Development of new oligomeric and polymeric materials for bulk heterojunction photovoltaic cells and photodetectors

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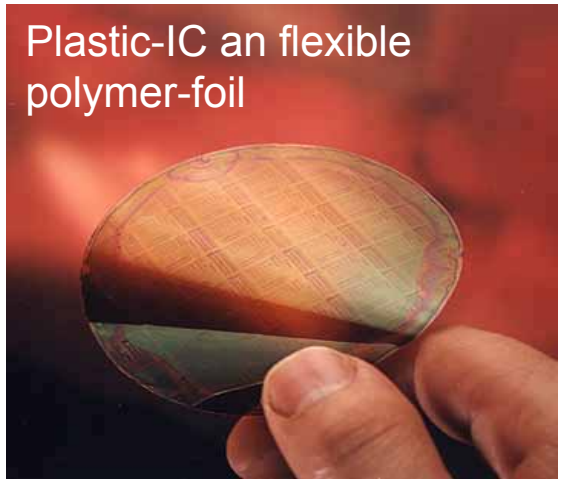
OUTLINE

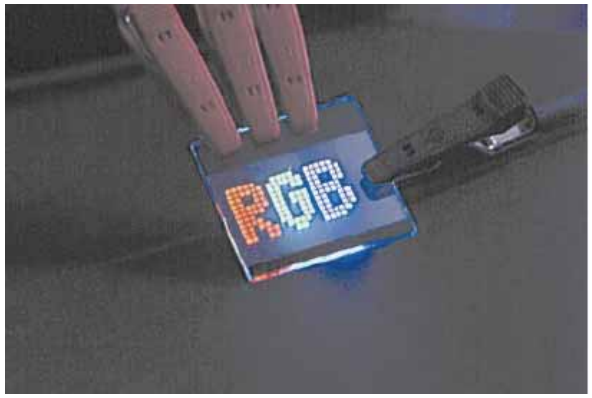
- Introduction
- Organosilicon derivatives of α,α’-dialkyloligothiophenes
- Oligothiophenesilanes
- Low band gap copolymers
- Conclusions

Organic electronics

Organic thin-film transistors (OTFTs, OFETs) and IC



Organic light emitting diodes (OLEDs) and displays



NATURE | VOL 421 | 20 FEBRUARY 2003

Organic photovoltaics (solar cells & photodetectors)

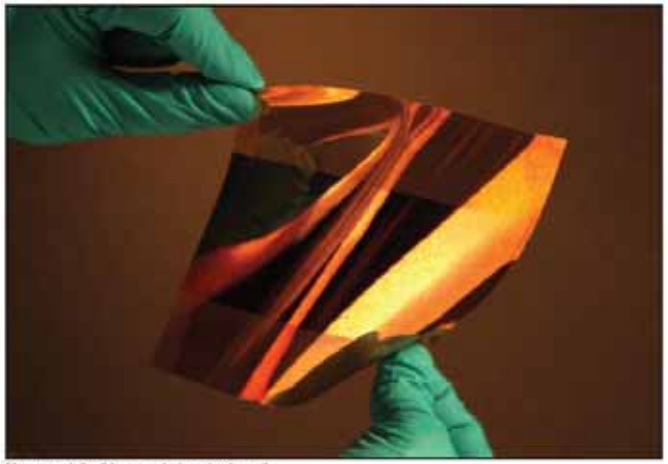


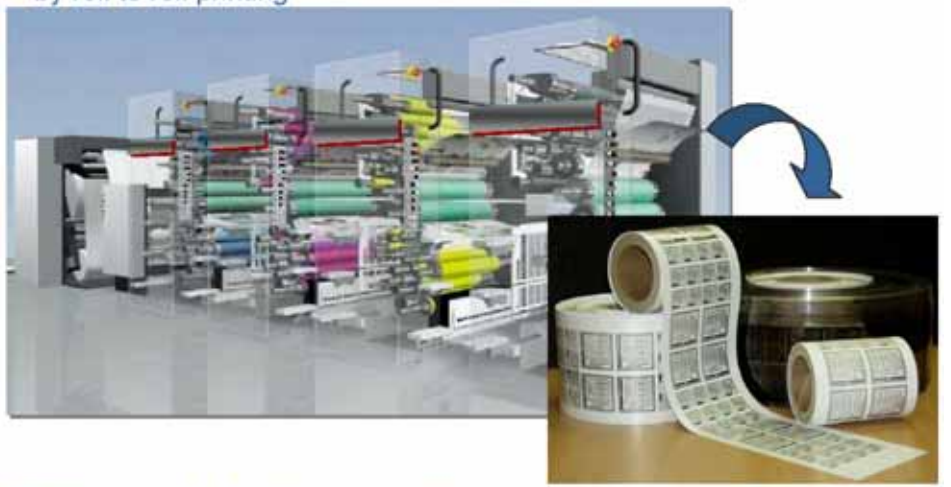
Figure 1. A flexible, organic-based solar cell

NATURE | VOL 428 | 29 APRIL 2004

The production of plastic chips tomorrow

Continuous printing methods for low cost polymerelectronics

- by roll to roll printing

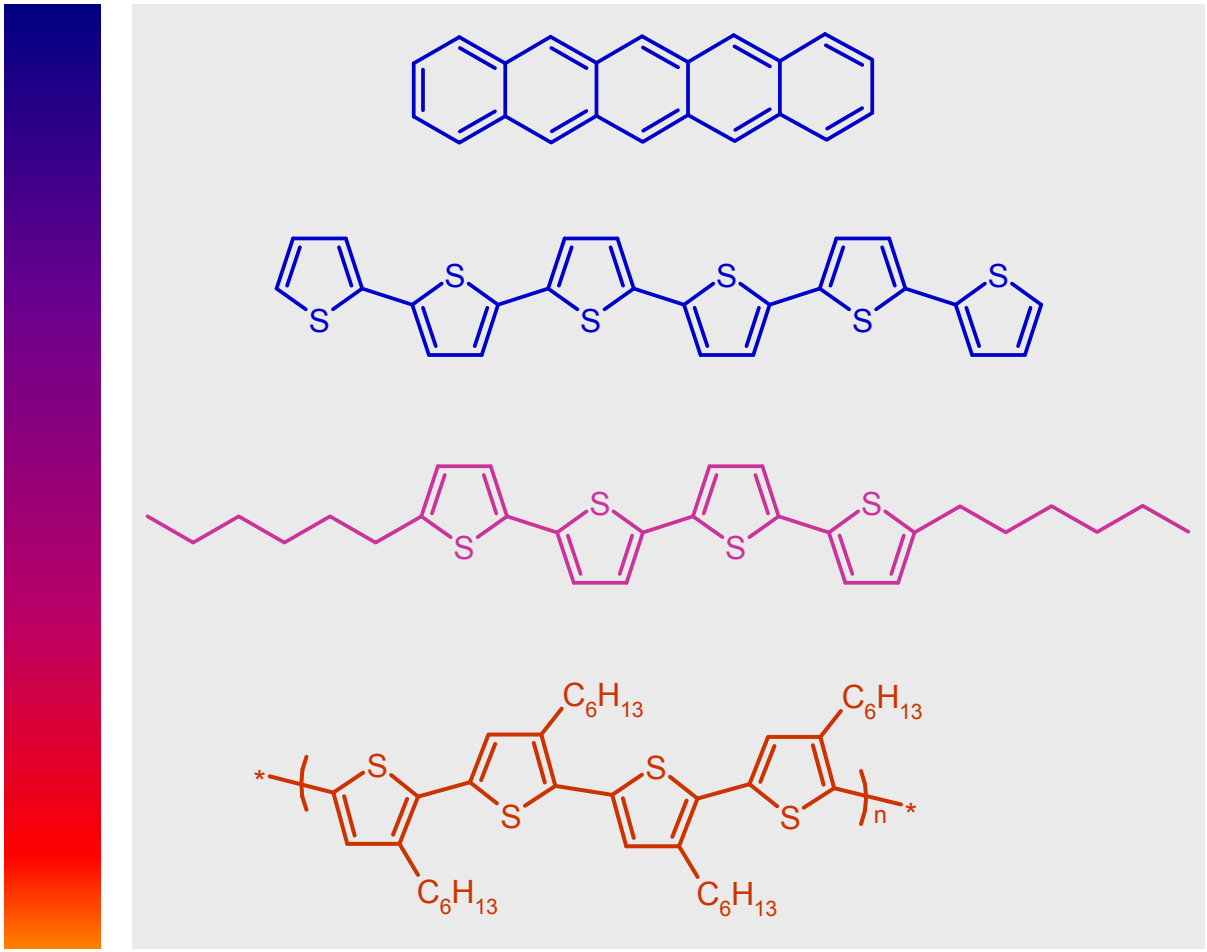


"let´s print electronics like a newspaper"

NDIP

Organic Semiconductors

Evaporation



Pentacene

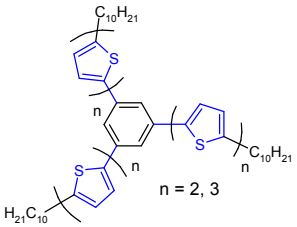
Sexithiophene

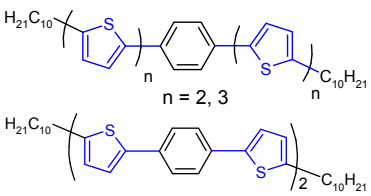
α, α’ -dihexyl-quaterthiophene

Poly(hexylthiophene)

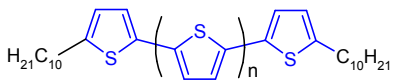
Spincoating

Functional materials for Organic Electronics and Photonics @ ISPM RAS

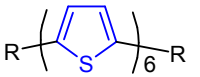




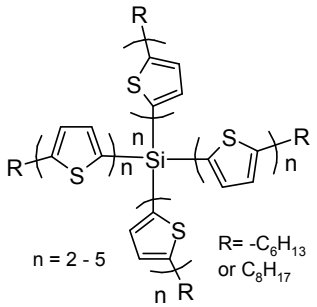
Linear oligomers



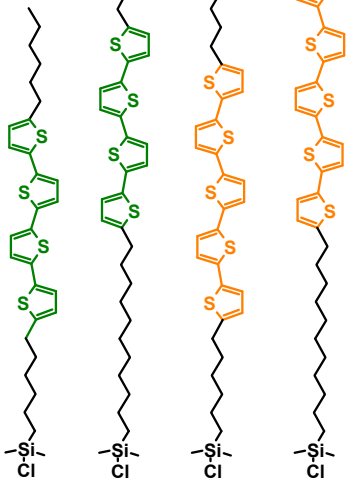
n = 2 Dec-4T-Dec
n = 3 Dec-5T-Dec
n = 4 Dec-6T-Dec

