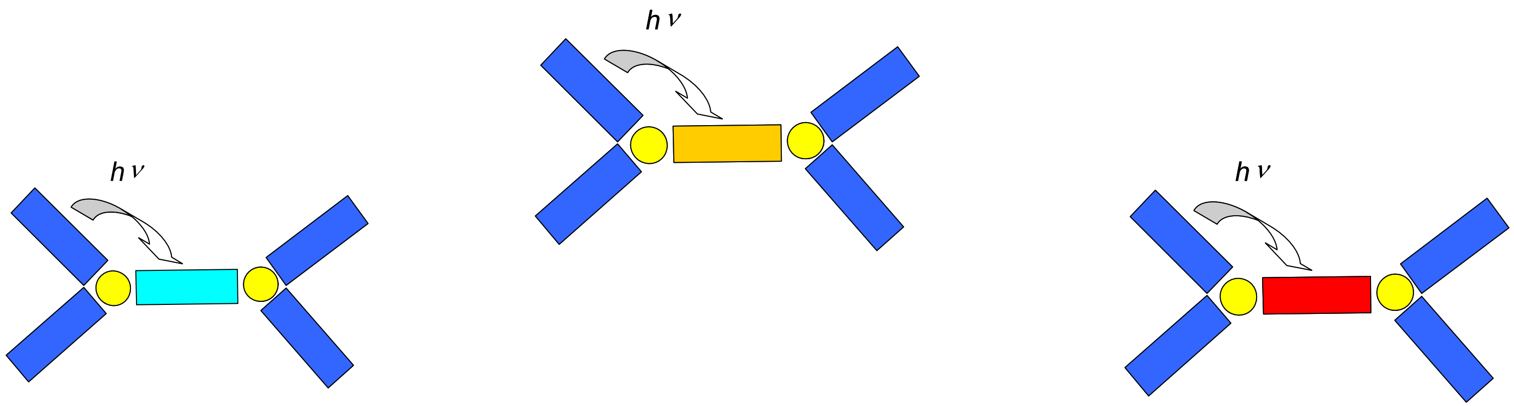
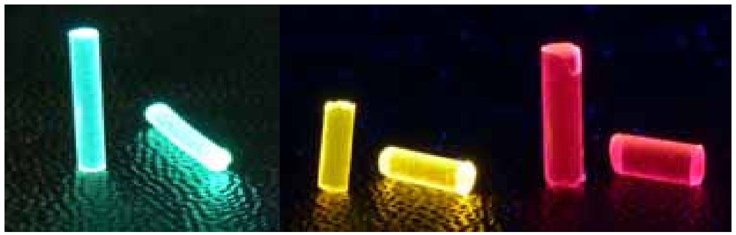
New materials for organic photodetectors, wavelength sifters and plastic scintillators



<u>Sergey Ponomarenko</u>, Oleg Borschev, Nikolay Surin

Institute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS), Moscow, Russia

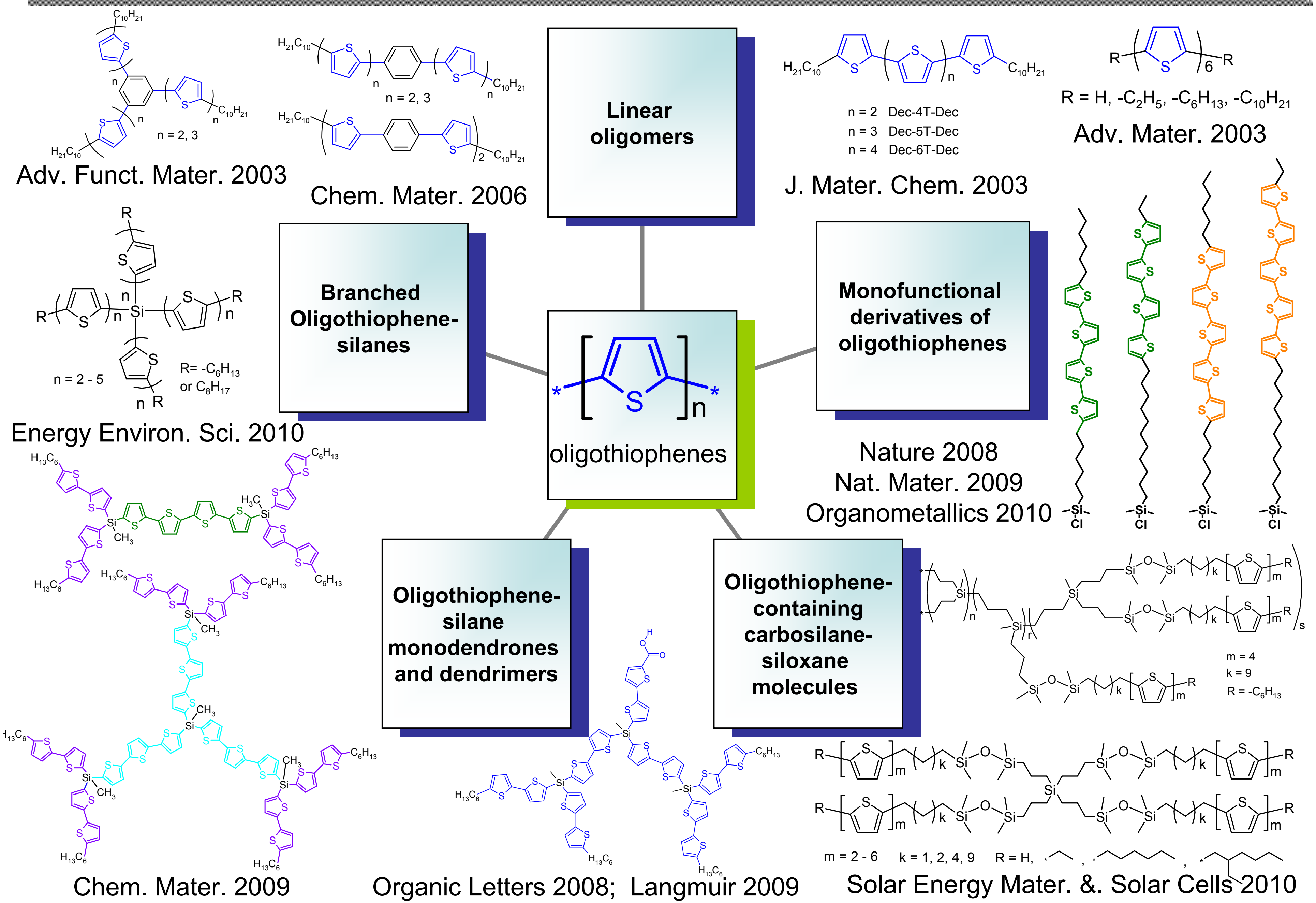
Luminescent Innovation Technologies LLC, Skolkovo (Moscow region), Russia



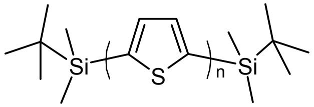
OUTLINE

- Introduction
- Materials for organic solar cells and photodetectors
- Organosilicon nanostructured luminophores (ONL)
- Plastic scintillators with ONL
- Organosilicon wavelength shifters (Si-WLS)

Functional materials for Organic Electronics and Photonics @ ISPM RAS



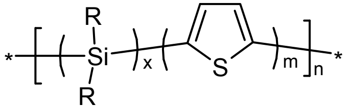
Oligo- and polyarylsilanes of different molecular structure



n = 3 - 6

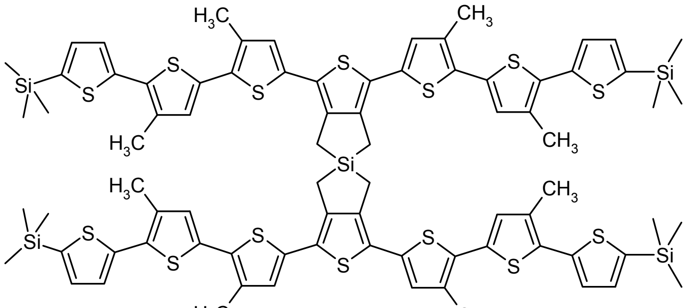
***t*BuMe$_2$Si-Tn-Si-Me$_2$*t*Bu**

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



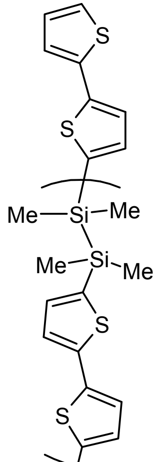
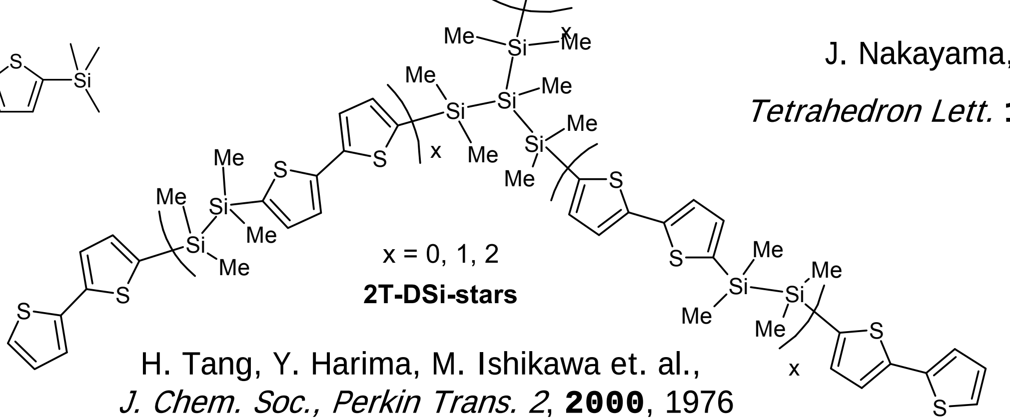
MSmT, x=1, m = 3-5, R=Et
DSmT, x=2, m = 3-5, R=Et
TSmT, x=3, m = 3-5, R=Me

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



Spiro-Si-7T

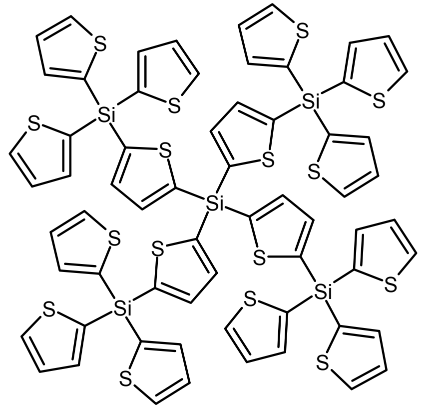
Guay J, Diaz A, Wu R, Tour JM, *J Am Chem Soc* **1993**, 115, 1869

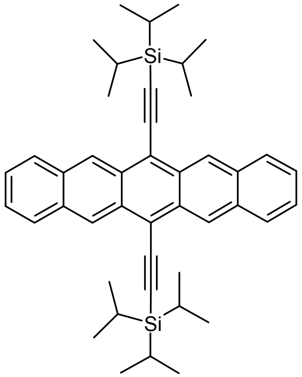
x = 0, 1, 2

2T-DSi-stars

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

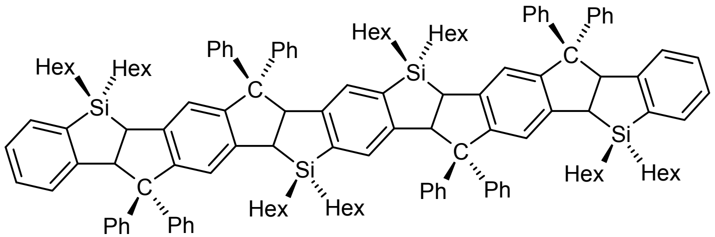


J. Nakayama, J.-S. Lin, *Tetrahedron Lett.* **1997**, 38, 6043

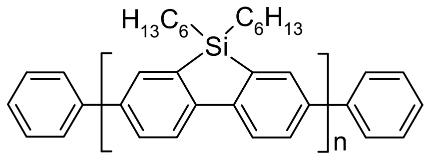


TIPS-5AC

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



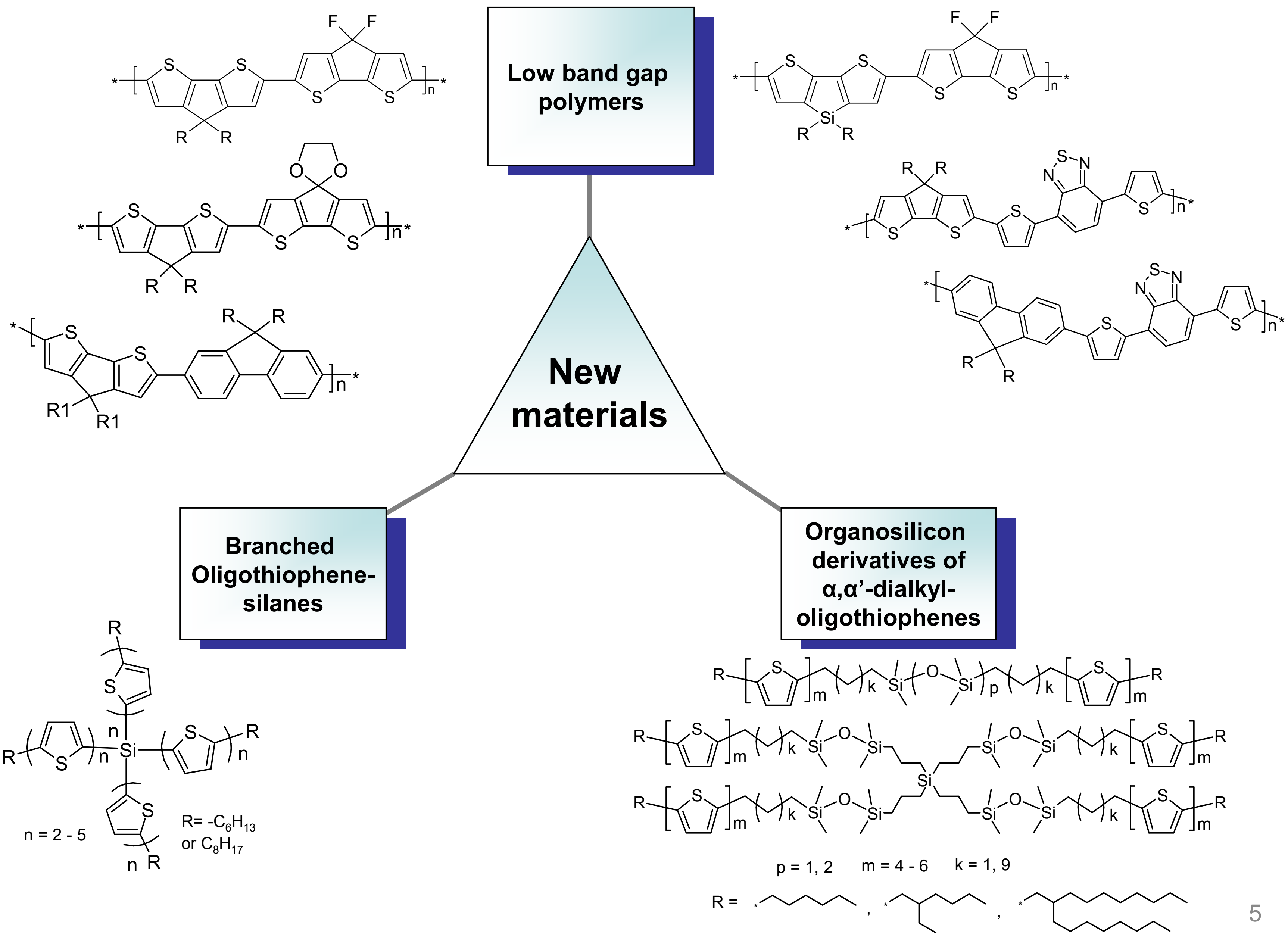
Xu C, Wakamiya A, Yamaguchi S *J Am Chem Soc* **2005**, 127, 1638



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

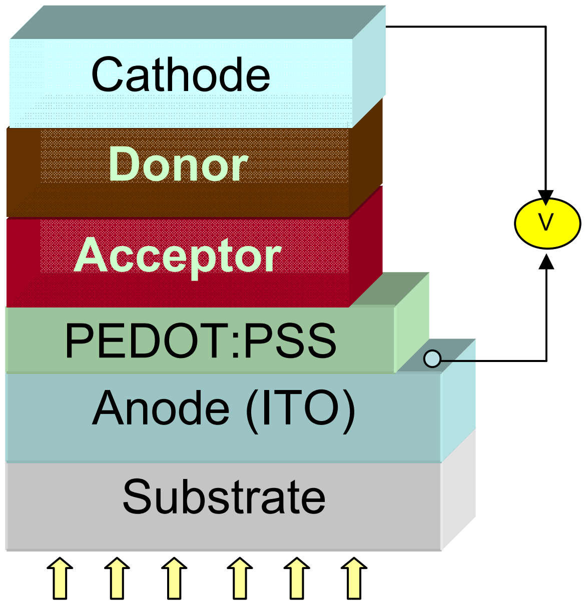
See review: S.A. Ponomarenko, S. Kirchmeyer, ***Adv. Polym. Sci.*, 2011**, 235, 33 - 110.

