymer (but not too low)
- Optimized side chain volume fraction
- Planarized conjugated backbone + high ordering
- Moderate stacking ability
- Face-on alignment on the substrate

Favored by branched side chains



PCPDTBT



R = 2-ethylhexyl

PTB7

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