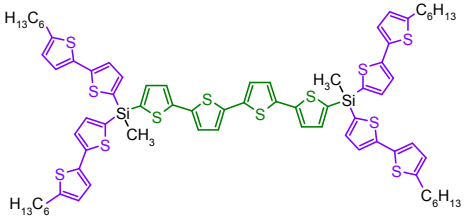


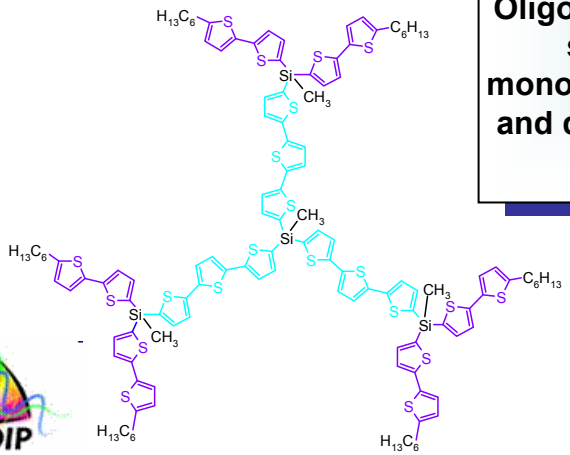
R = H, -C_2H_5, -C_6H_{13}, -$C_{10}H_{21}$



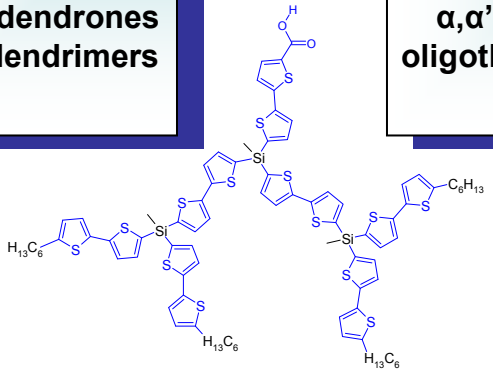
Branched Oligothiophene-silanes



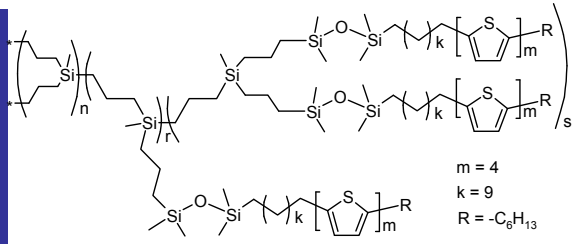


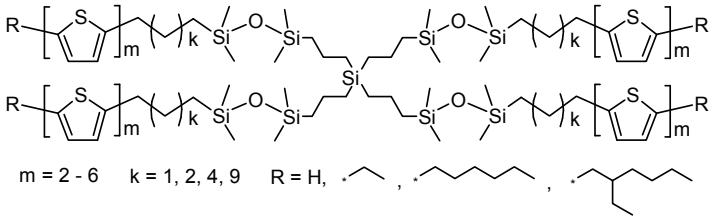


Oligothiophene-silane monodendrones and dendrimers



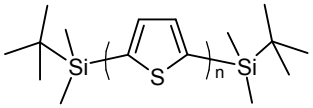
Organosilicon derivatives of α,α'-dialkyl-oligothiophenes





oligothiophenes

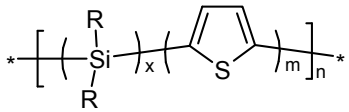
Oligo- and polyarylsilanes of different molecular structure



n = 3 - 6

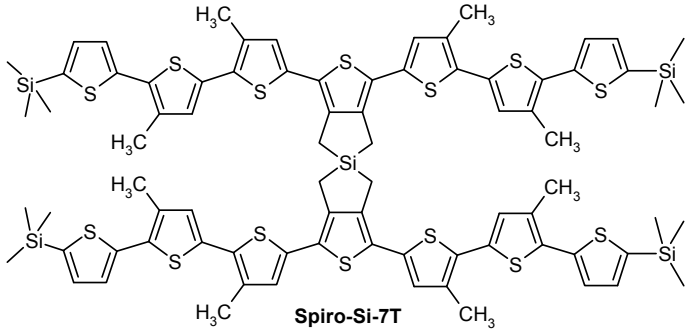
***t*BuMe$_2$Si-Tn-Si-Me$_2$*t*Bu**

Barbarella G, at. al., *Chem. Mater.* **1998**, 10, 3683



MSmT, x=1, m = 3-5, R=Et
DSmT, x=2, m = 3-5, R=Et
TSmT, x=3, m = 3-5, R=Me

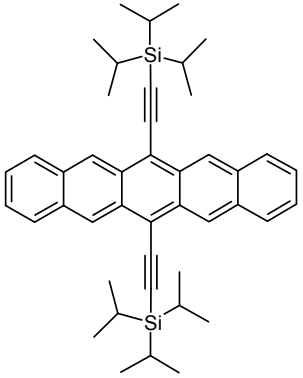
Kunai A. et.al., *Organometallics* **1996**, 15, 2000



Guay J, Diaz A, Wu R, Tour JM, *J Am Chem Soc* **1993**, 115, 1869

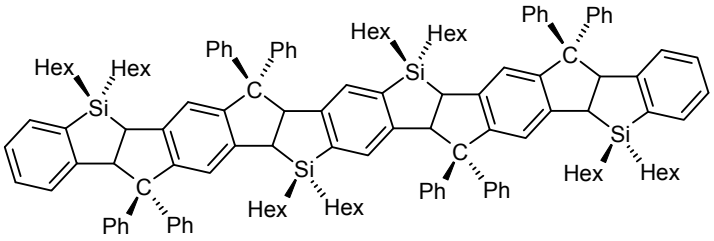
H. Tang, Y. Harima, M. Ishikawa et. al., *J. Chem. Soc., Perkin Trans. 2*, **2000**, 1976

J. Nakayama, J.-S. Lin, *Tetrahedron Lett.* **1997**, 38, 6043

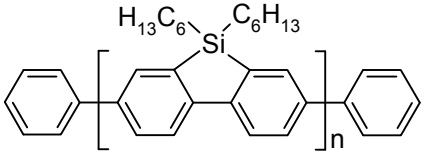


TIPS-5AC

Anthony JE et. al. *Chem Soc* **2001**, 123, 9482



Xu C, Wakamiya A, Yamaguchi S *J Am Chem Soc* **2005**, 127, 1638



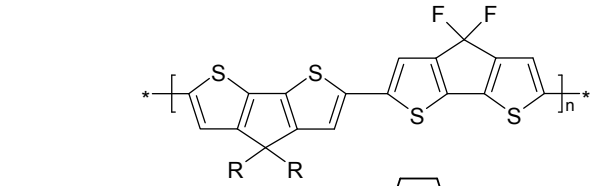
Holmes AB, at. al., *J Am Chem Soc* **2005,** 127, 7662

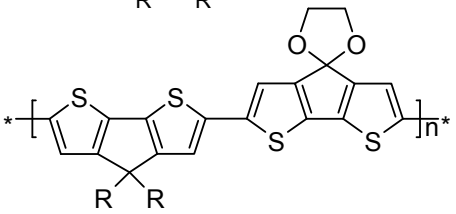
See review: S.A. Ponomarenko, S. Kirchmeyer, ***Adv. Polym. Sci.*, 2011**, 235, 33 - 110.

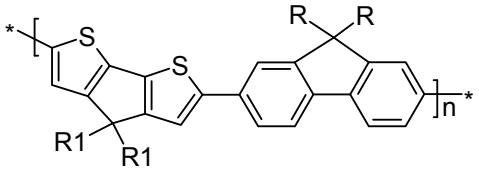
New materials for polymer BHJ solar cells and photodetectors

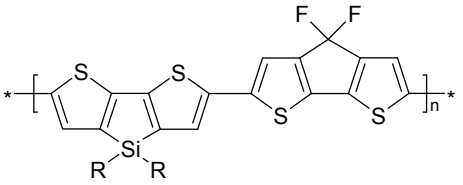
New materials

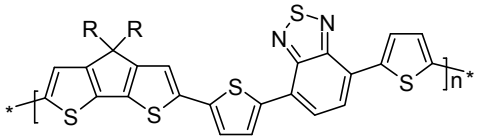
Low band gap polymers

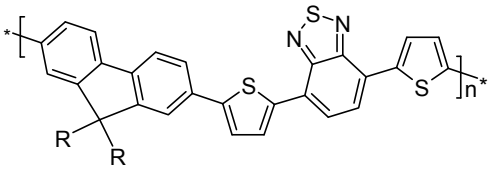




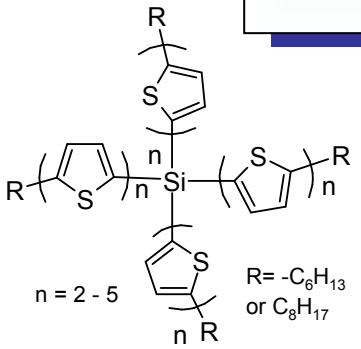




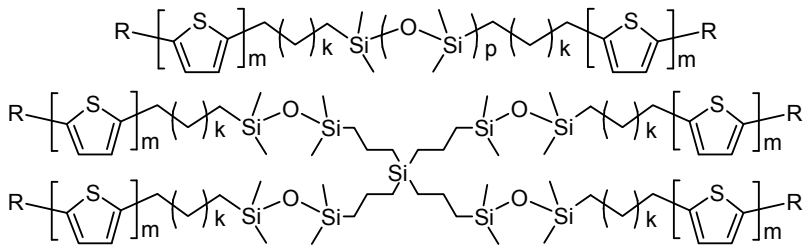




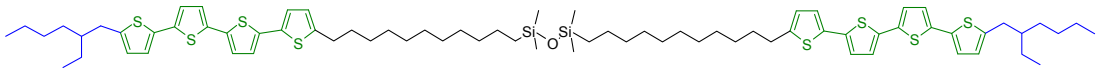
Branched Oligothiophene-silanes



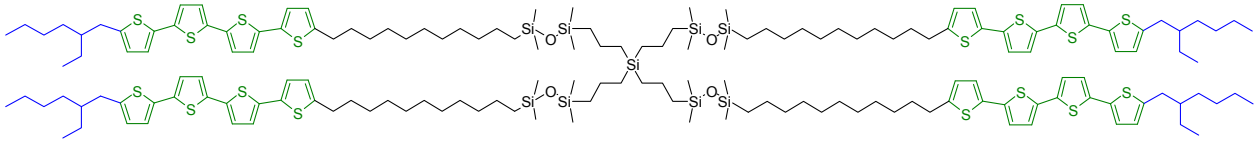
Organosilicon derivatives of α,α'-dialkyl-oligothiophenes