New materials for polymer BHJ solar cells and photodetectors

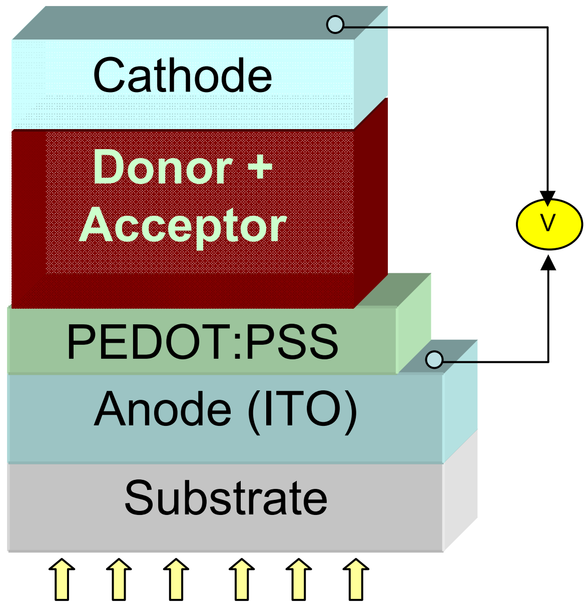


Organic Photovoltaic Cells

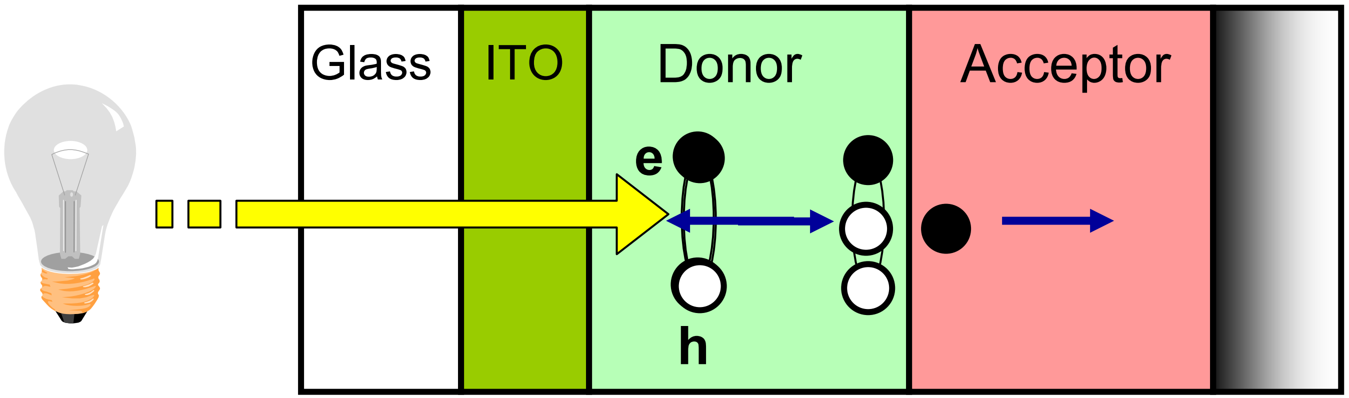
Bilayer device



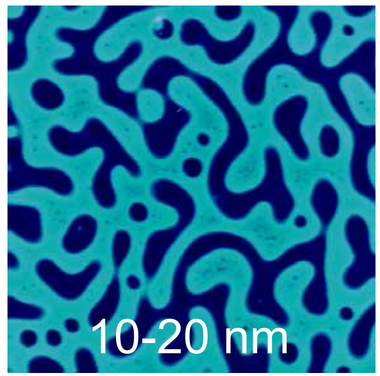
Bulk-heterojunction device



Photoinduced Charge Generation



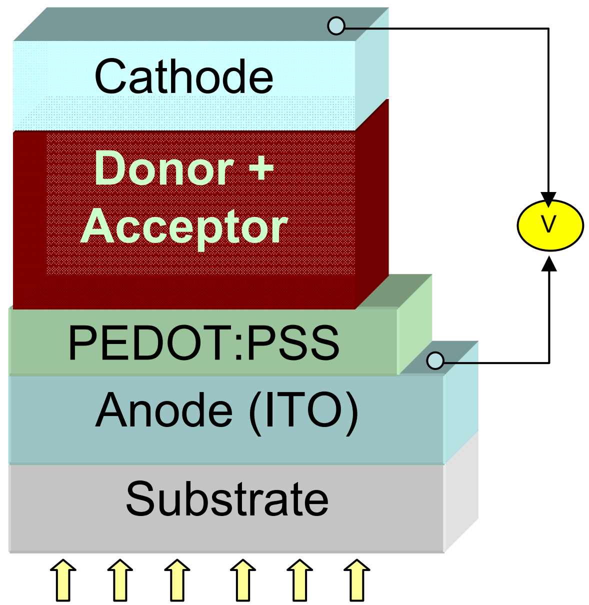
Donor-acceptor nanocomposite

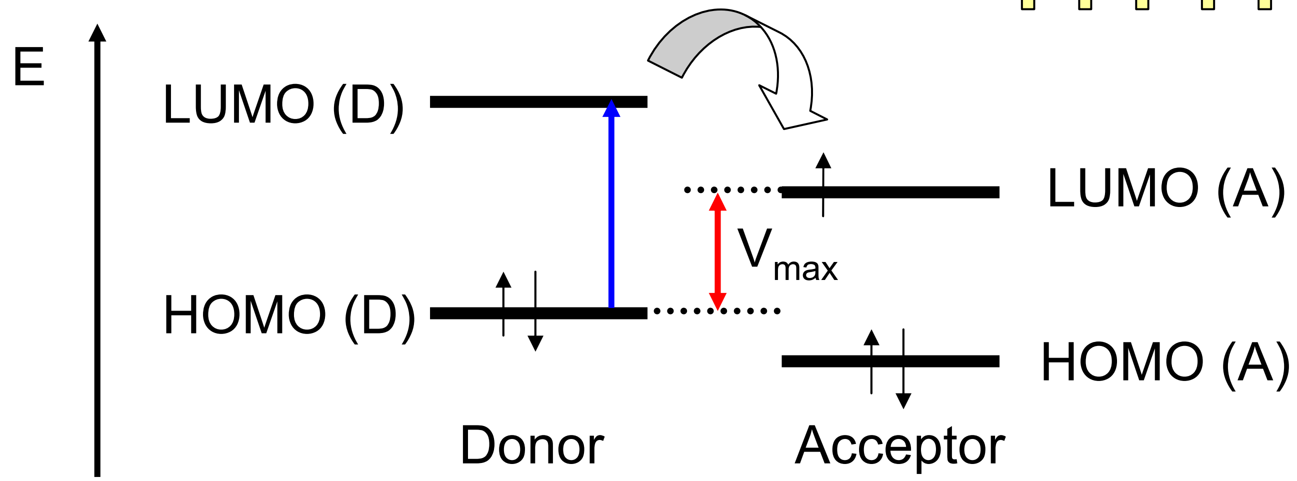


Control:

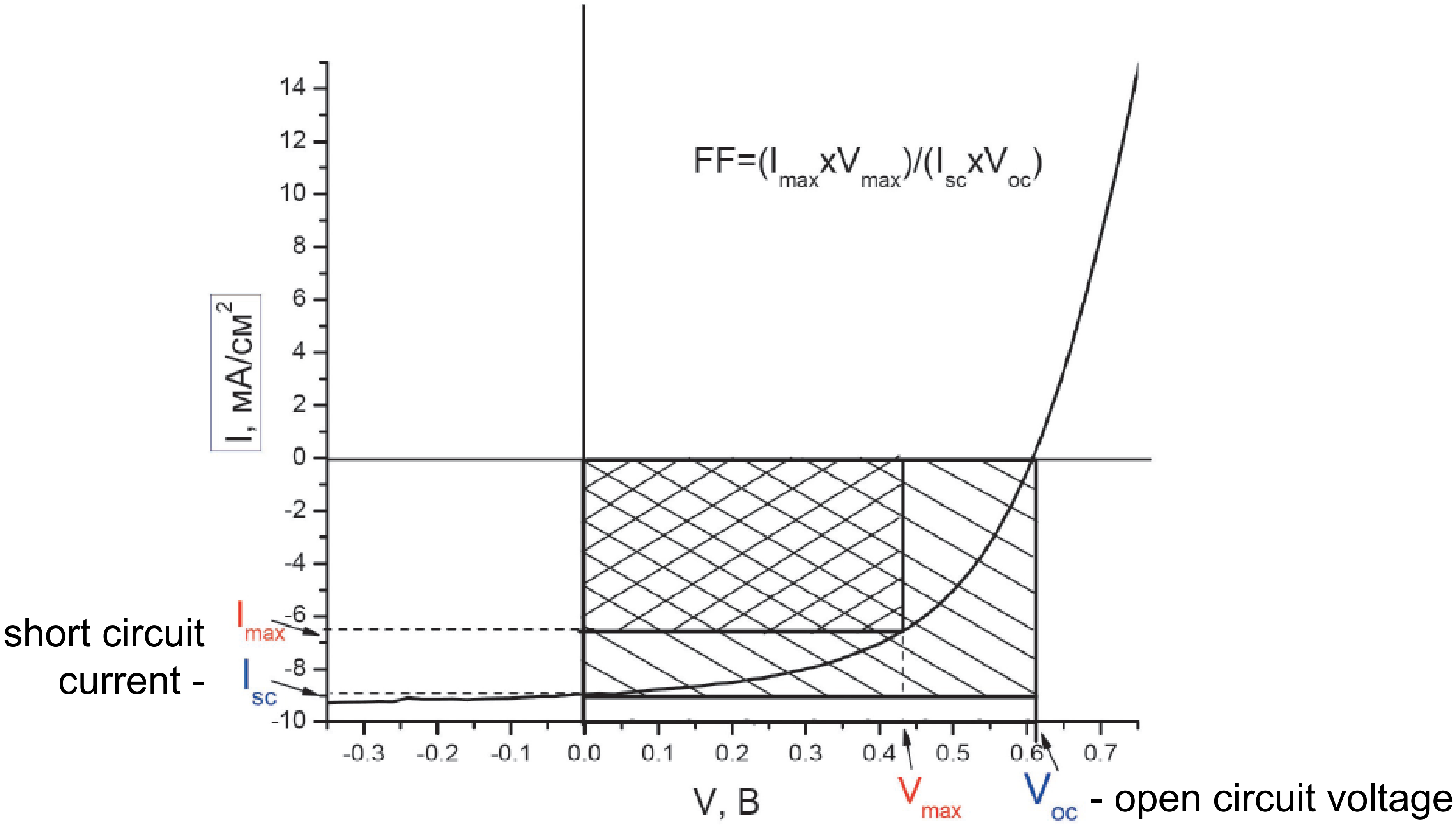
- Absorption of the solar light
- Charge transport
- Solubility
- Morphology
- HOMO and LUMO energy levels of donor and acceptor

Bulk-heterojunction device





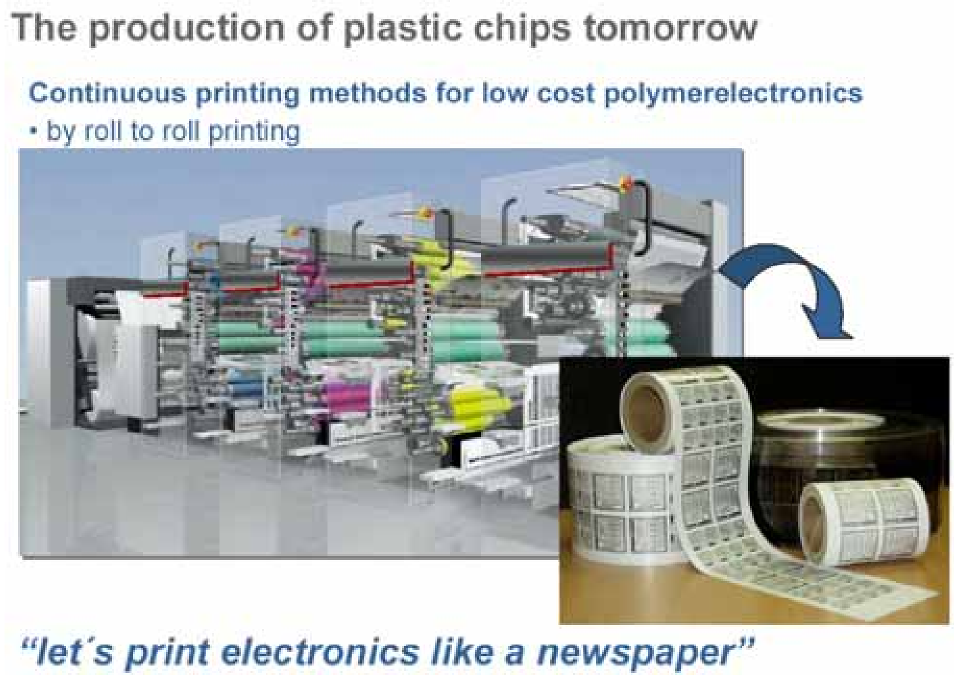
Typical electrical characteristics of photovoltaic cells



Power conversion efficiency $\eta = \dfrac{I_{\max} V_{\max}}{P_{light}} \times 100\% = \dfrac{I_{sc} V_{os} FF}{P_{light}} \times 100\%$

Advantages of organic electronics

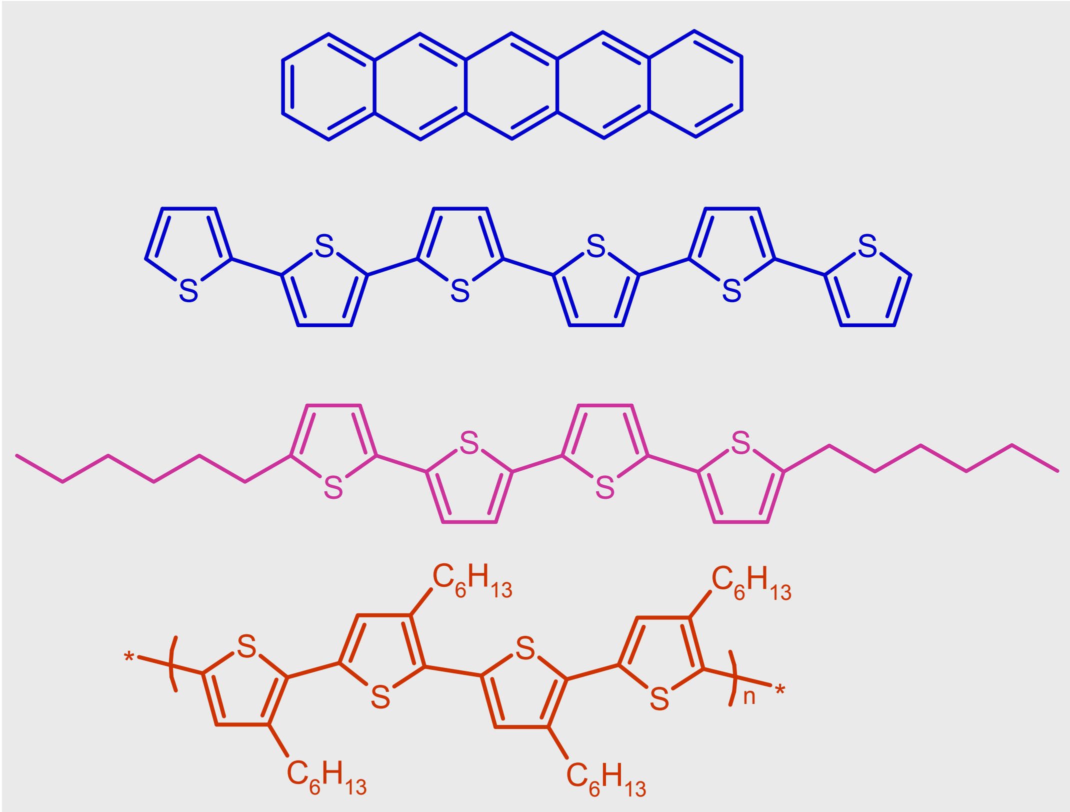
- Light weight
- Flexibility
- Large area
- Transparent
- Low-Cost
  - No vacuum processing
  - No lithography (printing)
  - Low-cost substrates (plastic, paper, even cloth…)
  - Direct integration on package (lower insertion costs)



Organic Semiconducting materials

Evaporation

p-type (donors)