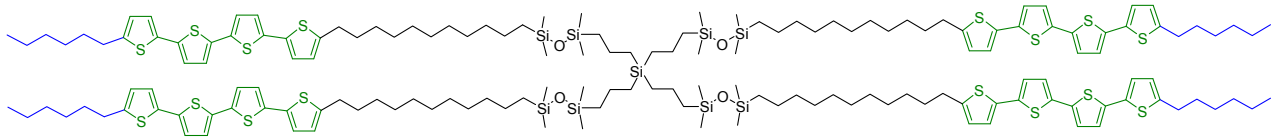
Organosilicon derivatives of α,α'-dialkyloligothiophenes



D1

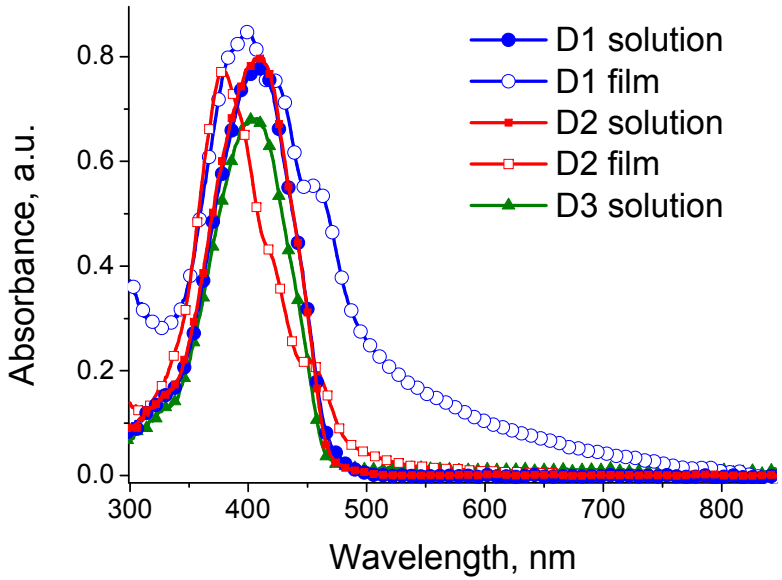


D2

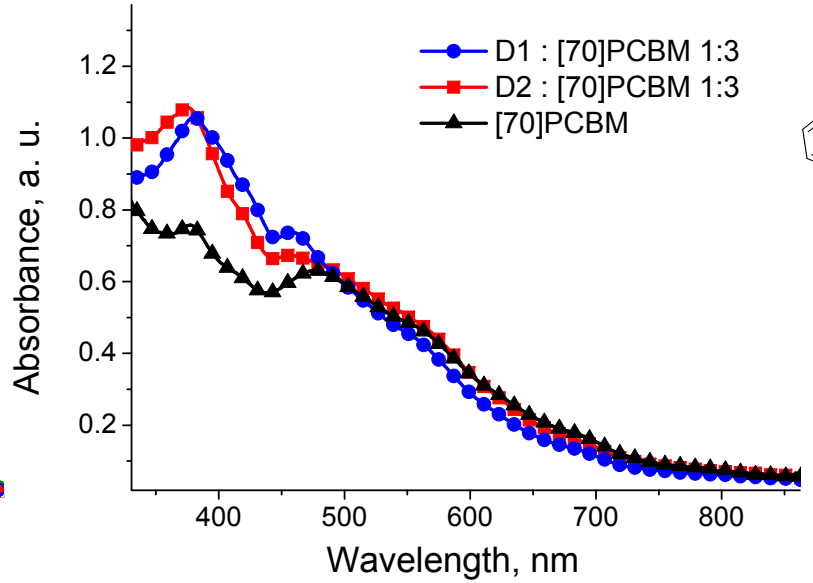


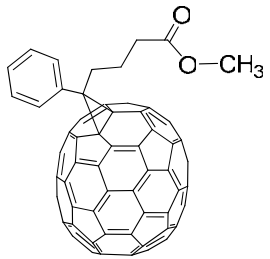
D1

UV- Vis absorption spectra



Thin films absorption spectra

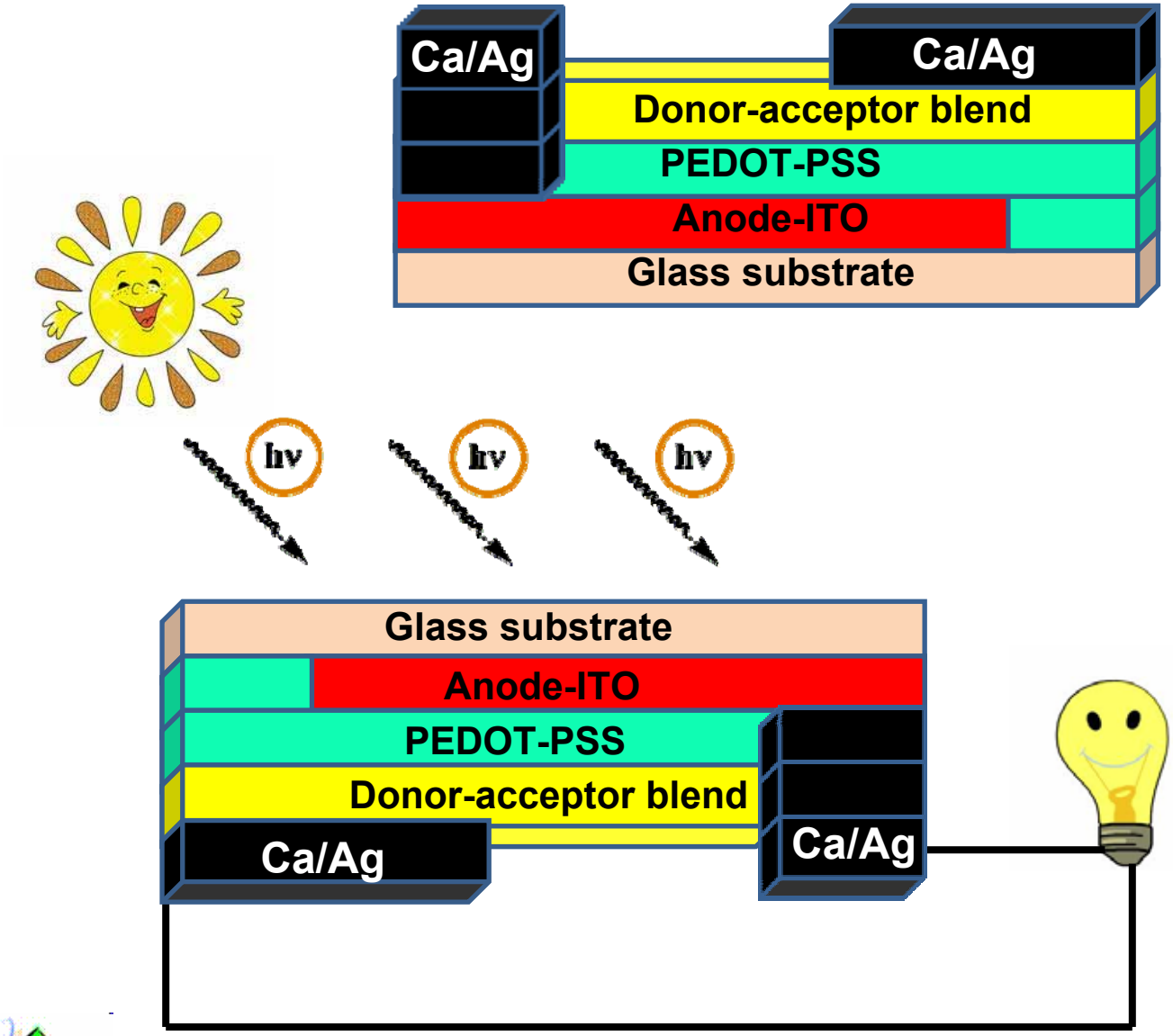




[70]PCBM

Solar Energy Materials and Solar cells **2010**, 94, 2064

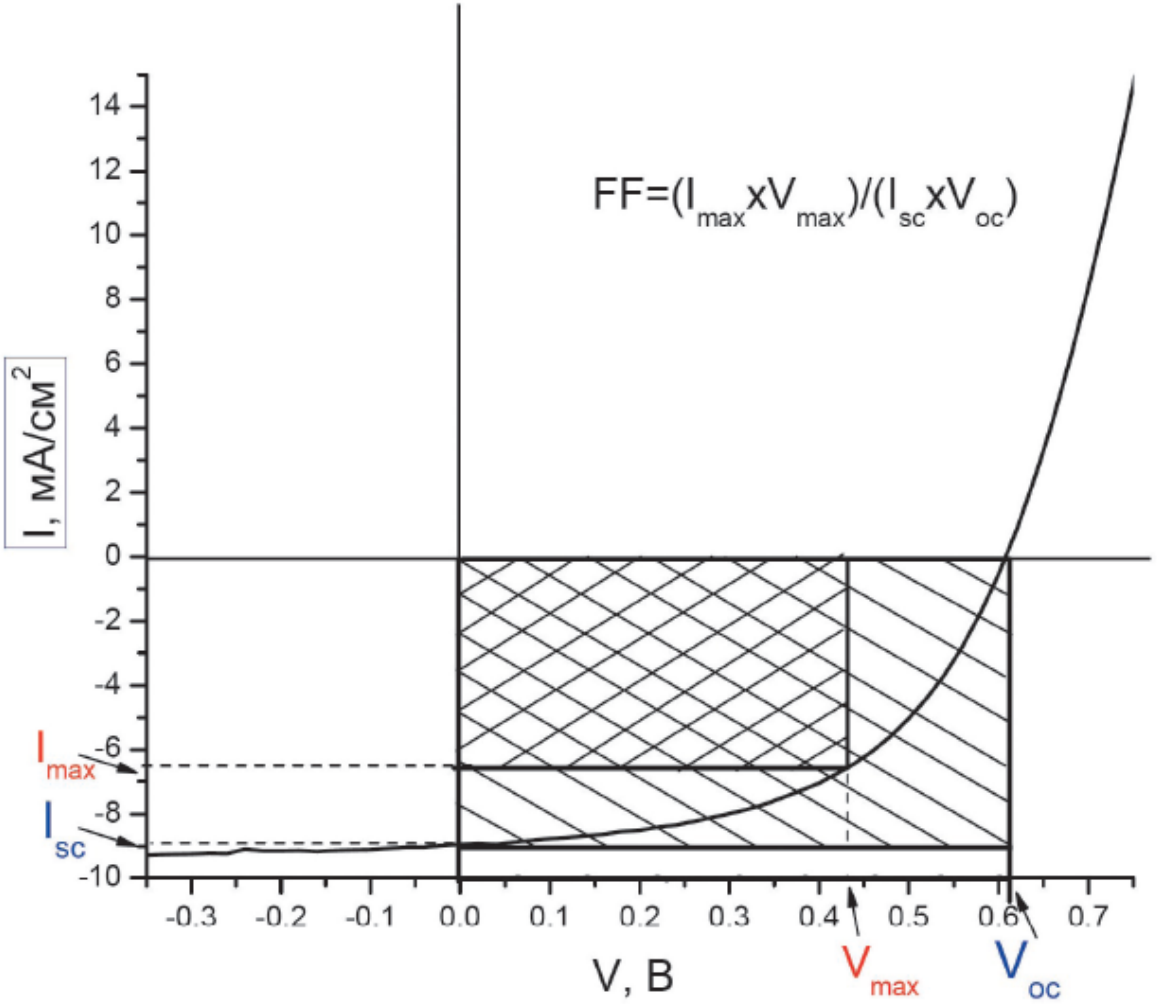
Preparation of test devices for organic photovoltaic cells



Schematic

Photograph

Typical electrical characteristics of photovoltaic cells



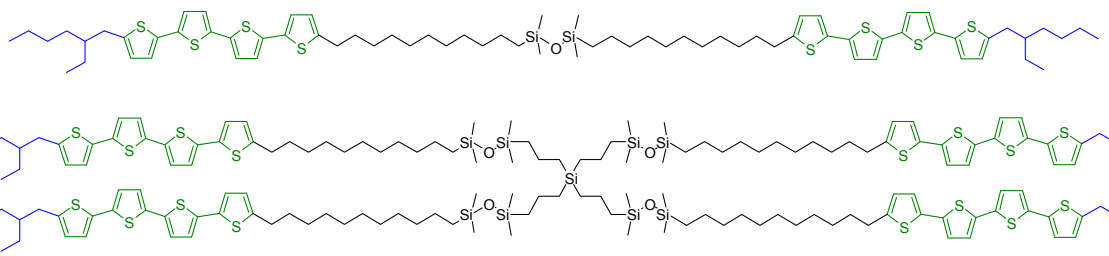
I_{sc} – short circuit current

V_{oc} – open circuit voltage

FF – fill factor

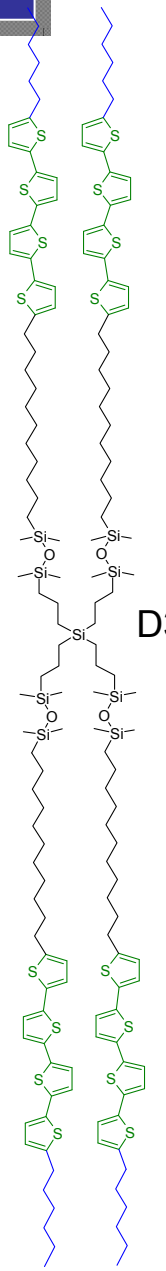
$$\eta = \frac{I_{\max} V_{\max}}{P_{light}} \times 100\% = \frac{I_{sc} V_{os} FF}{P_{light}} \times 100\%$$

Organosilicon derivatives of α,α'-dialkyloligothiophenes



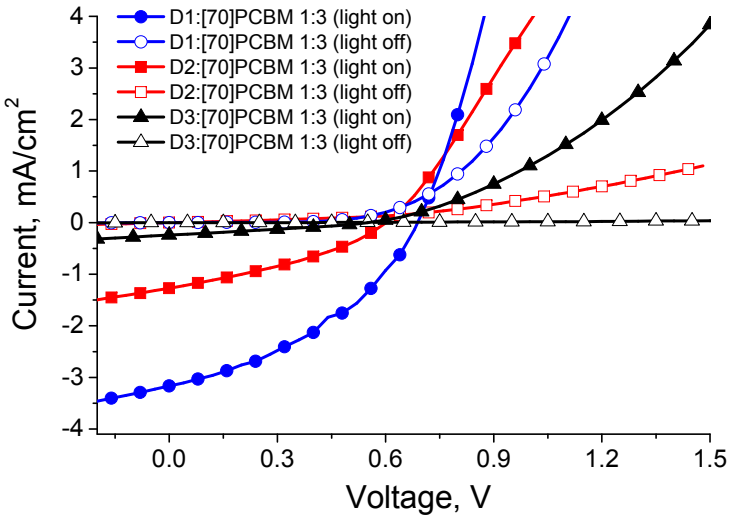
D1

D2

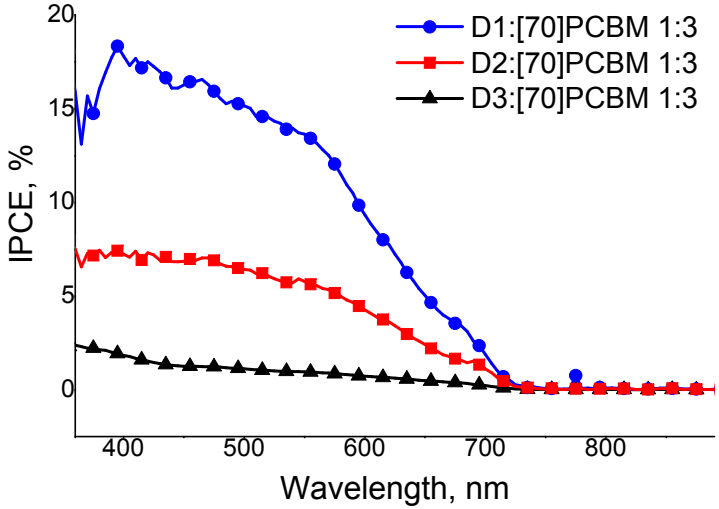


D3

Light-on and light-off I-V curves



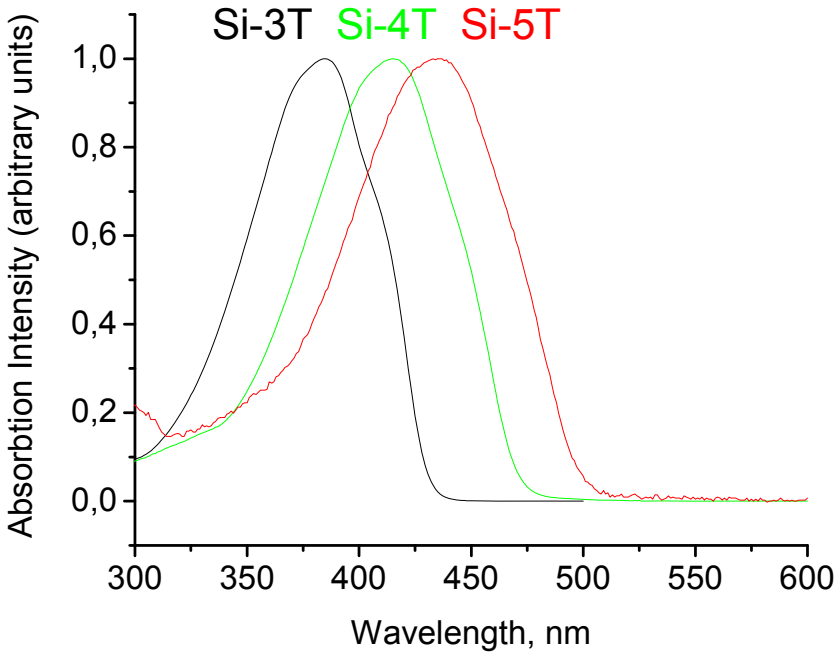
IPCE spectra



Com-pound	OFETs		Photovoltaic cells			
	μ, cm^2/Vs	On/Off Ratio	V_{oc}, mV	FF, %	I_{sc}, mA/cm^2	PCE, %
D1	-	-	**680**	**40**	**3.2**	**0.9**
D2	0,0002	260	600	35	1.3	0.27
D2	**0,02**	**10^6**	360	29	0.45	0.05

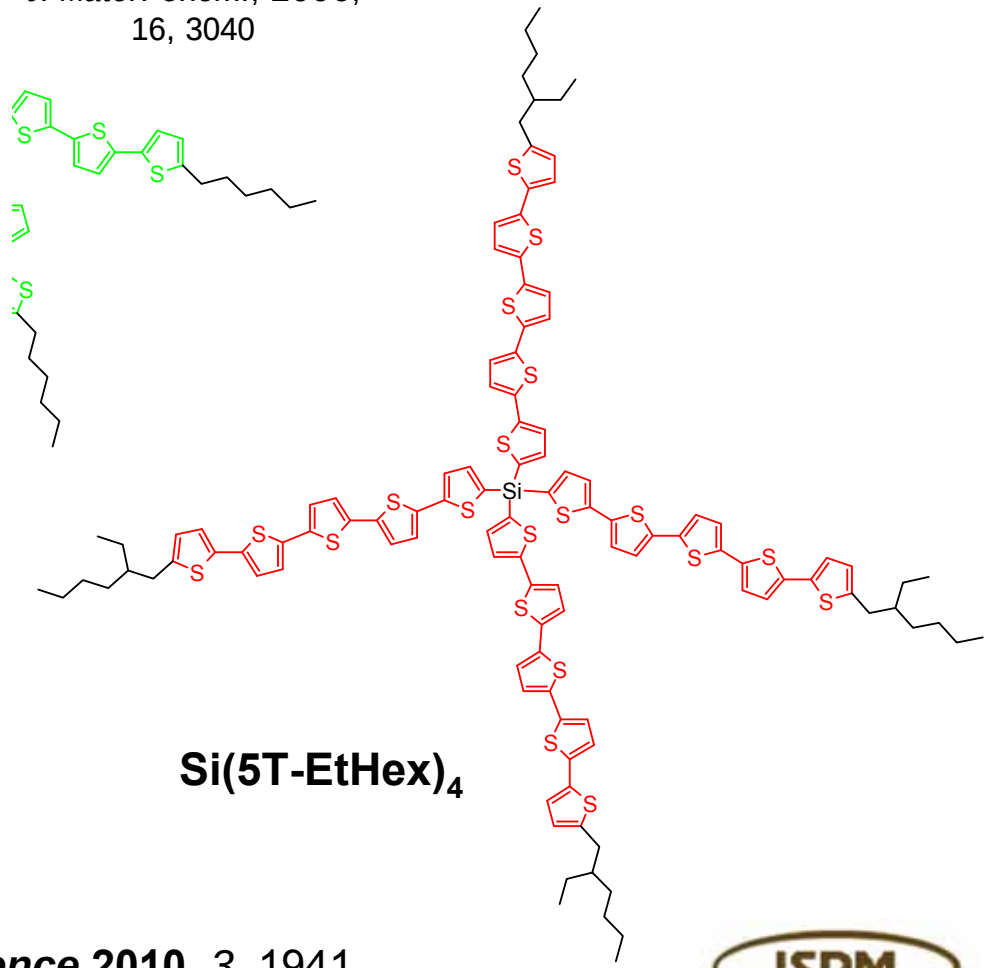
***Energy & Environmental Science* 2010**, *3*, 1941