Pentacene

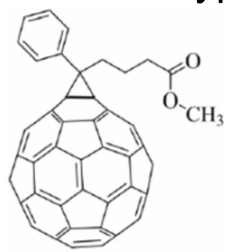
Sexithiophene

α, α' -dihexyl-
quaterthiophene

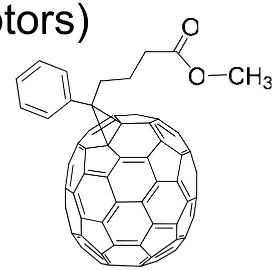
Poly(hexylthiophene)
P3HT

Spincoating

n-type (acceptors)



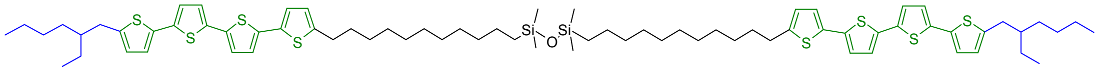
PCBM



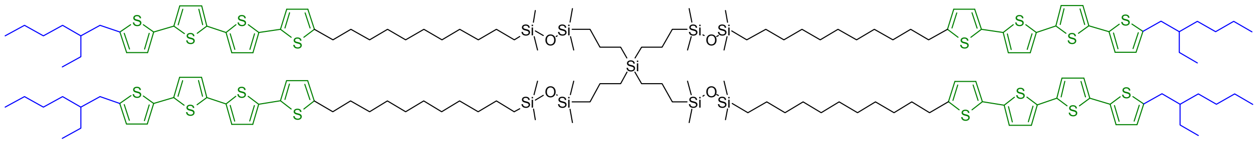
[70]PCBM

Soluble Fullerene
derivatives

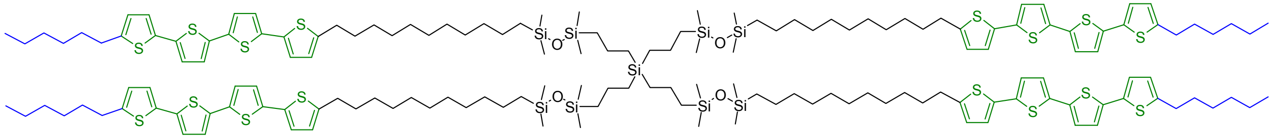
Organosilicon derivatives of α,α’-dialkyloligothiophenes



D1

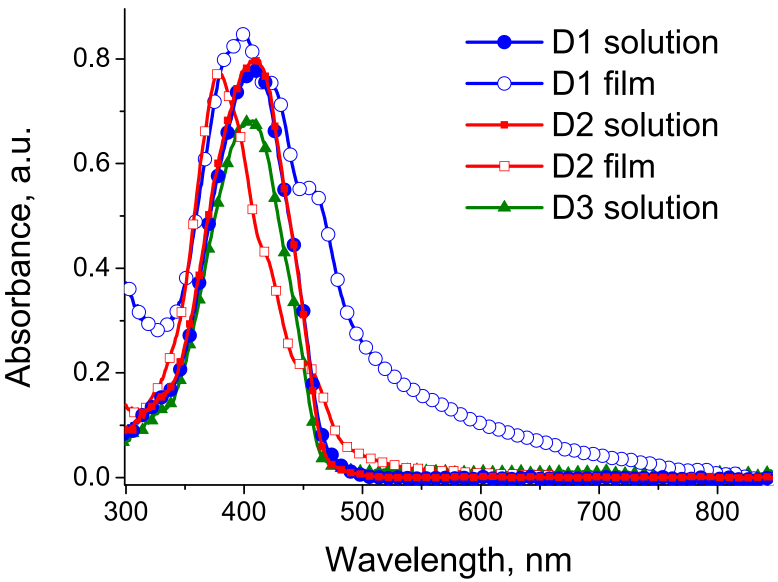


D2

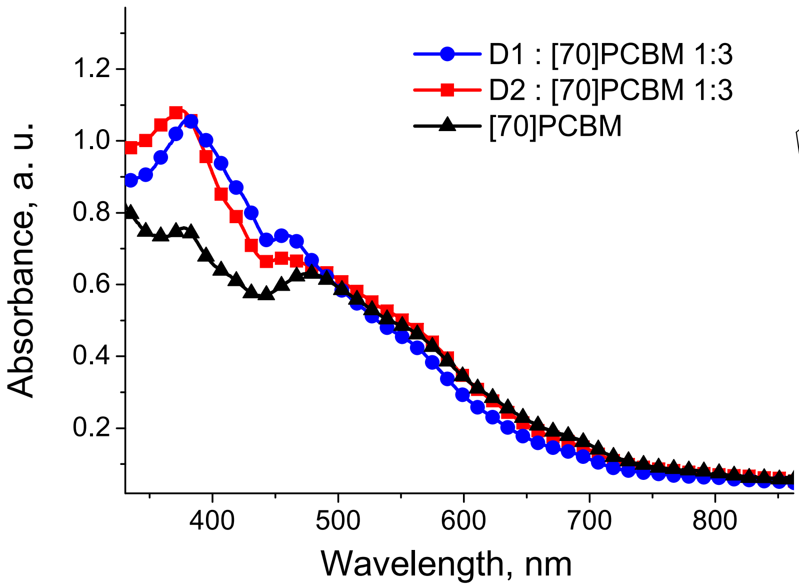


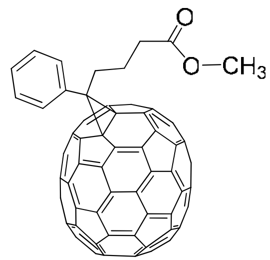
D1

UV- Vis absorption spectra



Thin films absorption spectra

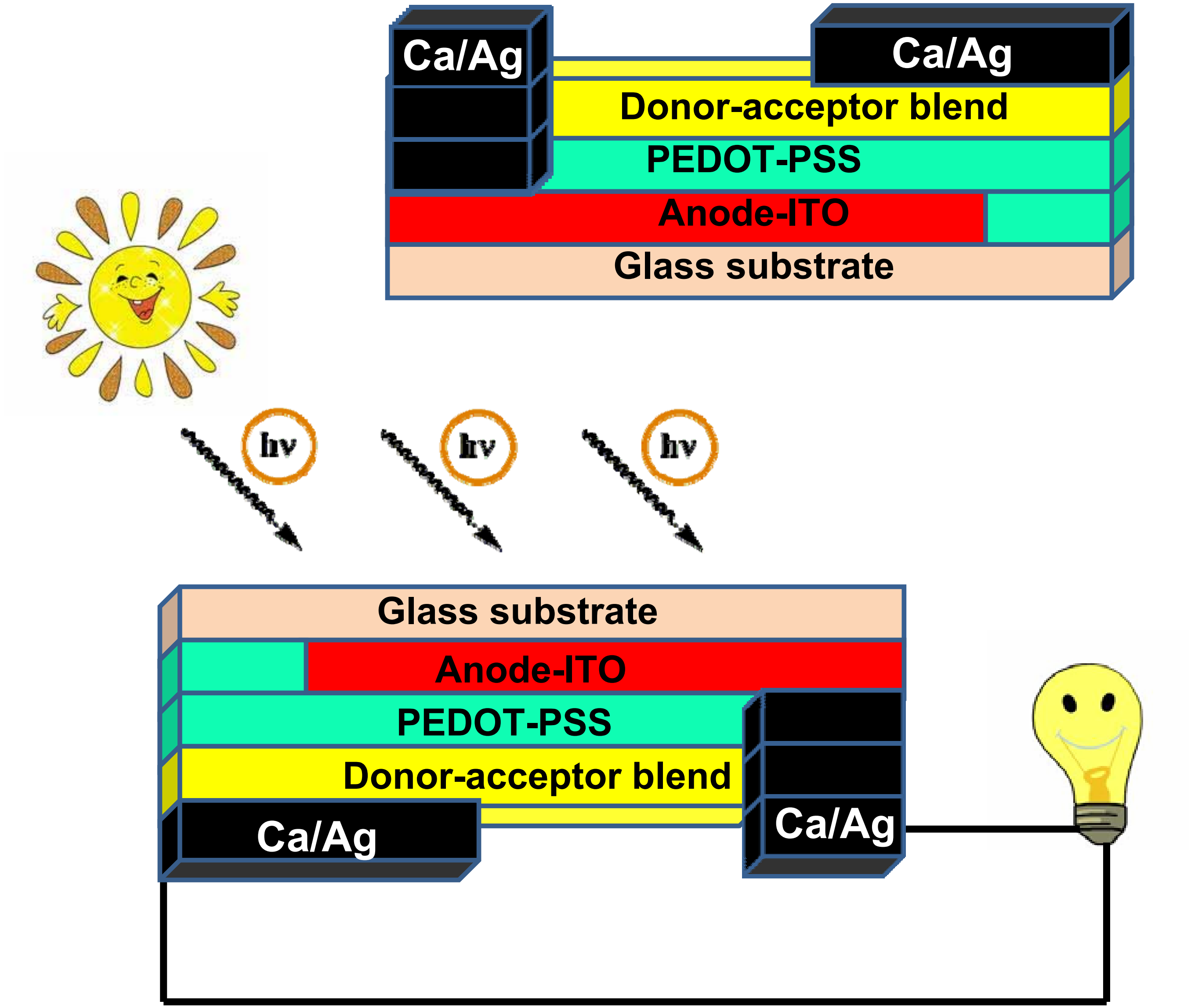




[70]PCBM

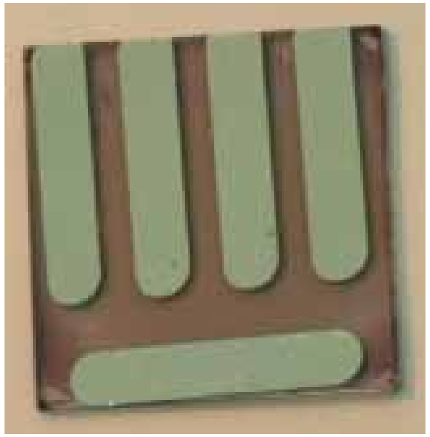
***Solar Energy Materials and Solar cells* 2010**, 94, 2064

Preparation of test devices for organic photovoltaic cells

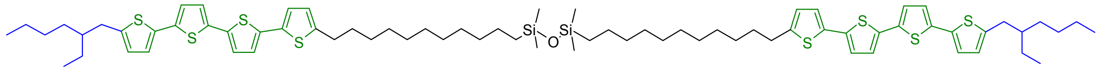


Schematic

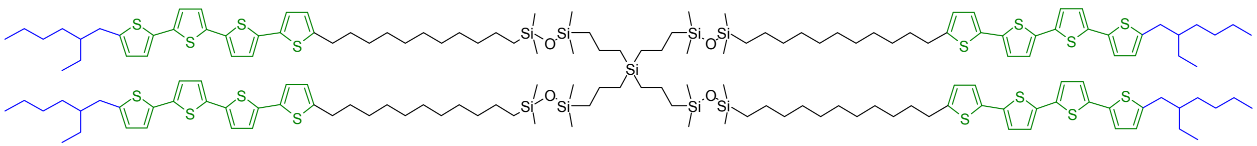
Photograph



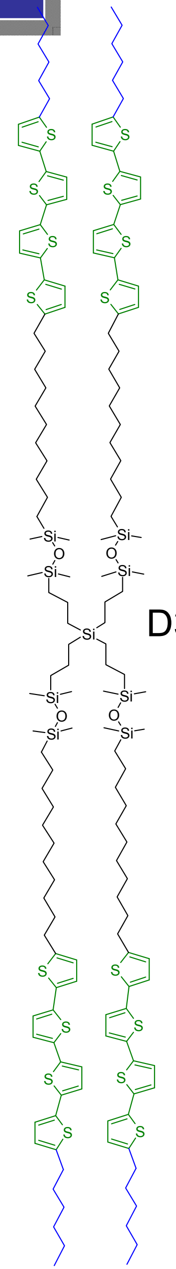
Organosilicon derivatives of α,α’-dialkyloligothiophenes



D1

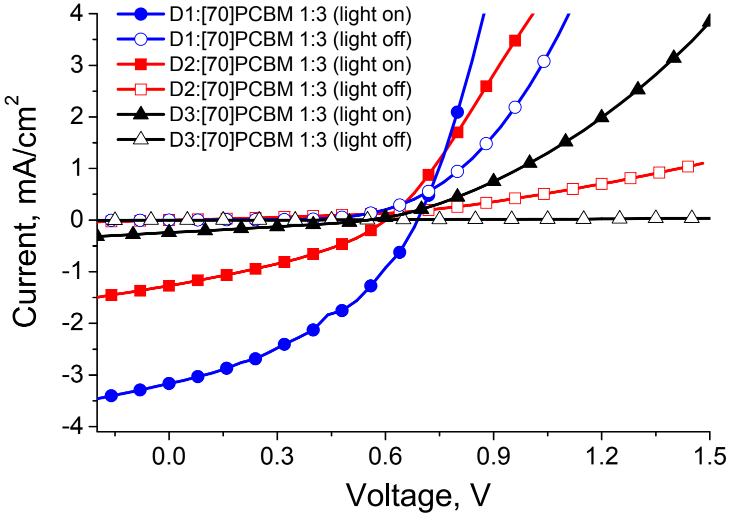


D2

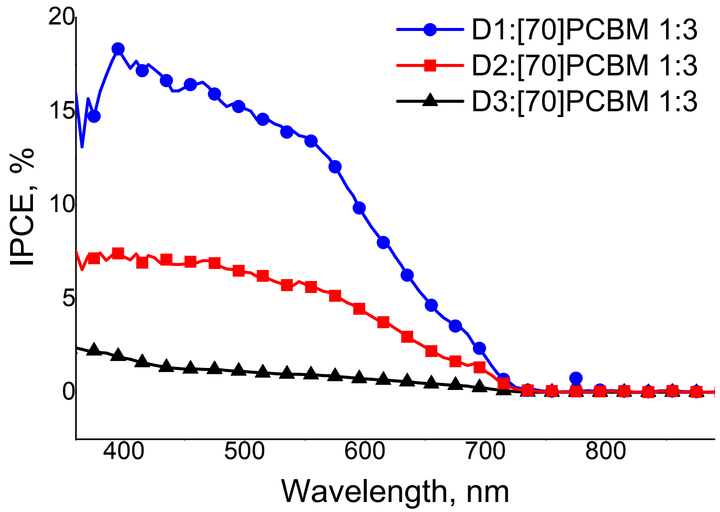


D3

Light-on and light-off I-V curves



IPCE spectra



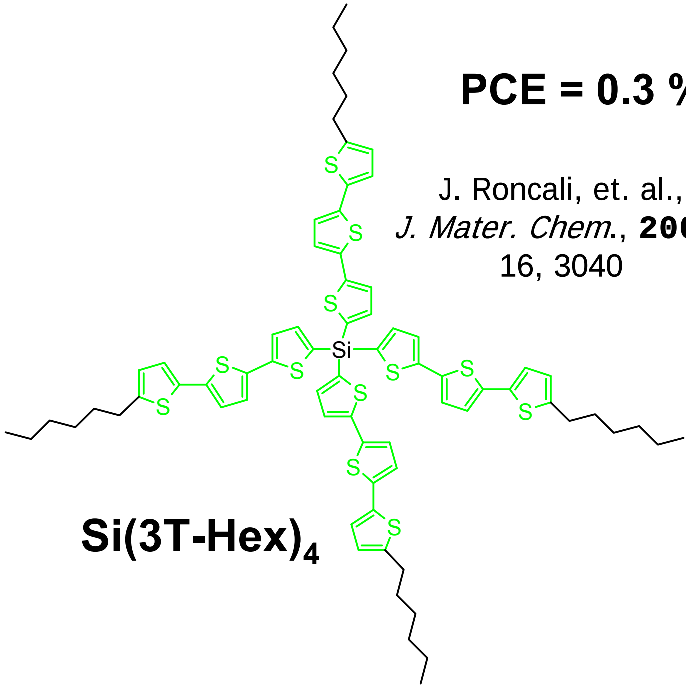
Com-pound	OFETs		Photovoltaic cells			
	μ, cm^2/Vs	On/Off Ratio	V_{oc}, mV	FF, %	I_{sc}, mA/cm^2	PCE, %
D1	-	-	**680**	**40**	**3.2**	**0.9**
D2	0,0002	260	600	35	1.3	0.27
D2	**0,02**	**10^6**	360	29	0.45	0.05