Tetrakis(ter-, quater- and quinquethiophene)silanes



PCE = 0.3 %

J. Roncali, et. al.,
J. Mater. Chem., **2006**,
16, 3040

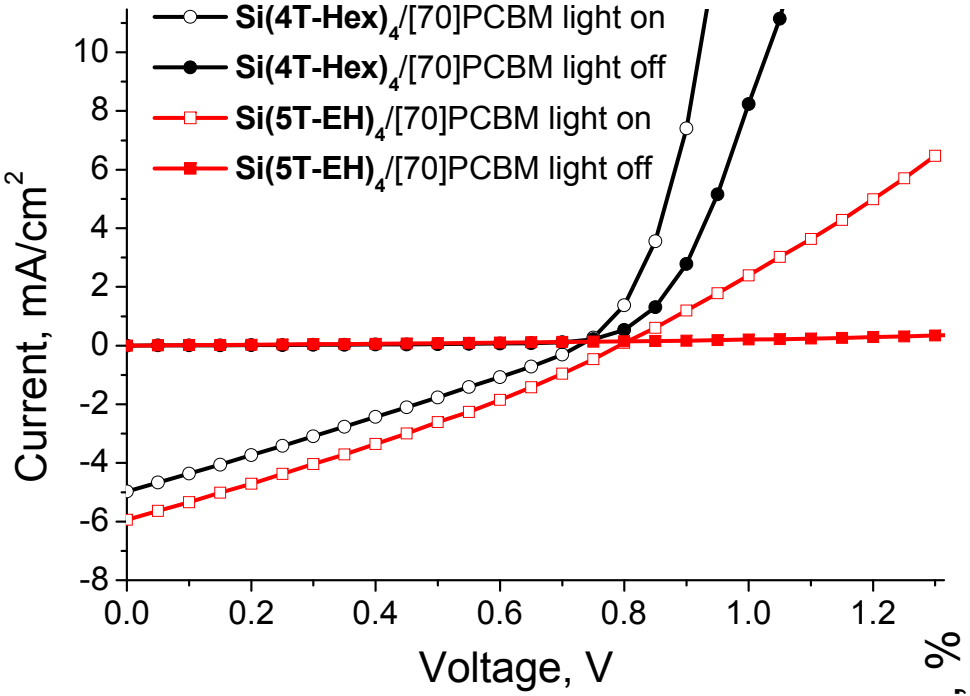


Si(5T-EtHex)$_4$

Com-pound	Photovoltaic cells			
	V_{oc}, mV	FF, %	I_{sc}, mA/cm^2	PCE, %
Si-3T	830	25	2.9	0.6
Si-4T	750	26	5.0	1.0
Si-5T	**800**	**28**	**6.0**	**1.4**

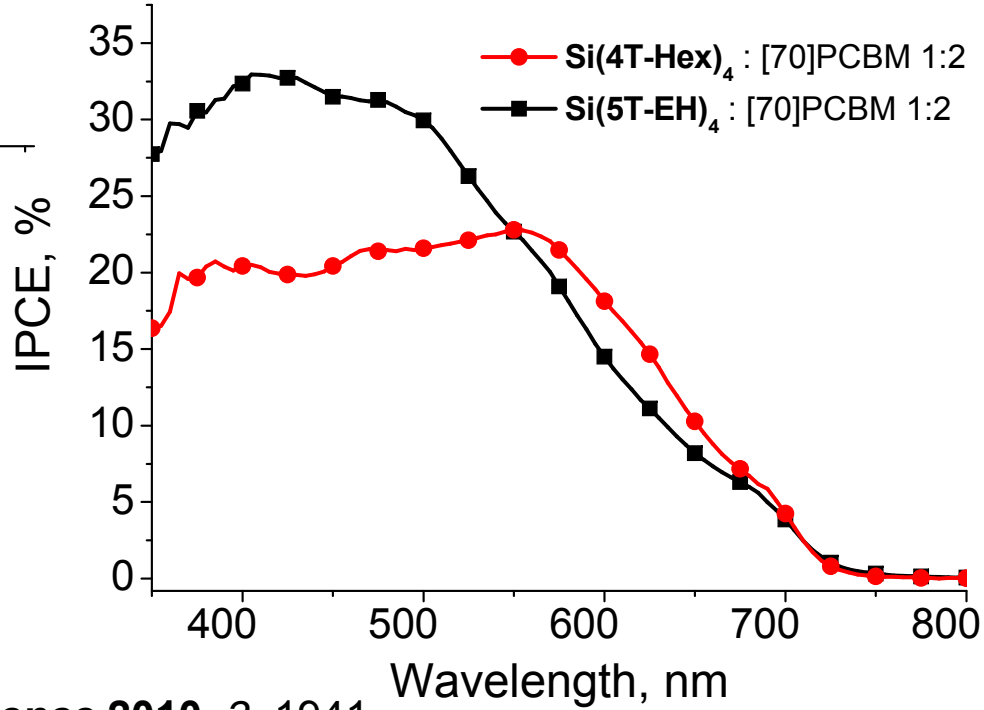
Energy & Environmental Science **2010**, *3*, 1941

I-V characteristics and IPCE spectra of photovoltaic cells based on oligothiophenesilanes



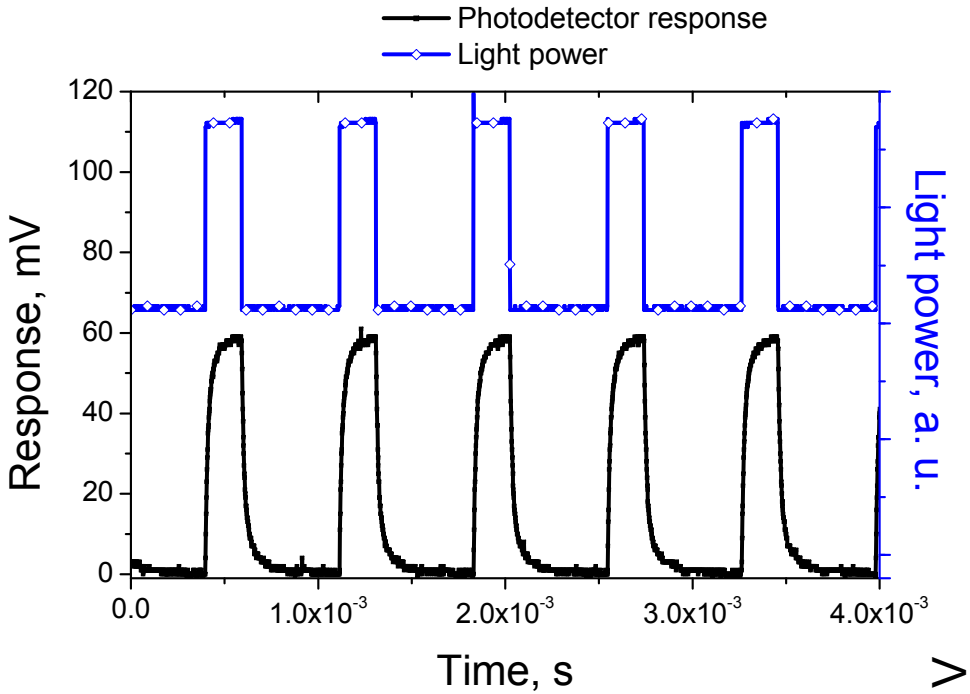
Light-on and light-off I-V curves for photovoltaic cells comprising blends **Si(4T-Hex)$_4$**/[70]PCBM and **Si(5T-EH)$_4$**/[70]PCBM in the photoactive layers

IPCE spectra for devices comprising **Si(4T-Hex)$_4$**/[70]PCBM and **Si(5T-EH)$_4$** /[70]PCBM blends in the active layers



Energy & Environmental Science **2010**, *3*, 1941

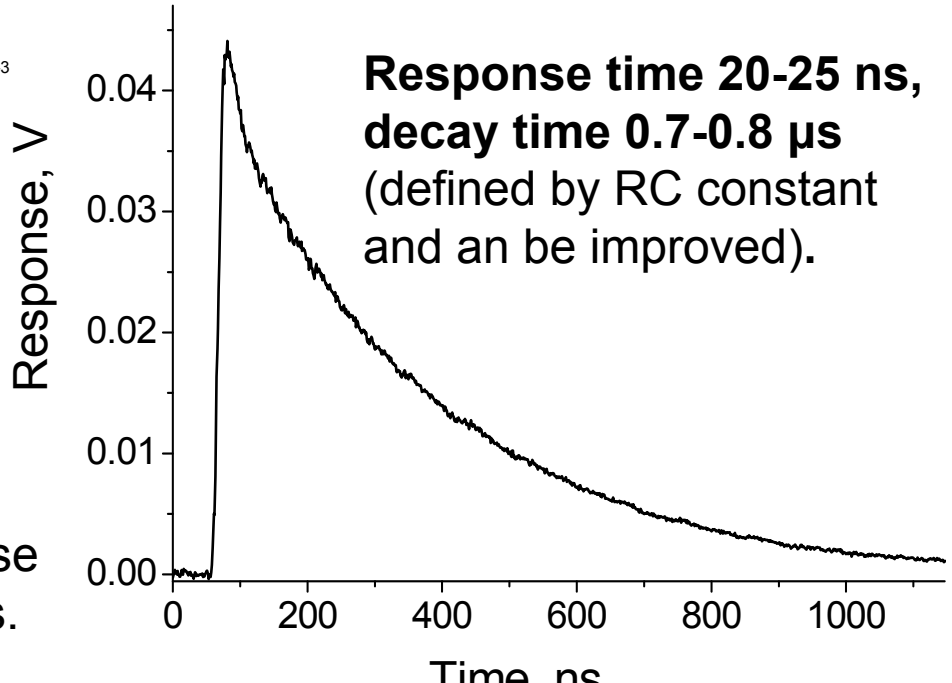
Photodetectors based on $Si(4T\text{-}Hex)_4$ / [70]PCBM BHJ



Detection of light pulses modulated at 5kHz with organic photodetector.

RC constant: 0.3 μs
Load resistance: 60 Ω
Device area: 0.12 cm^2

Transient response of organic photodetector to 10 ns light pulse from nitrogen laser (337 nm).