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

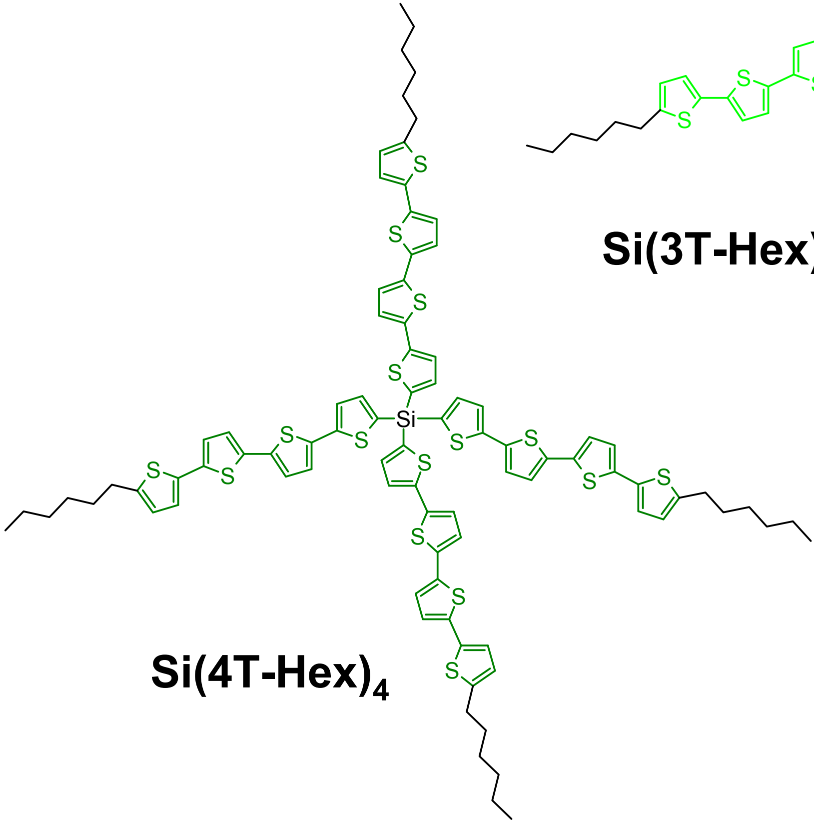
Tetrakis(ter-, quater- and quinquethiophene)silanes

PCE = 0.3 %

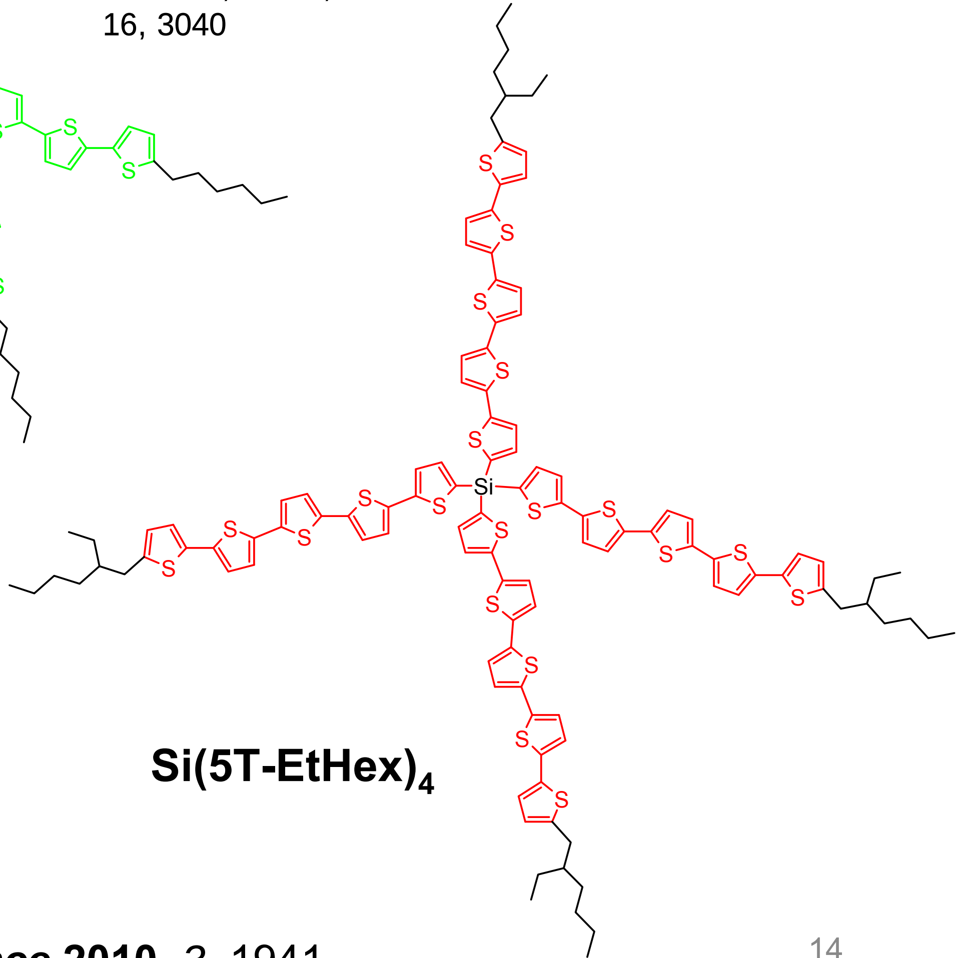
J. Roncali, et. al.,
J. Mater. Chem., **2006**,
16, 3040



Si(3T-Hex)$_4$



Si(4T-Hex)$_4$



Si(5T-EtHex)$_4$

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

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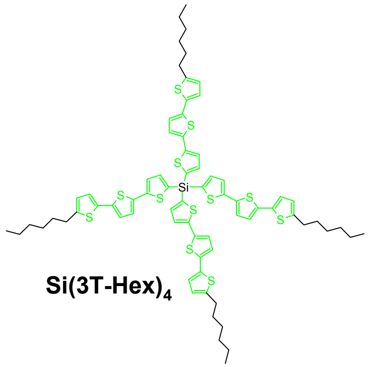
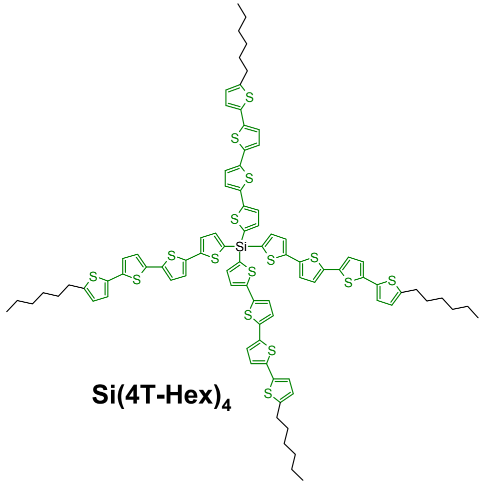
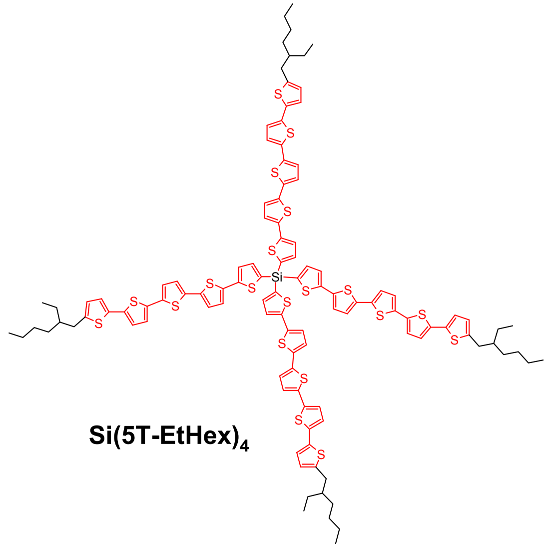
Tetrakis(ter-, quater- and quinquethiophene)silanes



$Si(3T\text{-}Hex)_4$

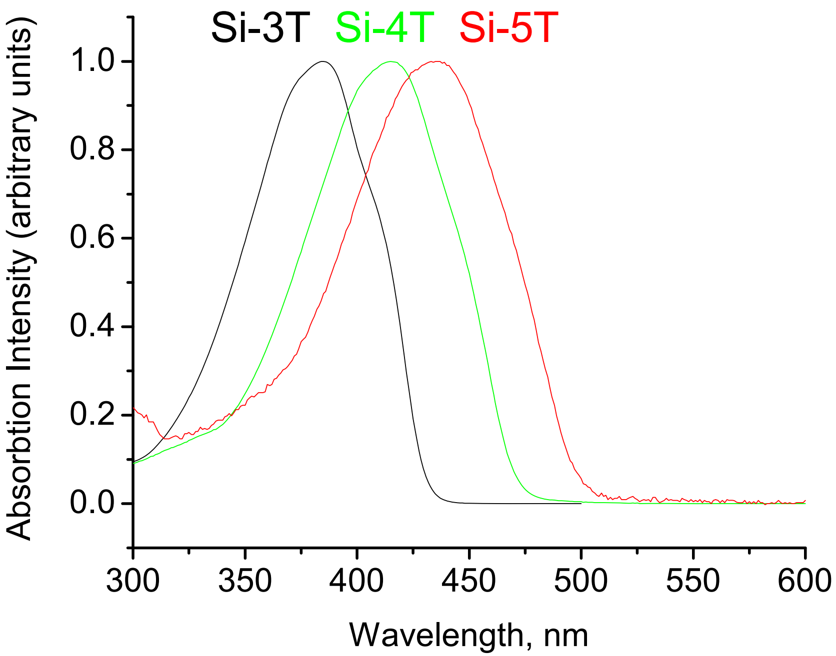


$Si(4T\text{-}Hex)_4$



$Si(5T\text{-}EtHex)_4$

Optical spectra



Photovoltaic Efficiency

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

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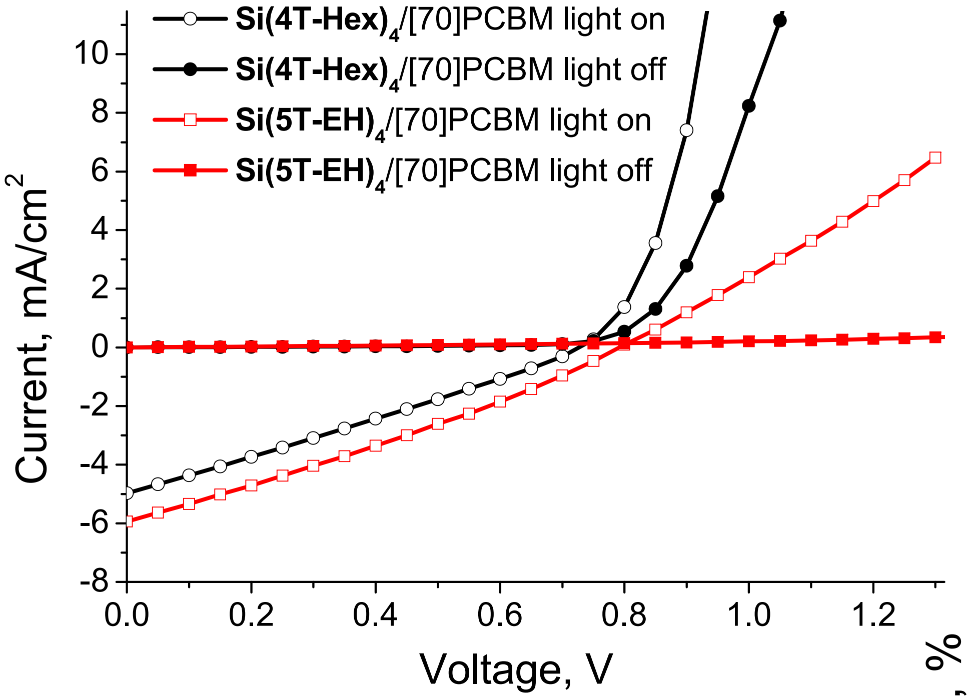
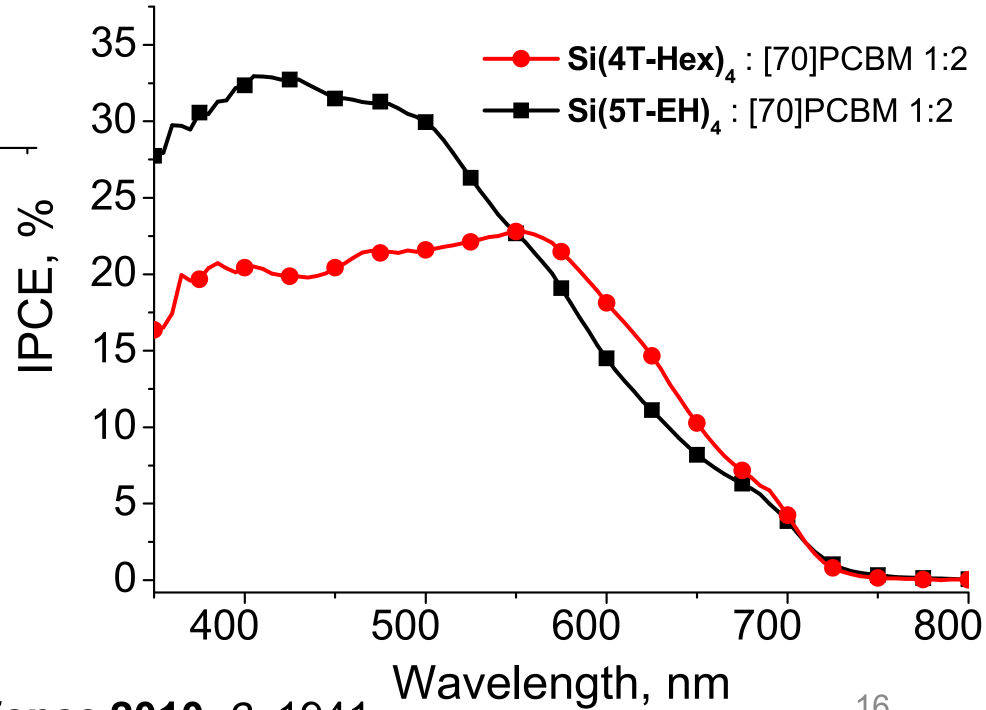
I-V characteristics and IPCE spectra of photovoltaic cells based on oligothiophenesilanes



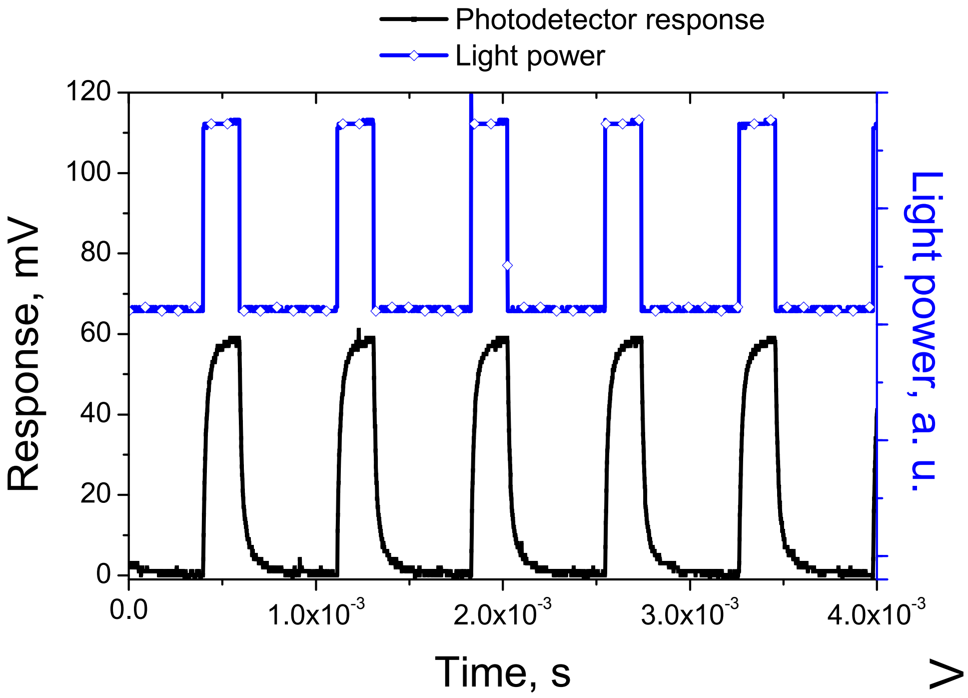
Light-on and light-off I-V curves for photovoltaic cells comprising blends **Si(4T-Hex)$_4$**/[70]PCBM and **Si(5T-EH)$_4$**/[70]PCBM in the photoactive layers

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

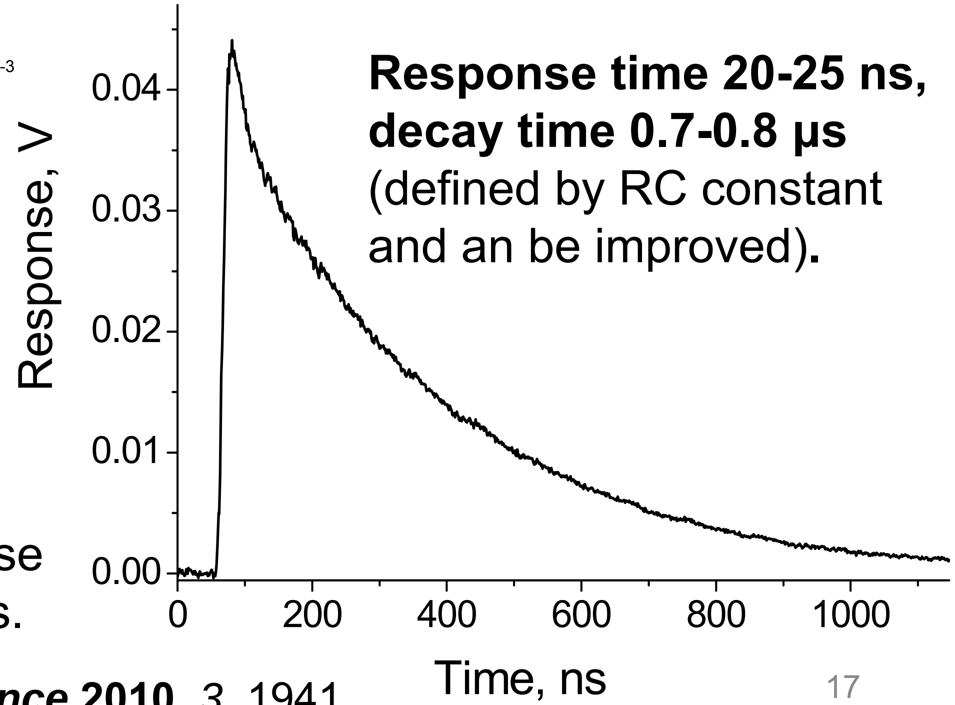
Photodetectors based on $Si(4T\text{-}Hex)_4$ / [70]PCBM BHJ



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).

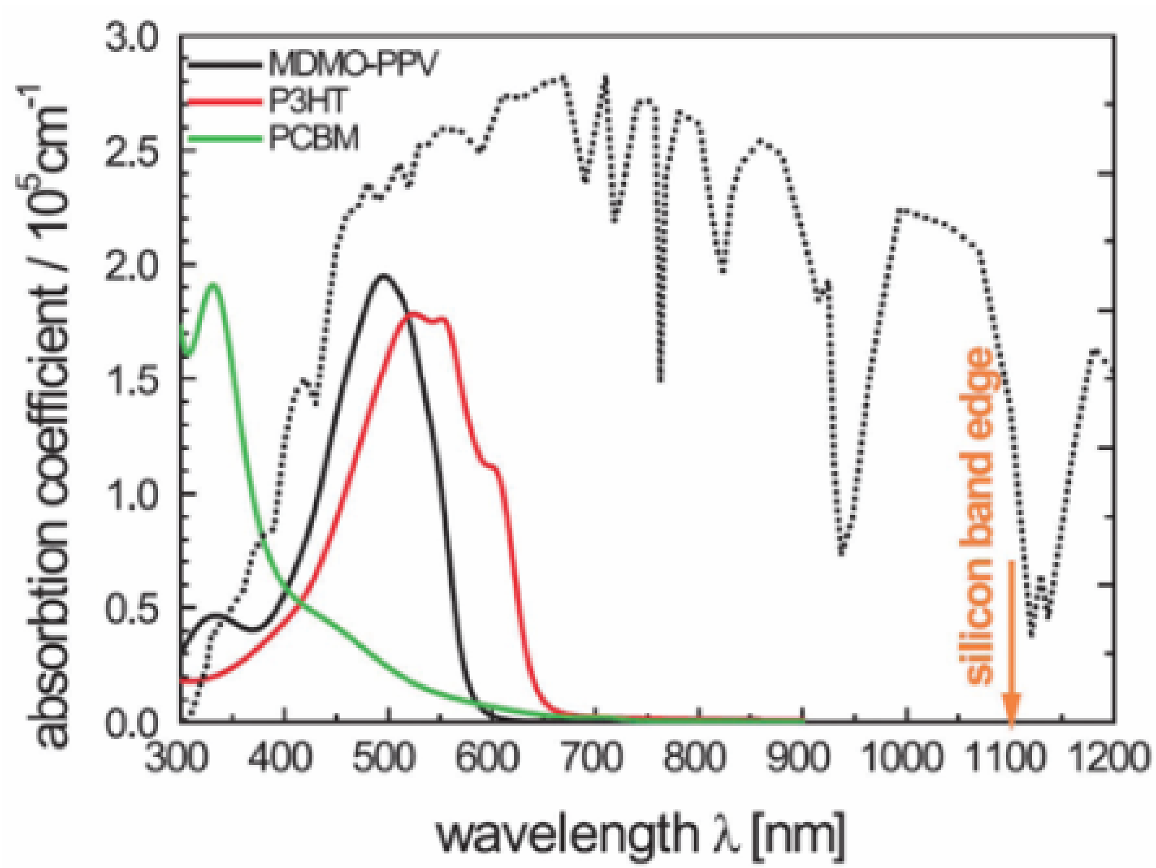


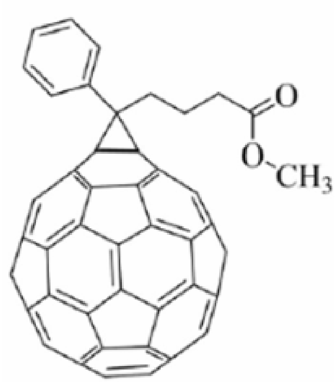
Response time 20-25 ns, decay time 0.7-0.8 µs (defined by RC constant and an be improved)**.**

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

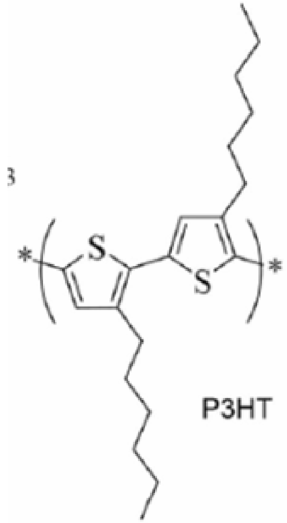
***Energy & Environmental Science* 2010**, *3*, 1941

Solar light spectra and absorption spectra of the mostly used materials

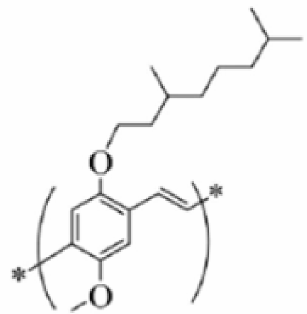




PCBM

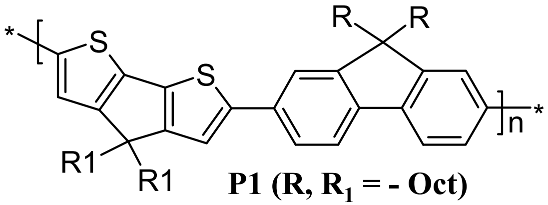


P3HT

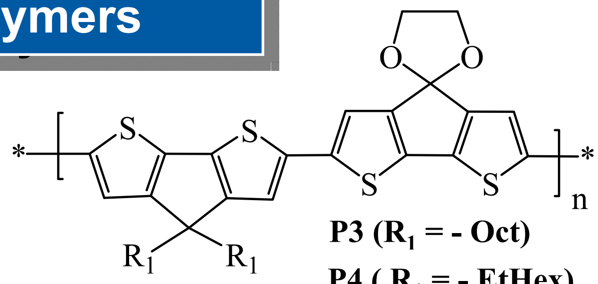


MDMO-PPV

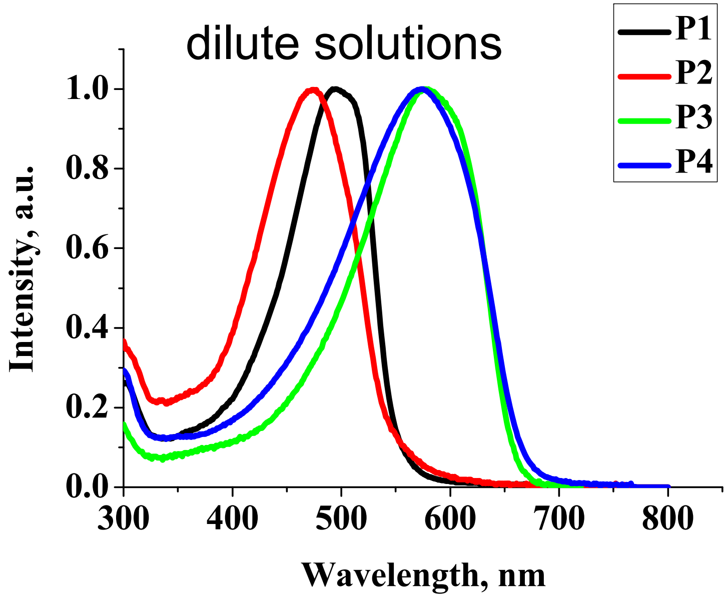
Low band gap copolymers

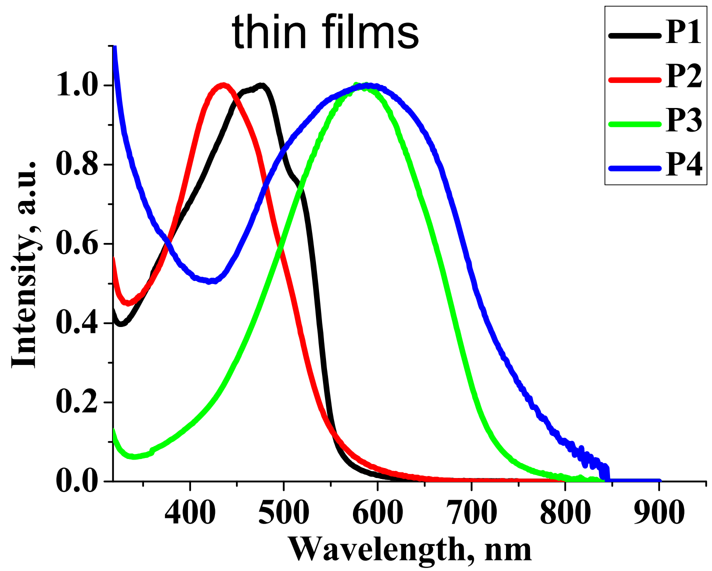


P1 (R, R_1 = - Oct)
P2 (R = Oct, R_1 = - EtHex)



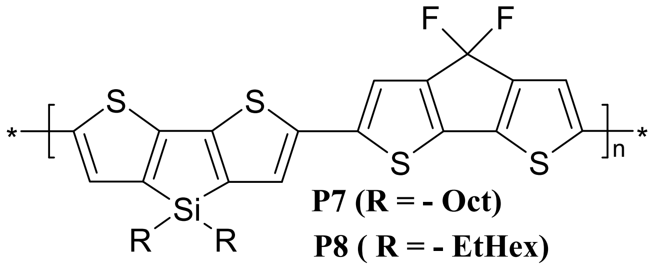
P3 (R_1 = - Oct)
P4 (R_1 = - EtHex)



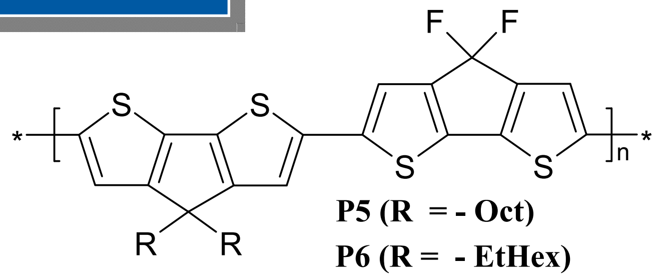


	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt}eV, (solution)	ΔE_{opt}, eV (film)
P1	8400	11900	1.42	495	478	2.24	2.21
P2	2700	4500	1.67	474	434	2.25	2.19
P3	7500	12500	1.67	574	585	1.89	1.69
P4	6700	10000	1.49	577	594	1.88	1.59

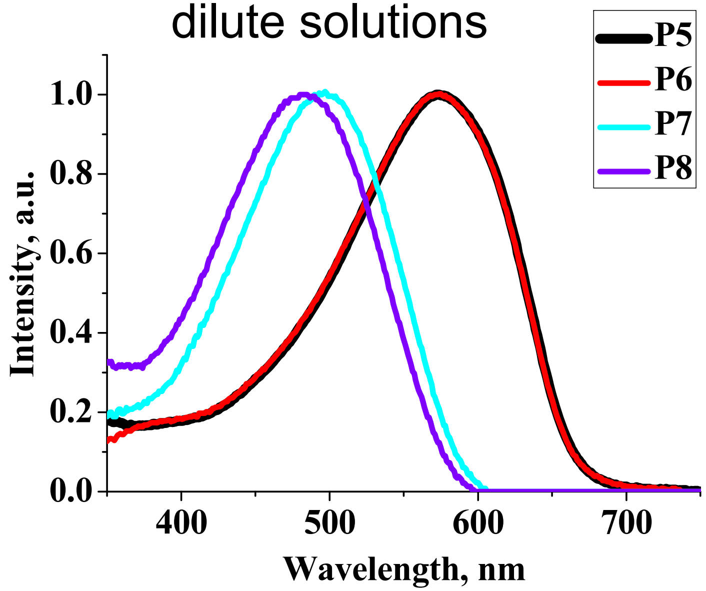
Low band gap copolymers

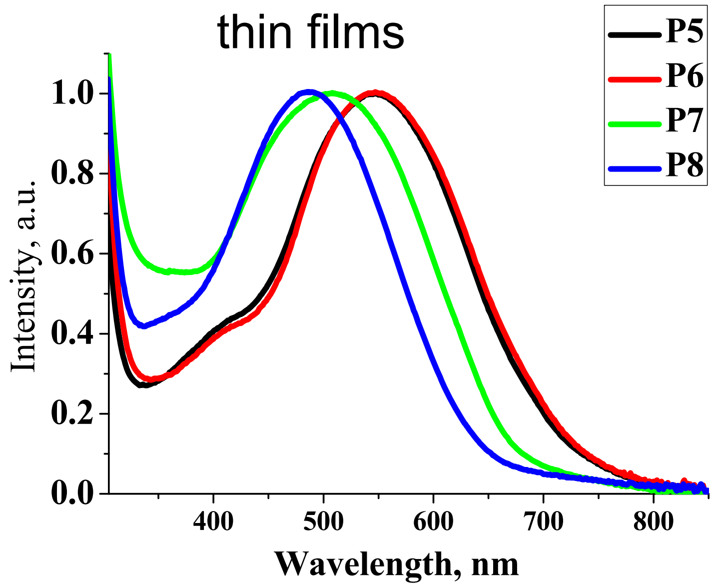


P7 (R = - Oct)
P8 (R = - EtHex)



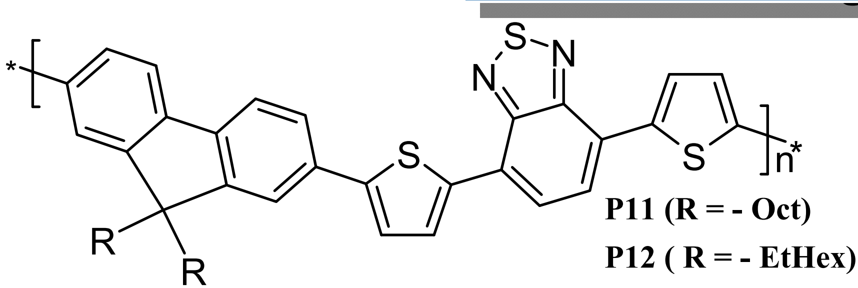
P5 (R = - Oct)
P6 (R = - EtHex)