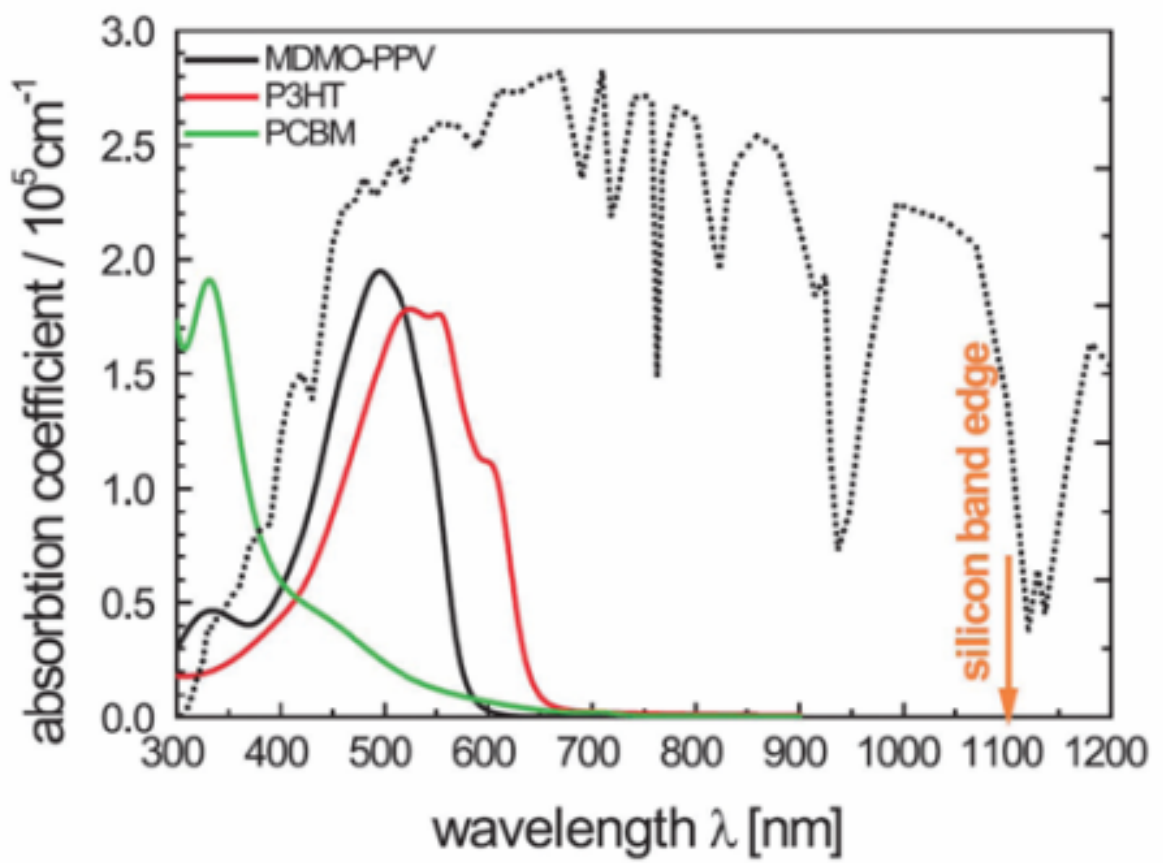
Response time 20-25 ns, decay time 0.7-0.8 μs (defined by RC constant and an be improved).

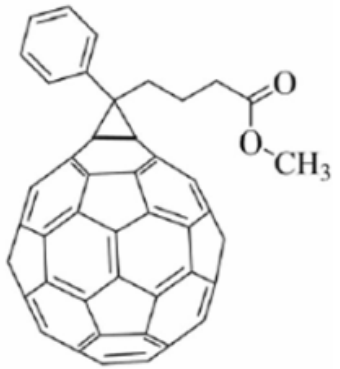
The reference devices based on P3HT/[70]PCBM blends yielded response time of 1–2 μs and decay time of 3–4 μs.

NDIP

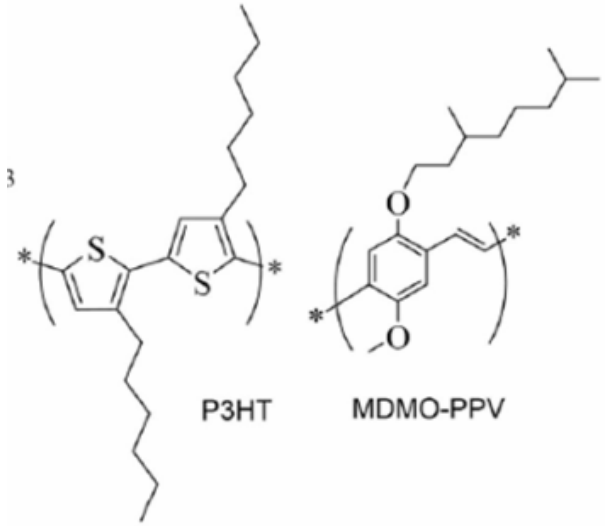
***Energy & Environmental Science* 2010**, *3*, 1941

Solar light spectra and absorption spectra of the mostly used materials



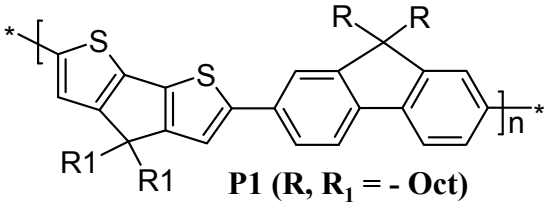


PCBM



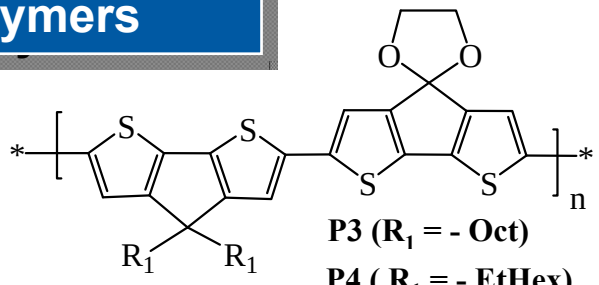
P3HT MDMO-PPV

Low band gap copolymers



P1 (R, R_1 = - Oct)

P2 (R = Oct, R_1 = - EtHex)



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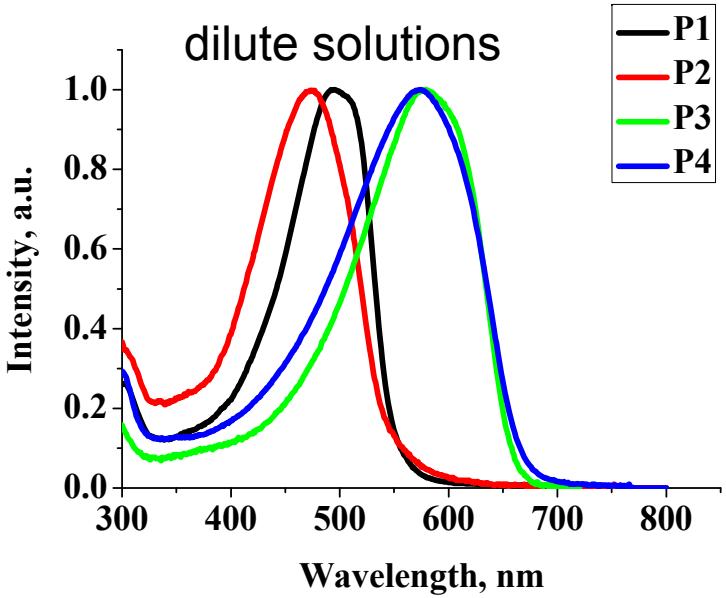
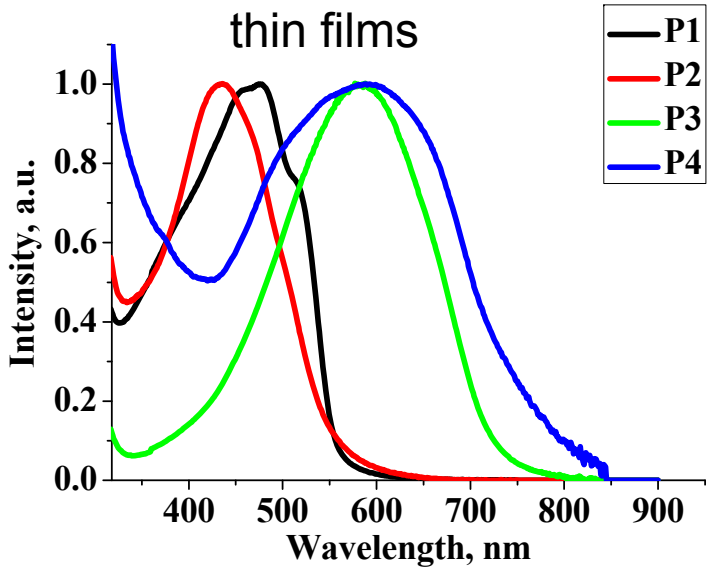
P4 (R_1 = - EtHex)

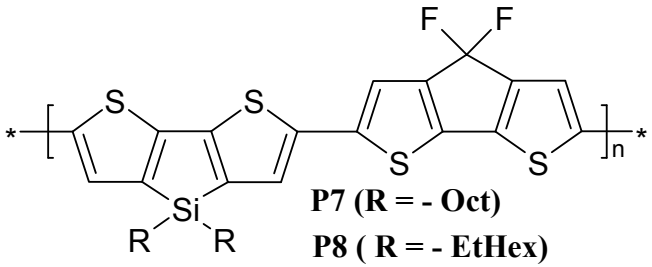




	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt} eV, (solution)	ΔE_{opt}, eV (film)
P1	8400	11900	1.42	495	478	2.24	2.21
P2	2700	4500	1.67	474	434	2.25	2.19
P3	7500	12500	1.67	574	585	1.89	1.69
P4	6700	10000	1.49	577	594	1.88	1.59

NDIP

Low band gap copolymers



P7 (R = - Oct)
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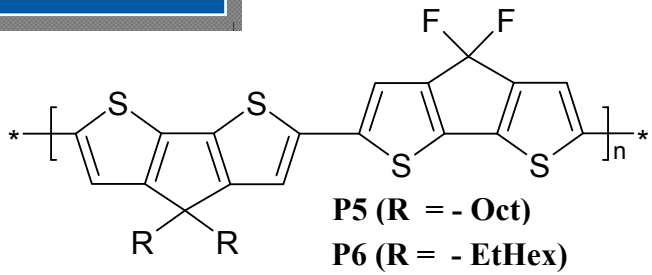