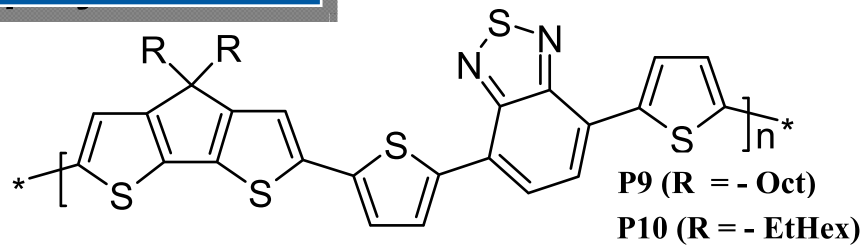


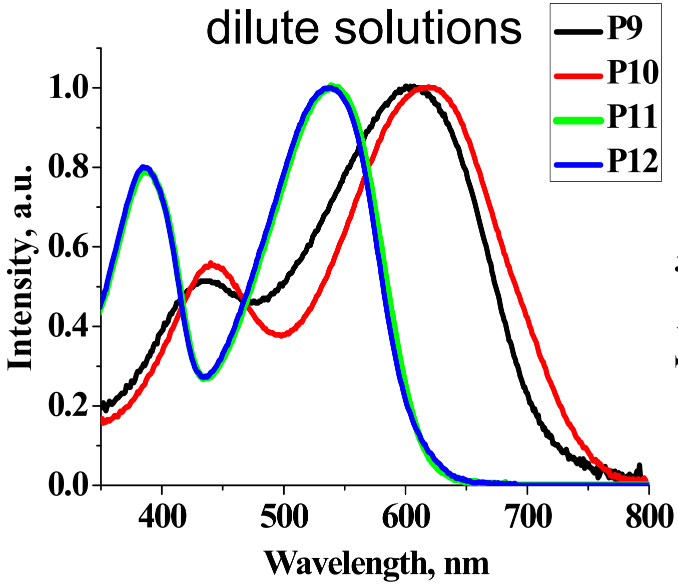


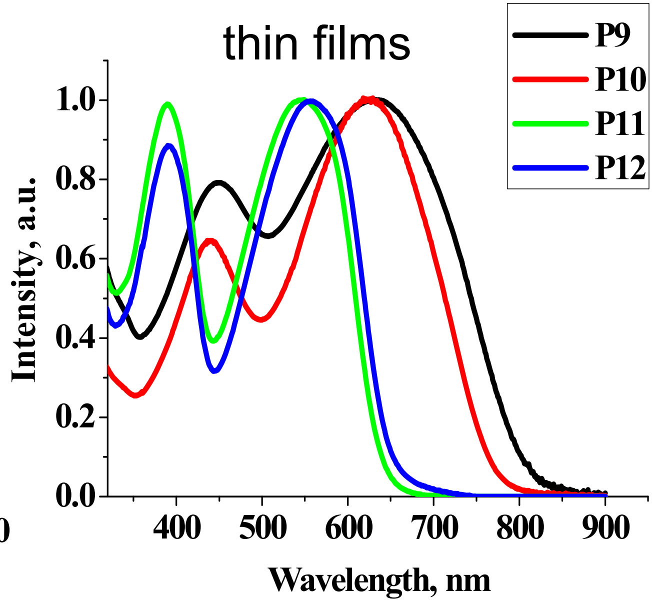
	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt}eV, (solution)	$\Delta E_{opt,}$ eV (film)
P5	11000	13900	1.26	573	547	1.85	1.60
P6	7900	10500	1.33	572	554	1.85	1.62
P7	4000	5000	1.20	495	510	2.11	1.79
P8	4600	6000	1.30	481	494	2.16	1.88

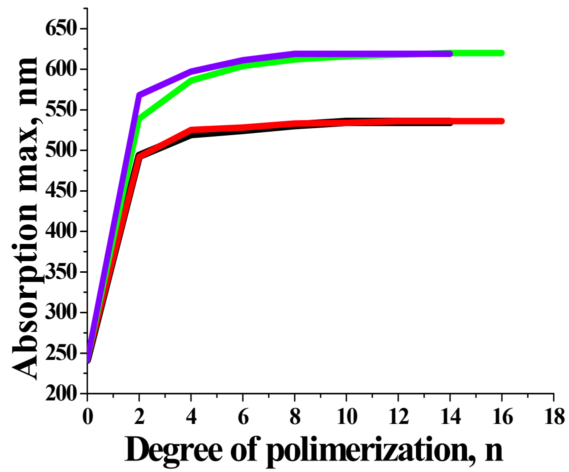
Low band gap copolymers





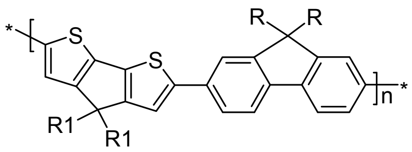






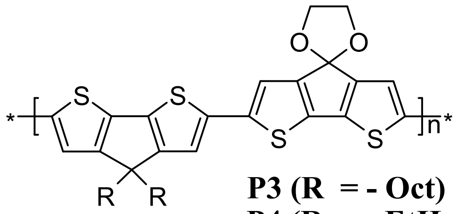
	Mn	Mw	DPI	λ_{max}, nm (solution)	λ_{max}, nm (film)	ΔE_{opt}eV, (solution)	$\Delta E_{opt,}$ eV (film)
P9	18200	25500	1.40	609	637	1.73	1.55
P10	10600	15000	1.42	617	624	1.65	1.60
P11	9300	15700	1.63	538	545	2.03	1.92
P12	8300	12300	1.47	539	560	2.02	1.90

Low band gap copolymers



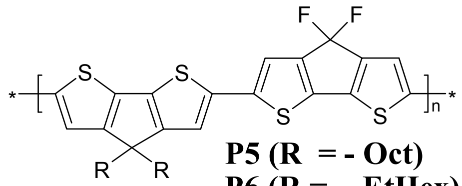
P1 (R, R_1 = - Oct)

P2 (R = Oct, R_1 = - EtHex)



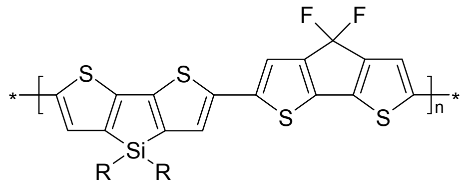
P3 (R = - Oct)

P4 (R = - EtHex)



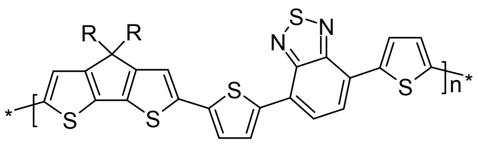
P5 (R = - Oct)

P6 (R = - EtHex)



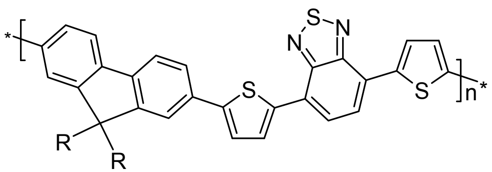
P7 (R = - Oct)

P8 (R = - EtHex)



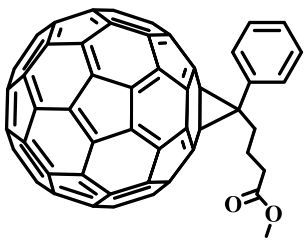
P9 (R = - Oct)

P10 (R = - EtHex)



P11 (R = - Oct)

P12 (R = - EtHex)

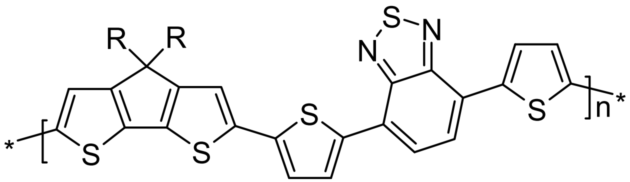


F1 - [60]PCBM

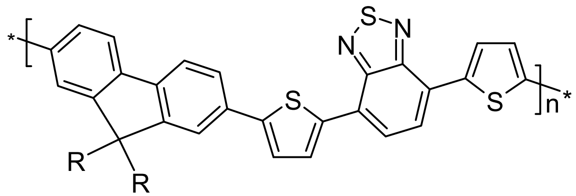
No.	ΔE_{opt} eV, in film	Px / F1	I_{sc}, mA/cm²	V_{oc}, мV	FF, %	η, %
P1	2.21	1 : 1	1.43	522	53	0.80
P2	2.19	1 : 2	2.94	561	32	0.20
P3	1.69	1 : 2	1.45	365	27	0.14
P4	1.59	1 : 2	3.10	565	41	0.70
P5	1.60	1 : 3	2.50	525	37	0.50
P6	1.62	1 : 3	2.10	516	37	0.41
P7	1.79	1 : 3	2.57	720	39	0.73
P8	1.88	1 : 4	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

Adv. Funct. Mater. **2010**, *20*, 4351

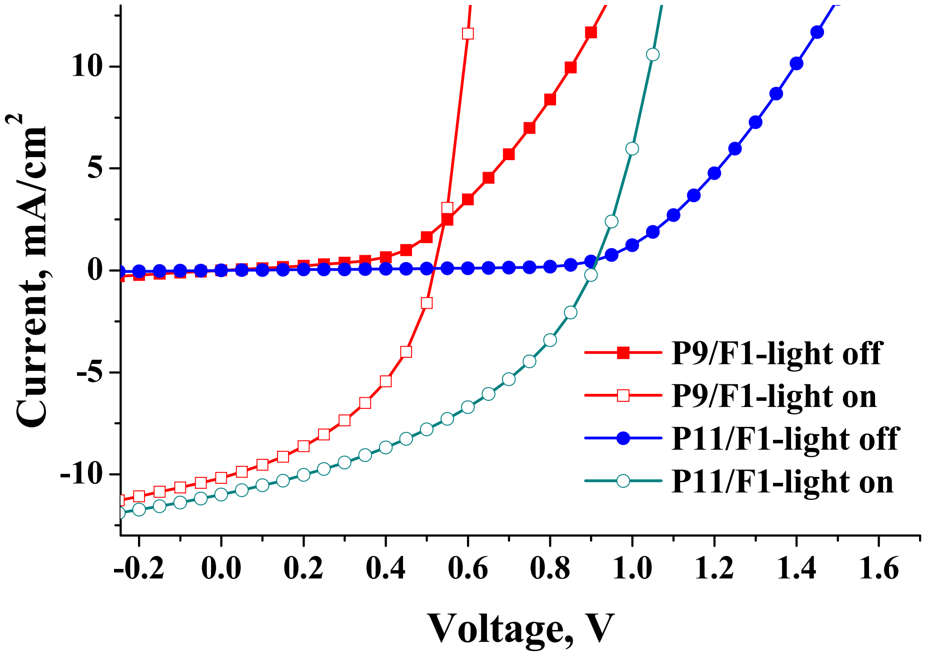
I-V characteristics and IPCE spectra of low band gap copolymers

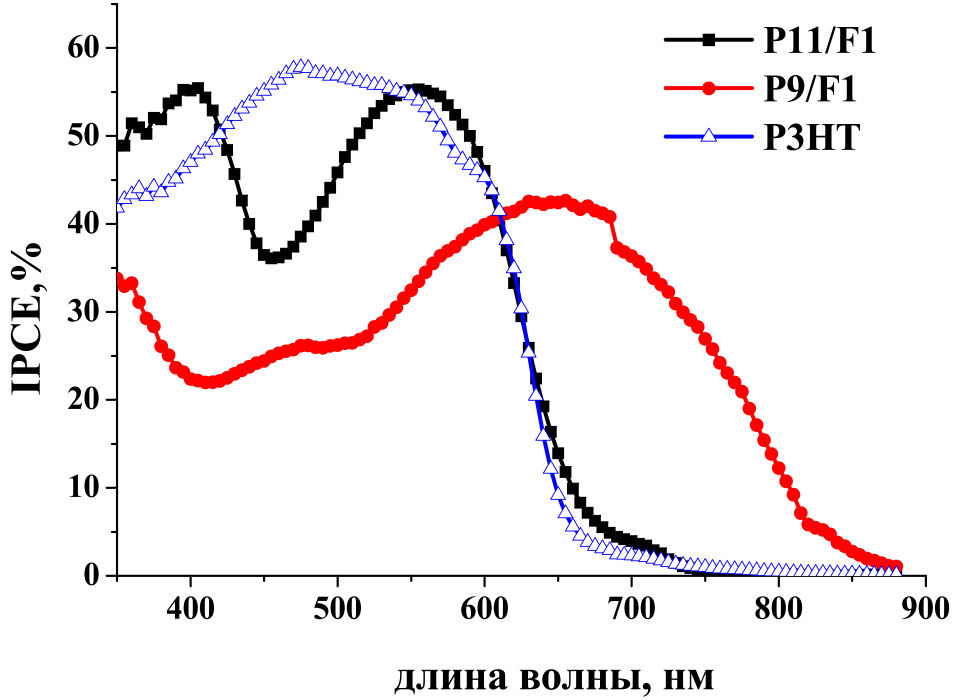


P9 (R = - Oct)



P11 (R = - Oct)

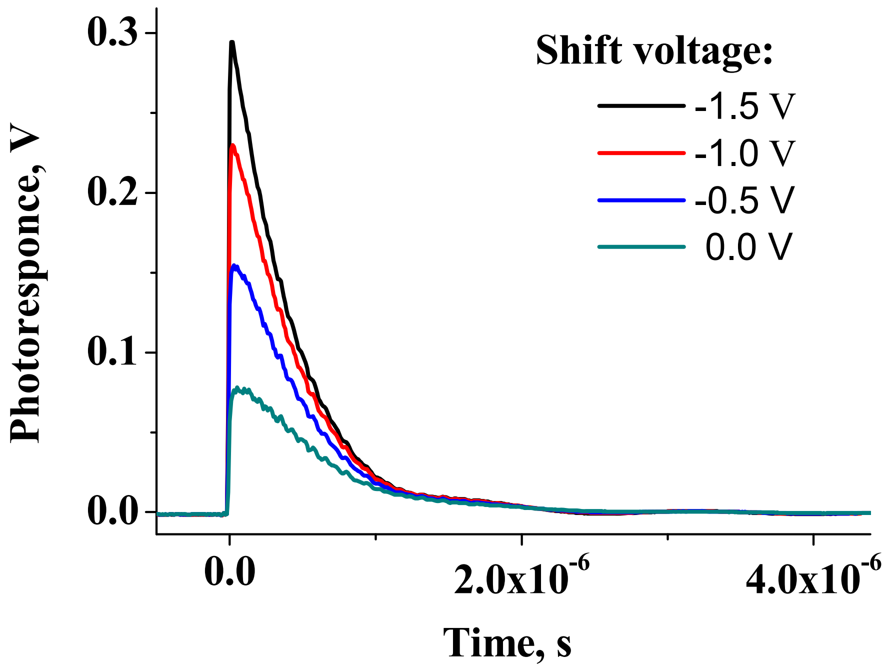




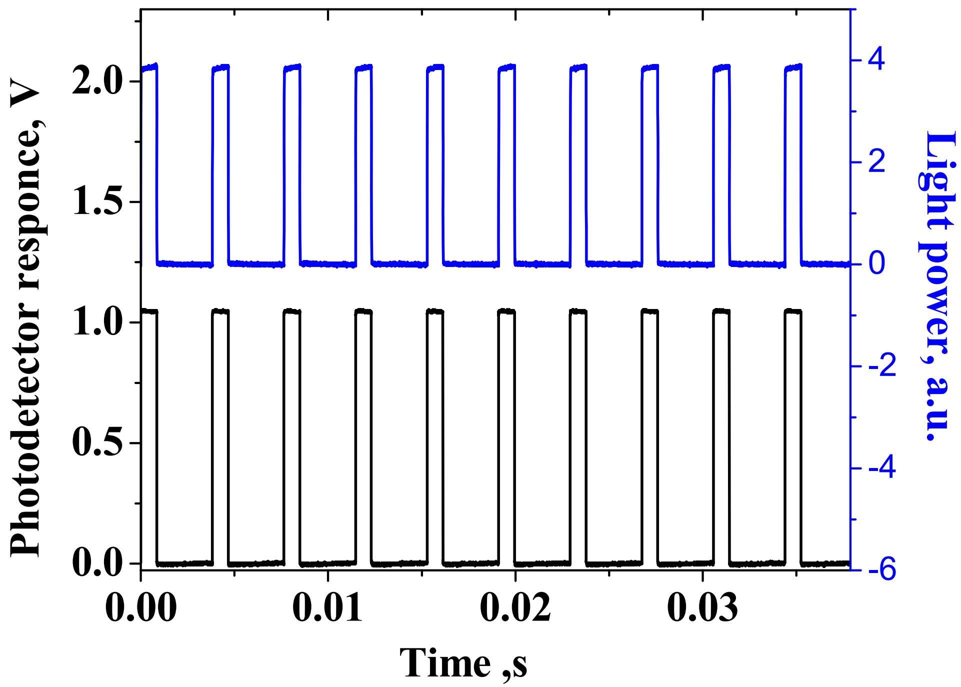
P9: I_{sc} = 10.23 mA/cm², V_{oc} = 0.5V, FF = 41%, PCE = 2.1%

P11: I_{sc} = 10.50 mA/cm², V_{oc} = 0.9V, FF = 42%, PCE = 4.0%

Photodetectors based on P11/[60]PCBM blend



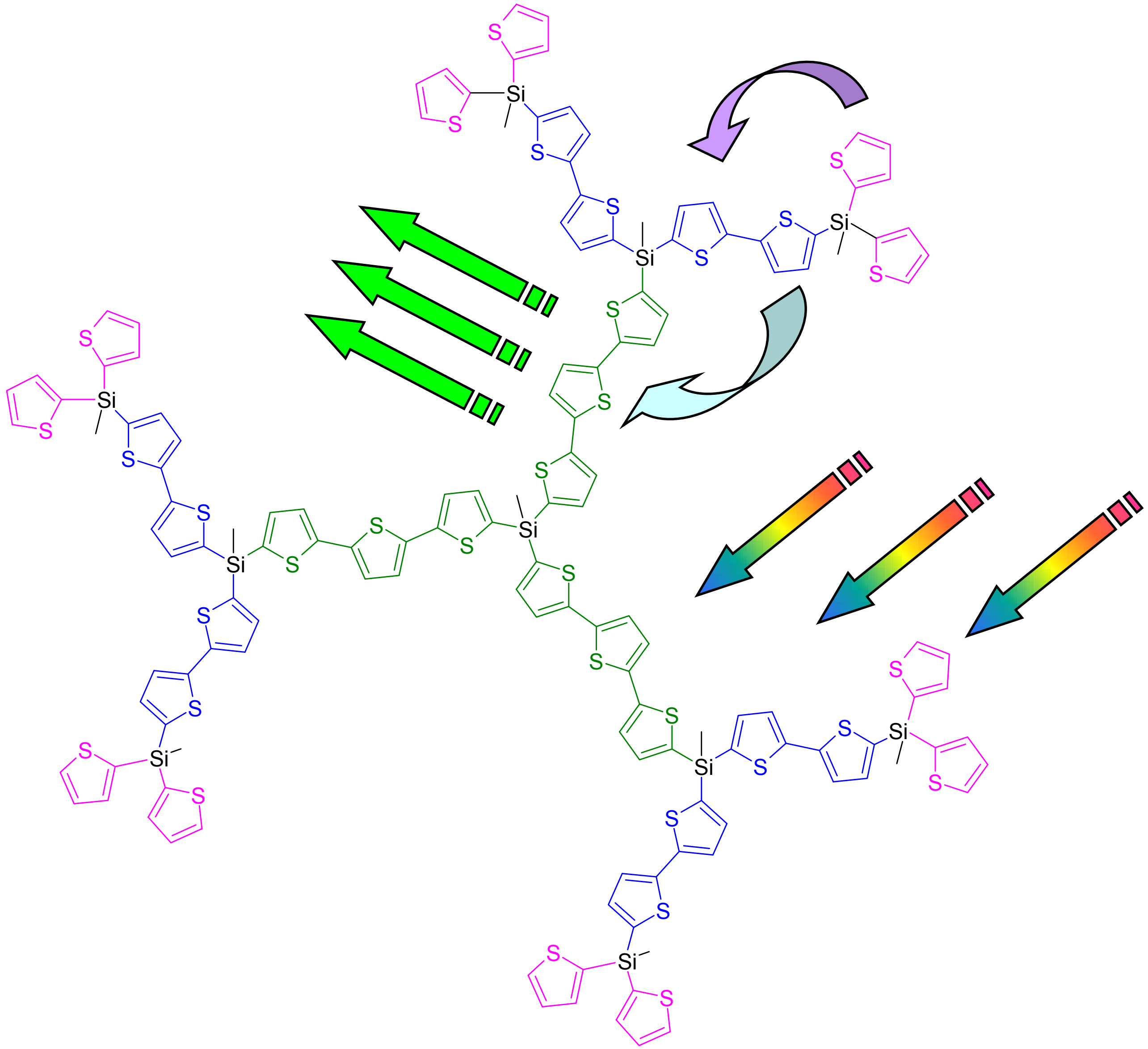
Transient response of the organic photodetector to a 10 ns light pulse from a nitrogen laser (337 nm) at different shift voltages. The active area was 0.5 cm^2 and a load resistance of 16 Ω.



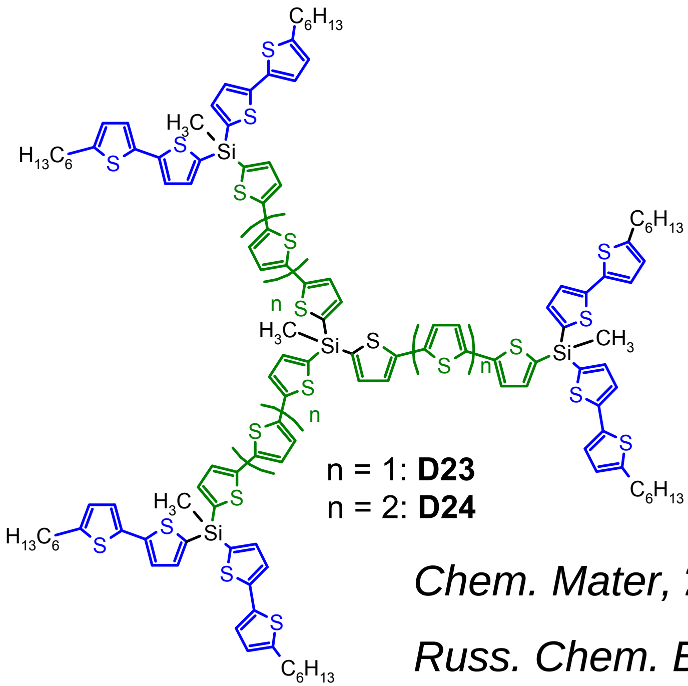
Detection of 1 ms light pulses of blue LED modulated at 250 Hz with the organic photodetector. Black line - photodetector response,
blue line - light power.

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

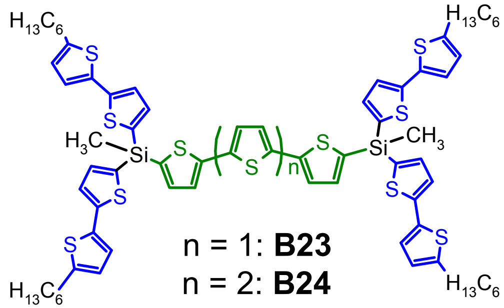
Organosilicon nanostructures luminophores and “molecular antennae” effect



The first organosilicon “molecular antennas”



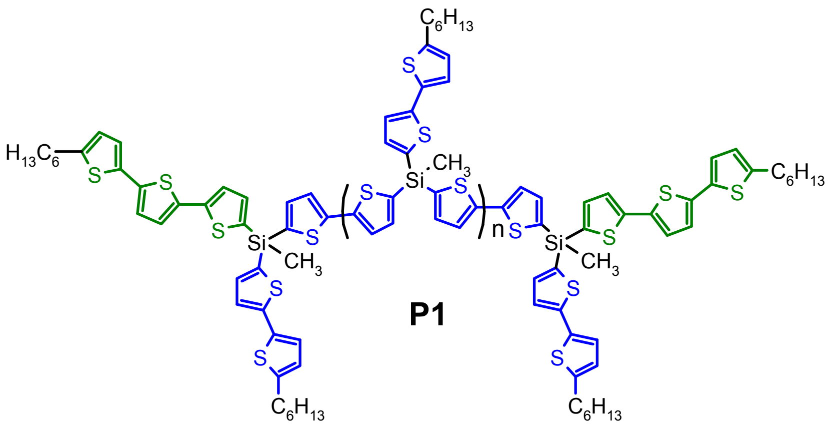
n = 1: **D23**
n = 2: **D24**



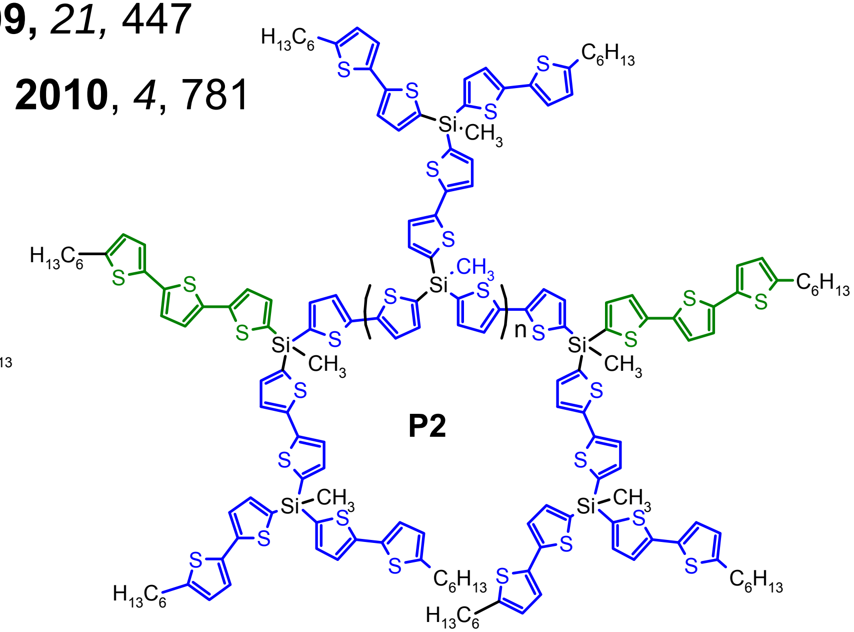
n = 1: **B23**
n = 2: **B24**

Chem. Mater, **2009,** *21*, 447

Russ. Chem. Bull, **2010**, *4*, 781



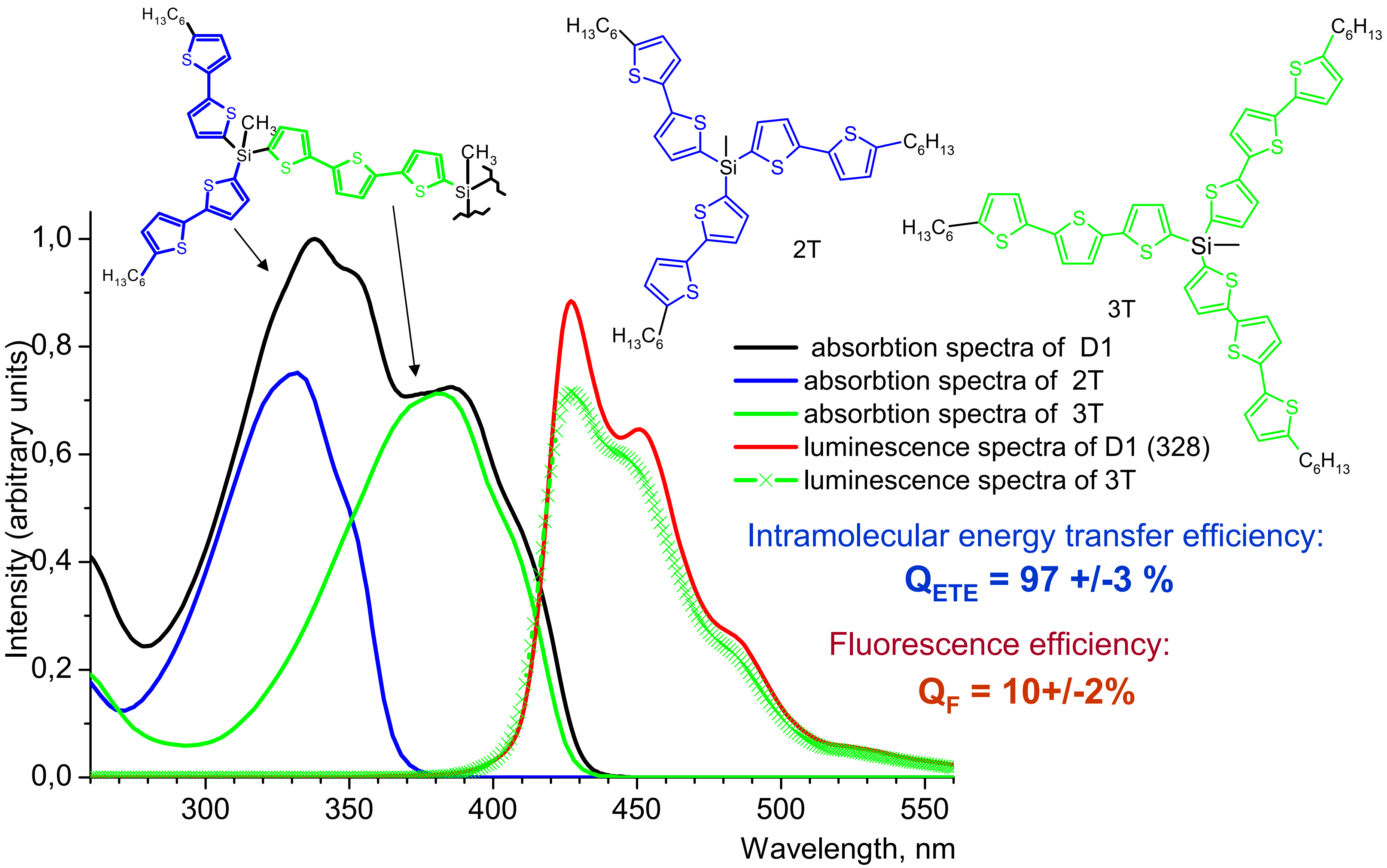
P1



P2

Macromolecules **2012**, *45*, 2014

Absorption and luminescence spectra of dendrimer D23 and model stars



Intramolecular energy transfer efficiency:

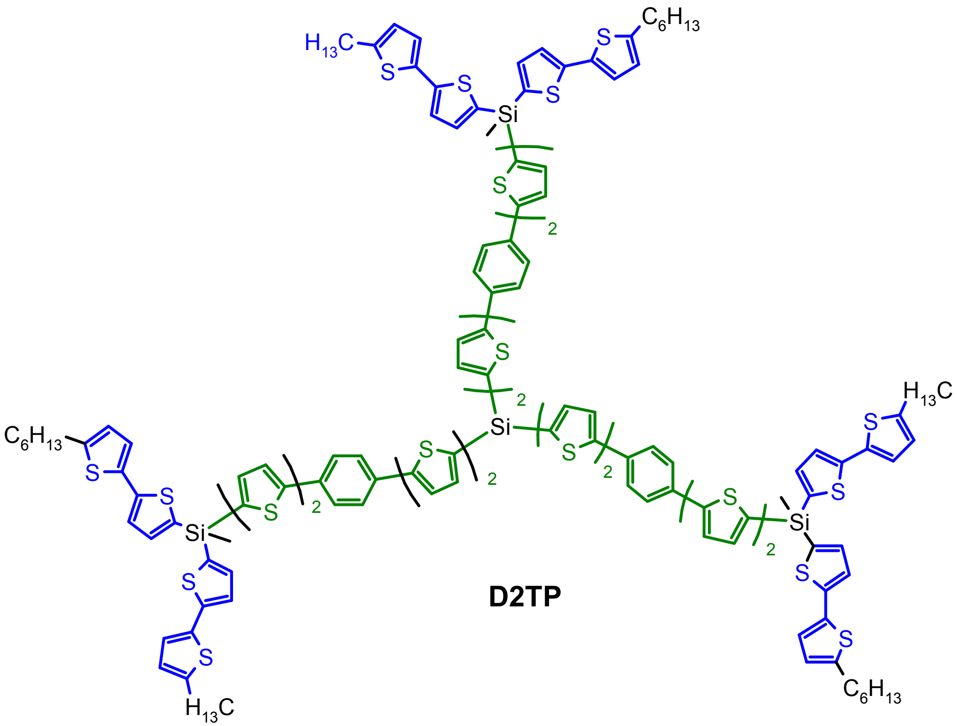
$$Q_{ETE} = 97 \pm 3\ \%$$

Fluorescence efficiency:

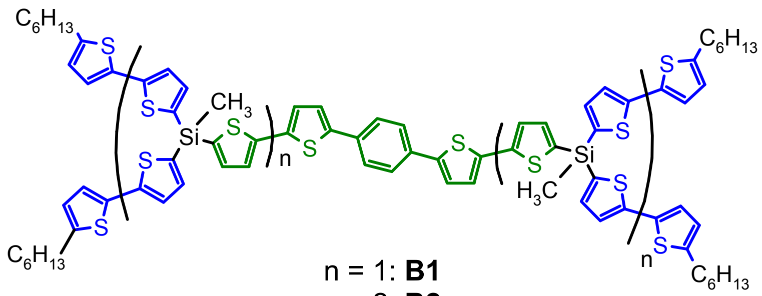
$$Q_F = 10 \pm 2\%$$

Absorption spectra of dendrimer D23 consists of a absorption bands of its 2T and 3T components, but its luminescence spectra coincides with those of 3T fragments independently of excitation wavelength

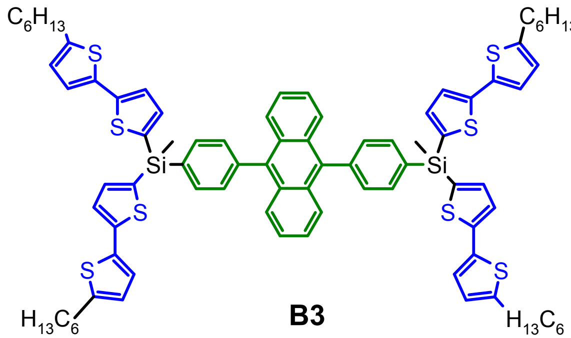
Highly luminescent oligoarylsilane "molecular antennas"