P5 (R = - Oct)
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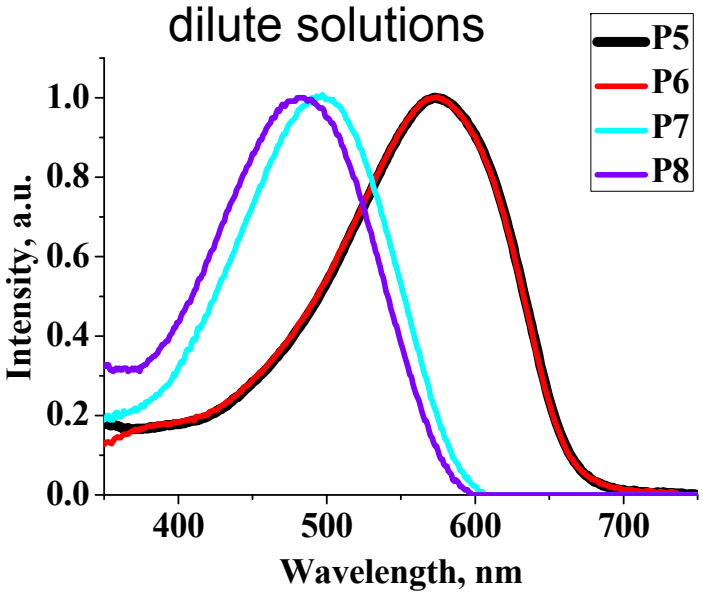
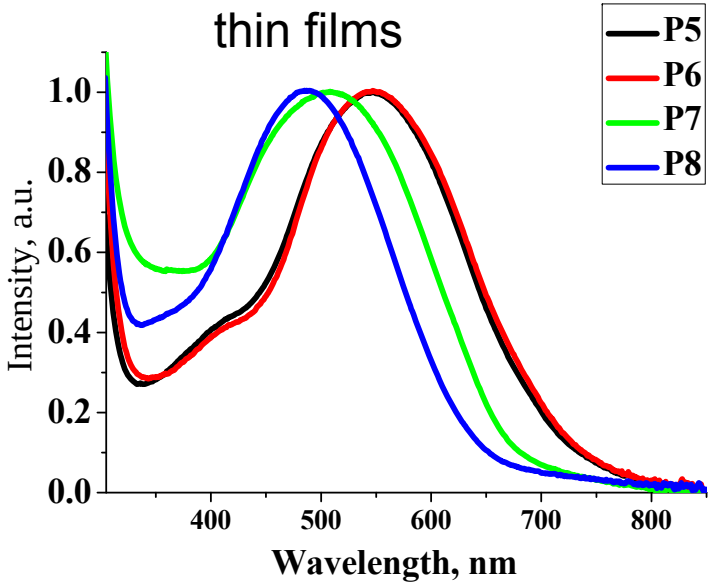
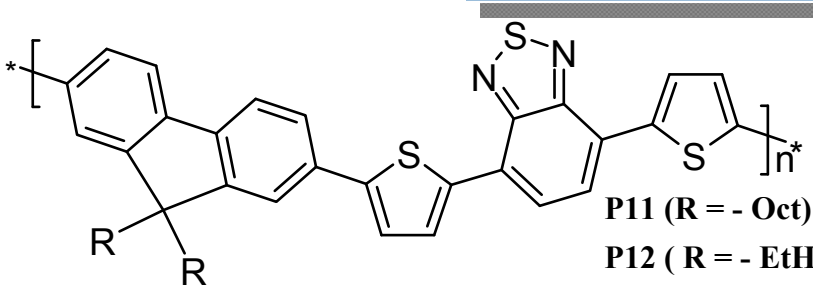




	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt} eV, (solution)	ΔE_{opt}, eV (film)
P5	11000	13900	1.26	573	547	1.85	1.60
P6	7900	10500	1.33	572	554	1.85	1.62
P7	4000	5000	1.20	495	510	2.11	1.79
P8	4600	6000	1.30	481	494	2.16	1.88

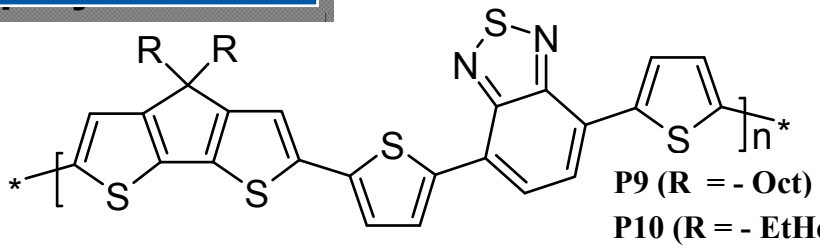
NDIP

Low band gap copolymers



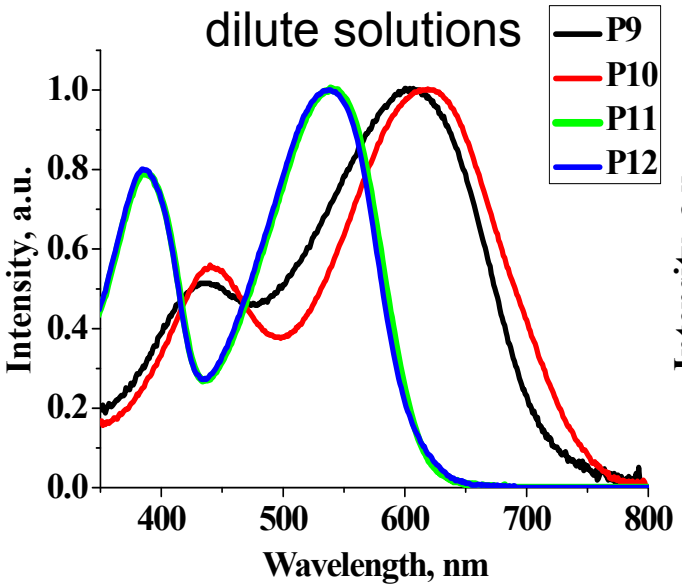
P11 (R = - Oct)

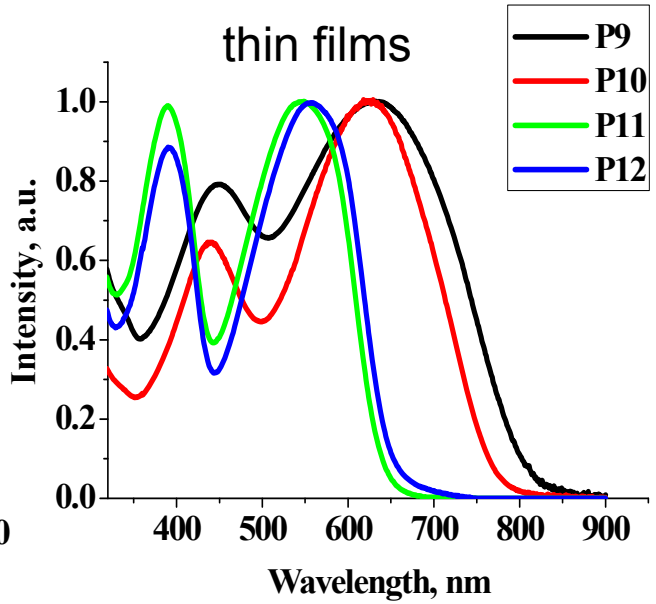
P12 (R = - EtHex)

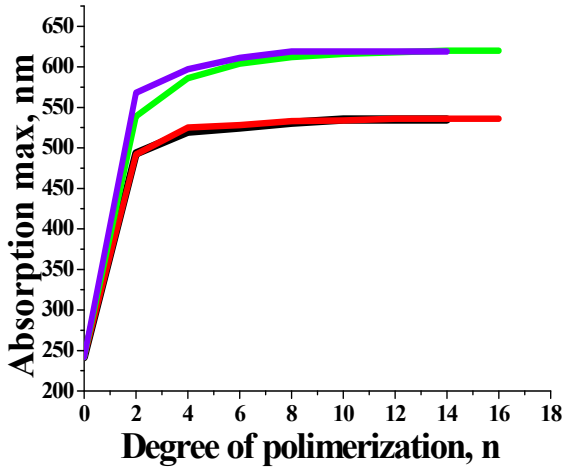


P9 (R = - Oct)

P10 (R = - EtHex)



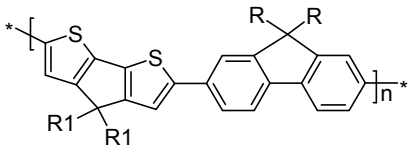




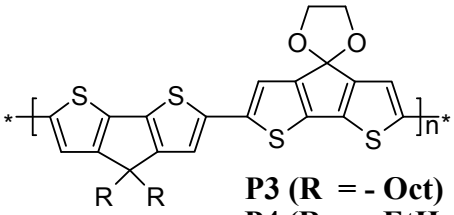
	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt} eV, (solution)	ΔE_{opt}, eV (film)
P9	18200	25500	1.40	609	637	1.73	1.55
P10	10600	15000	1.42	617	624	1.65	1.60
P11	9300	15700	1.63	538	545	2.03	1.92
P12	8300	12300	1.47	539	560	2.02	1.90

NDIP

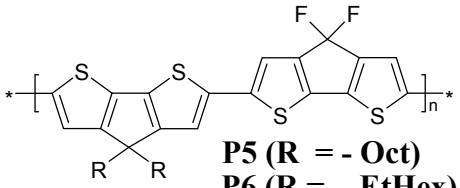
Low band gap copolymers



P1 (R, R_1 = - Oct)
P2 (R = Oct, R_1 = - EtHex)



P3 (R = - Oct)
P4 (R = - EtHex)



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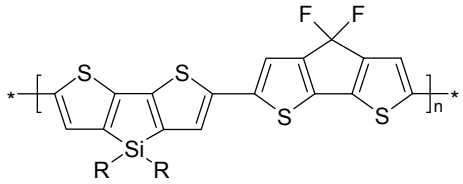

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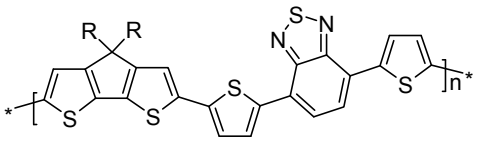
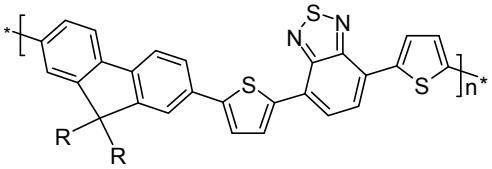
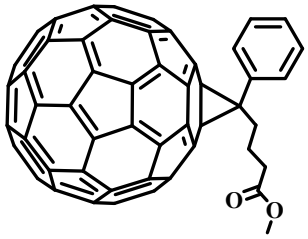


P9 (R = - Oct)
P10 (R = - EtHex)



P11 (R = - Oct)
P12 (R = - EtHex)



F1 - [60]PCBM

No.	ΔE_{opt} eV, in film	Px / F1	I_{sc}, mA/cm^2	V_{oc}, мV	FF, %	η, %
P1	2.21	1 : 1	1.43	522	53	0.80
P2	2.19	1 : 2	2.94	561	32	0.20
P3	1.69	1 : 2	1.45	365	27	0.14
P4	1.59	1 : 2	3.10	565	41	0.70
P5	1.60	1 : 3	2.50	525	37	0.50
P6	1.62	1 : 3	2.10	516	37	0.41
P7	1.79	1 : 3	2.57	720	39	0.73
P8	1.88	1 : 4	1.57	631	33	0.33
P9	1.55	1 : 2	10.23	500	41	2.09
P10	1.60	1 : 2	3.70	500	35	0.65
P11	1.92	1 : 4	10.50	900	42	3.97
P12	1.90	1 : 4	8.1	900	35	2.55

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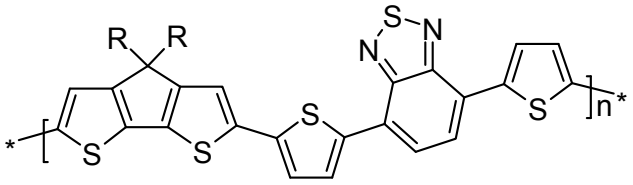
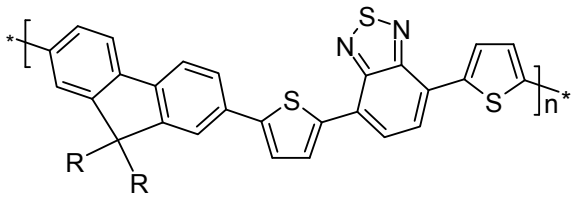
I-V characteristics and IPCE spectra of low band gap copolymers



P9 (R = - Oct)



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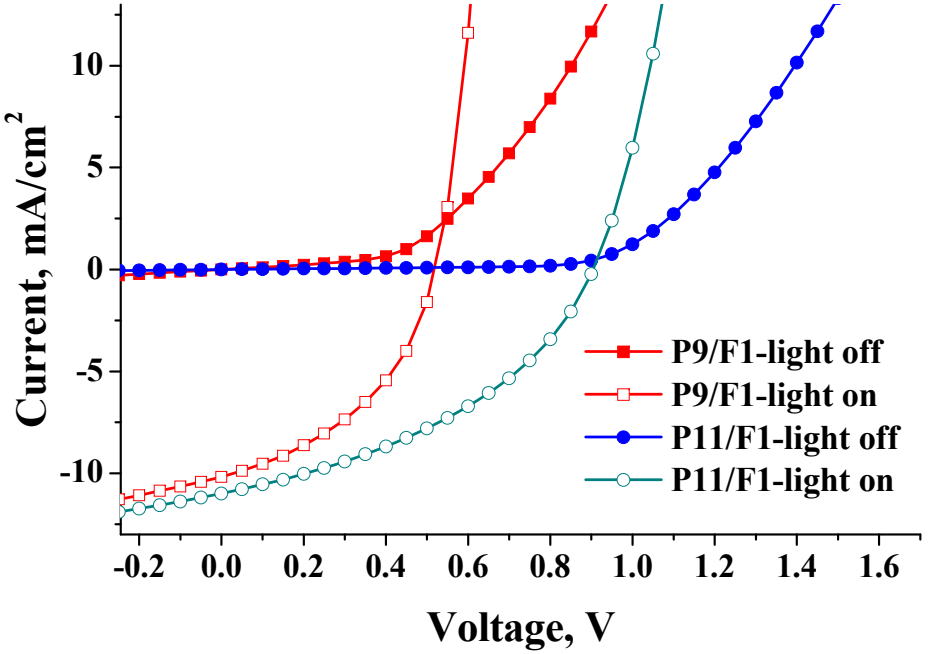
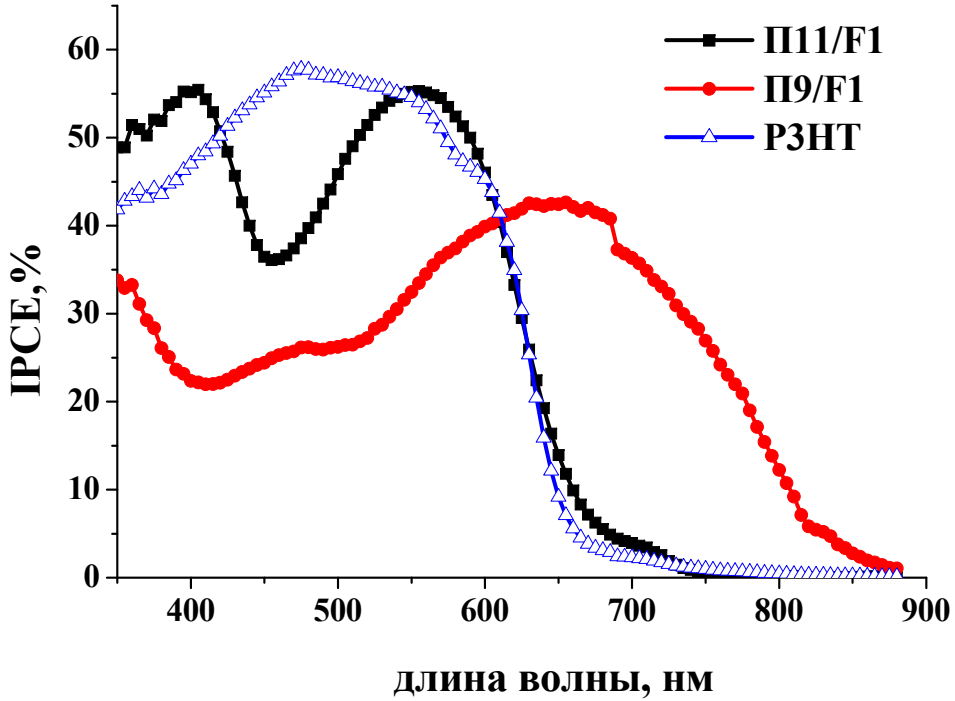
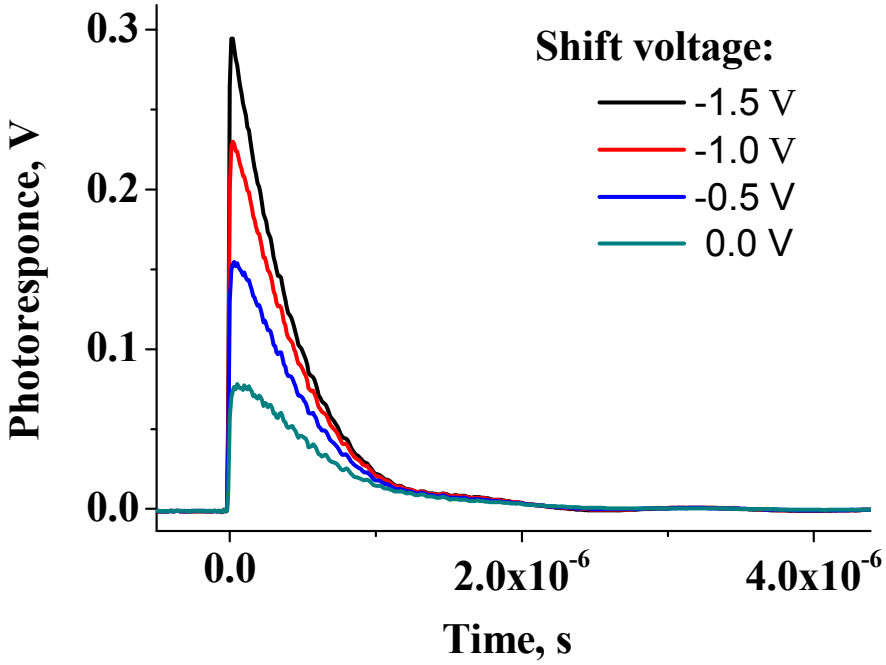


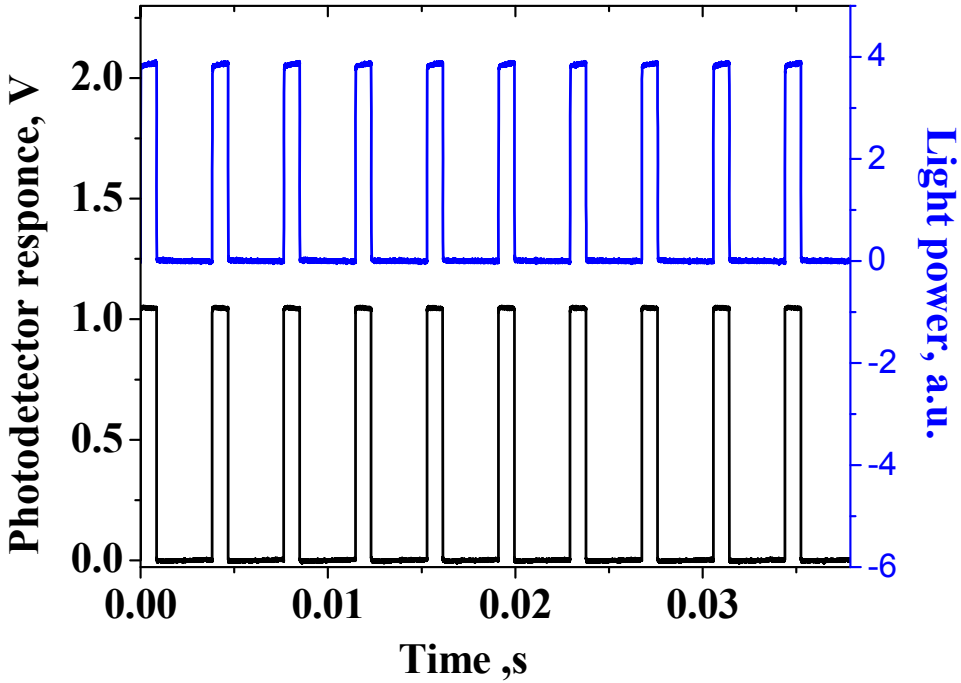


P9: I_{sc} = 10.23 mA/cm^2, V_{oc} = 0.5V, FF = 41%, PCE = 2.1%

P10: I_{sc} = 10.50 mA/cm^2, V_{oc} = 0.9V, FF = 42%, PCE = 4.0%

Photodetectors based on P11/[60]PCBM blend





Transient response of the organic photodetector to a 10 ns light pulse from a nitrogen laser (337 nm) at different shift voltages. The active area was 0.5 cm^2 and a load resistance of 16 Ω.

Detection of 1 ms light pulses of blue LED modulated at 250 Hz with the organic photodetector. Black line - photodetector response, blue line - light power.

Response time ~30-40 ns, decay time ~1 μs.

Conclusions

• Solution-processible organic organosilicon semiconducting materials based on α,α'-dialkyloligothiophenes can be used in organic BHJ solar cells .

• Soluble tetrasubstituted oligothiophenesilanes are interesting materials for organic BHJ solar cells and photodetectors.

• Robust design of low band gap copolymers allows creation polymer BHJ solar cells with improved efficiency and photodetectors.

• The solar cells obtained showed PCE up to 4.0%, while IPCE in the visible range reached 40-50% at maximum.

• The response time of organic photodetectors of 20 - 30 ns was achieved.

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Dr. A. Mourran

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Thank you for your attention!