D2TP



n = 1: **B1**
n = 2: **B2**



B3

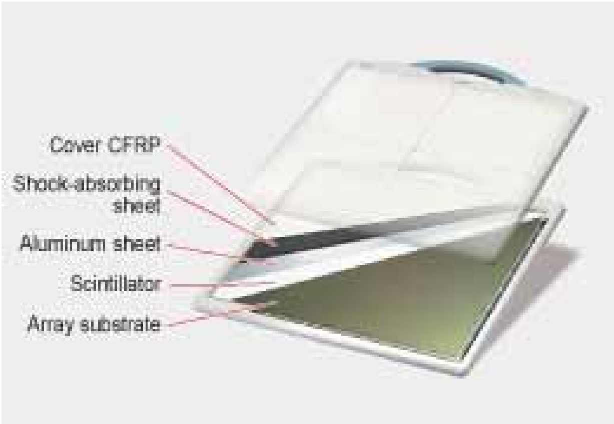
Mendeleev Commun. **2011**, *21*, 89

Compound	λ_{abs}, nm	Q_F,%	λ_{lum} nm	Q_{ETE},%
D2TP	336, 407	**46**	**456**/487	**88** +/- 3
B1	336, 404	**55**	**456**/487/521	**99** +/- 1
B2	337, 404	**55**	**456**/486/522	**90** +/- 10
B3	331, 375, 396	**80**	**418**	**82** +/- 10

Plastic scintillators and their applications

In medicine

Radiation control on nuclear power stations

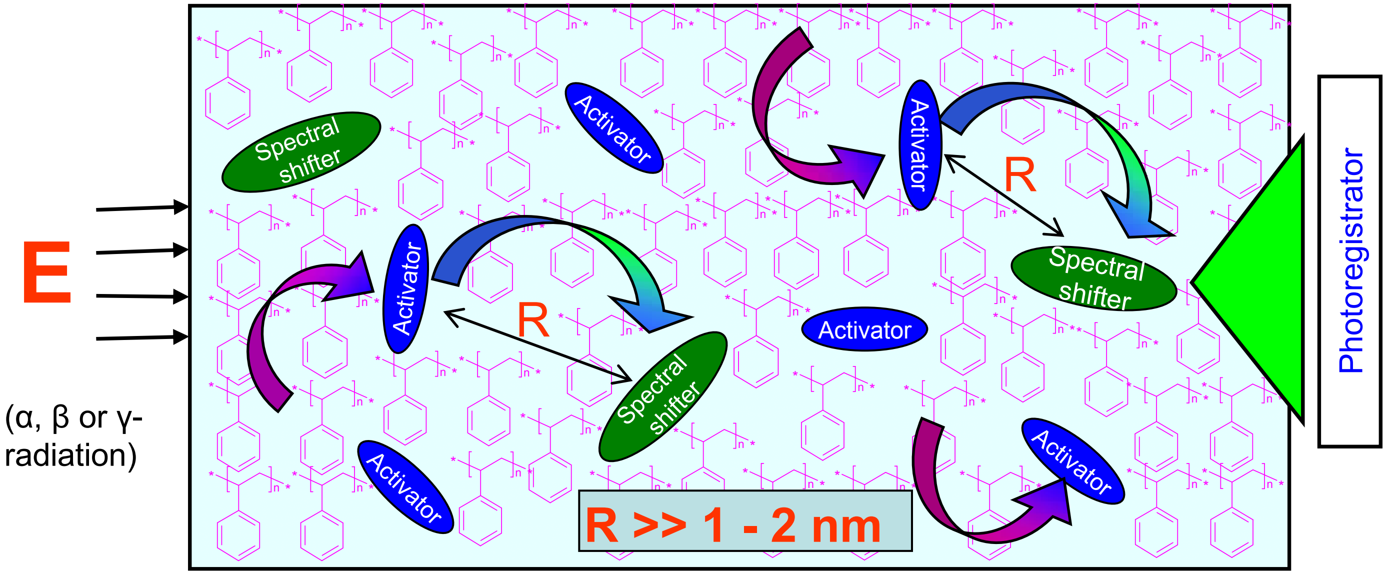


X-ray tomography

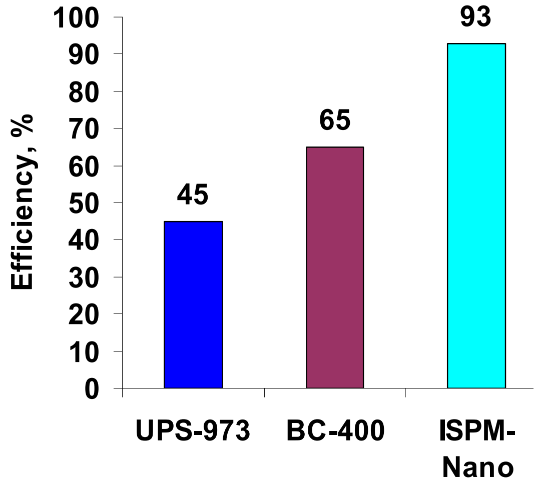
Radiation control at the boarders

Application in organic photonics: plastic scintillators

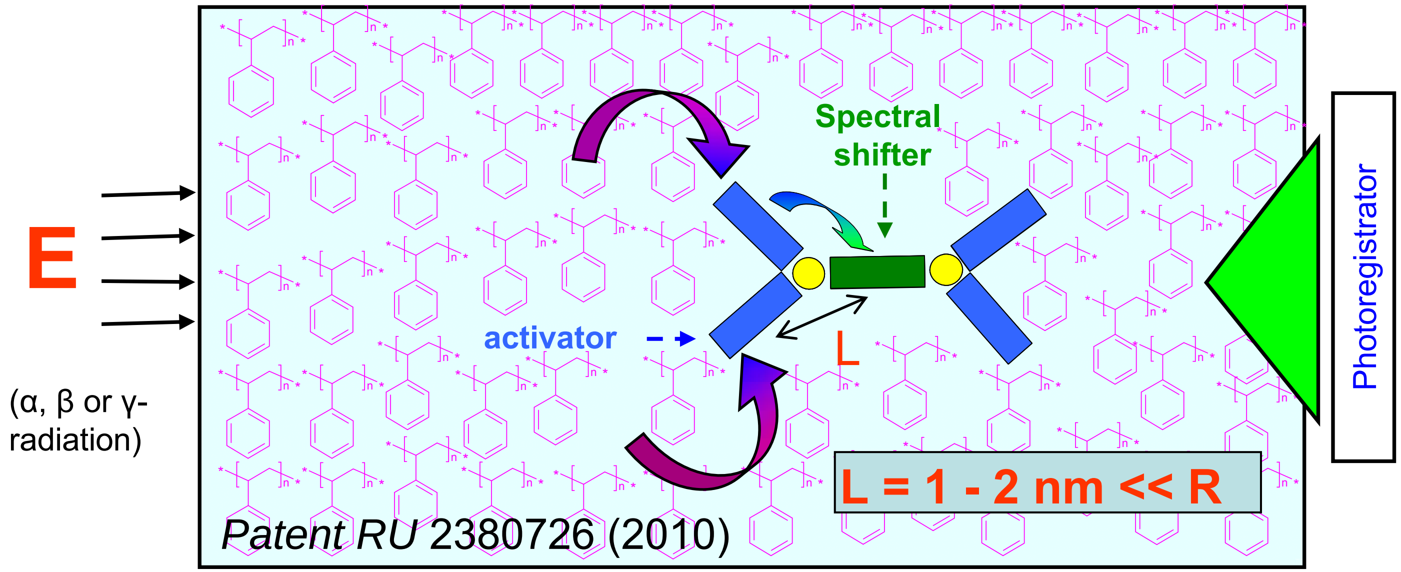
Classical polymeric scintillator



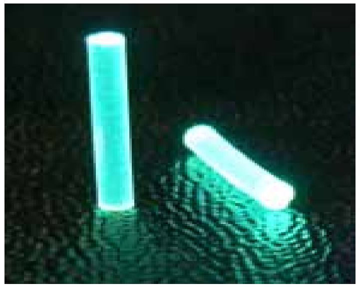
Efficiency relative to anthracene crystal



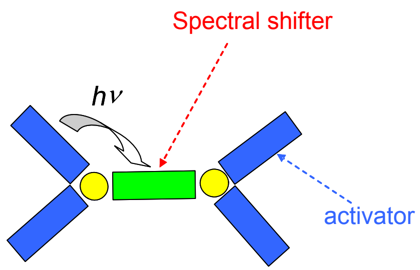
New scintillator with nanostructured luminophores



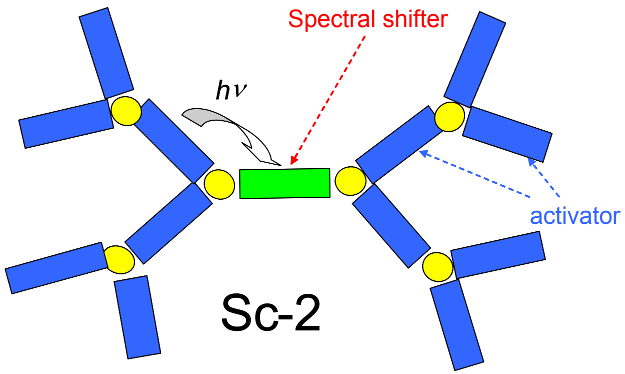
Nanoscintillator under UV irradiation



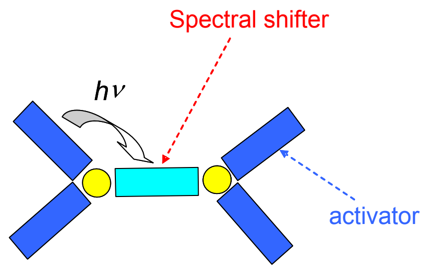
Polystyrene nanoscintillators



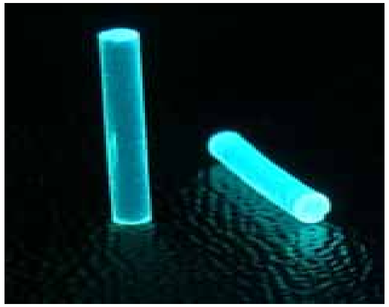
Sc-1

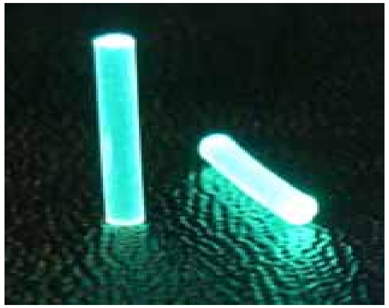


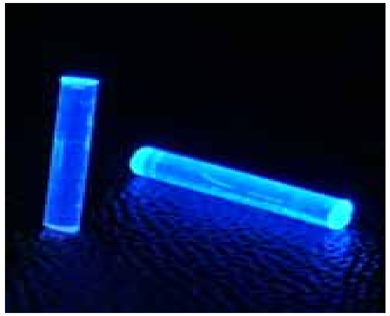
Sc-2



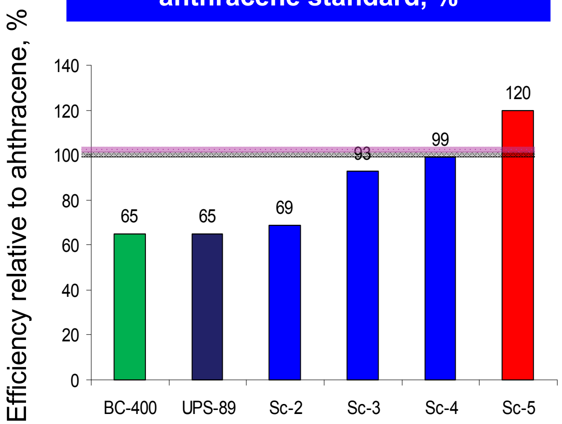
Sc-3



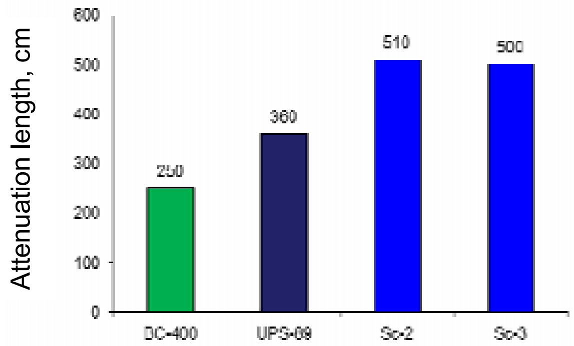




Scintillation efficiency relative to anthracene standard, %



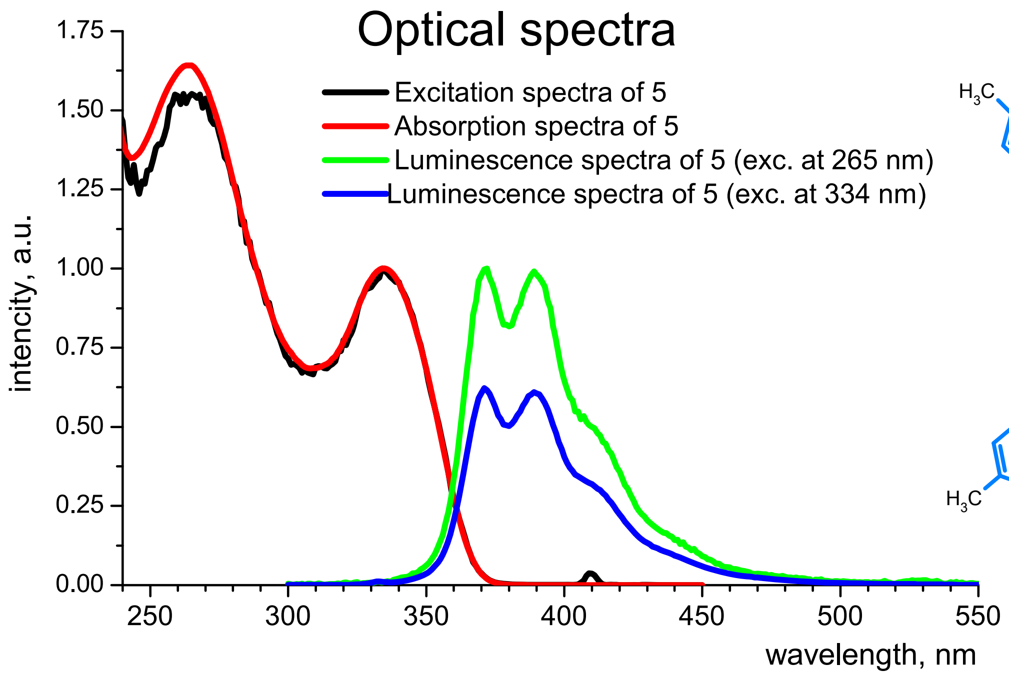
Attenuation length on the emission wavelength, cm

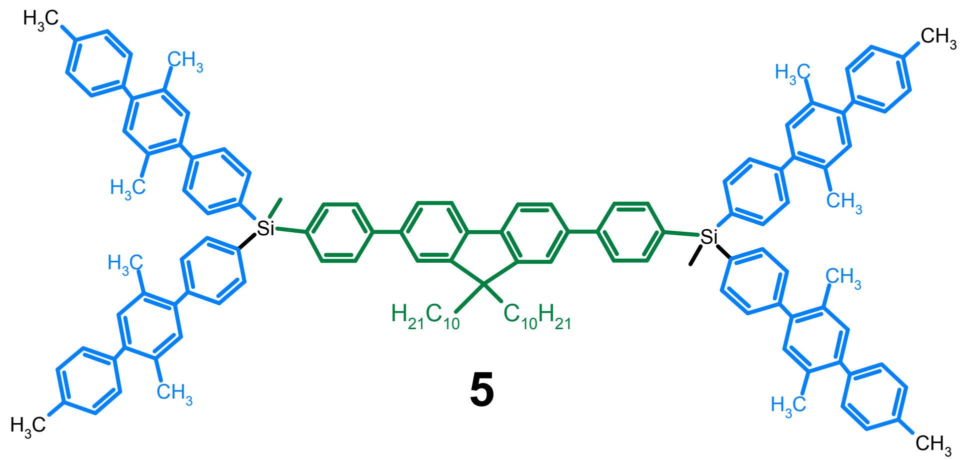


BC-400 – scintillator “Bicron”
UPS-973- scintillator “Amcrys-H”

Plastic scintillators with the efficiency exceeding those of anthracene crystals!

Polystyrene nanoscintillators

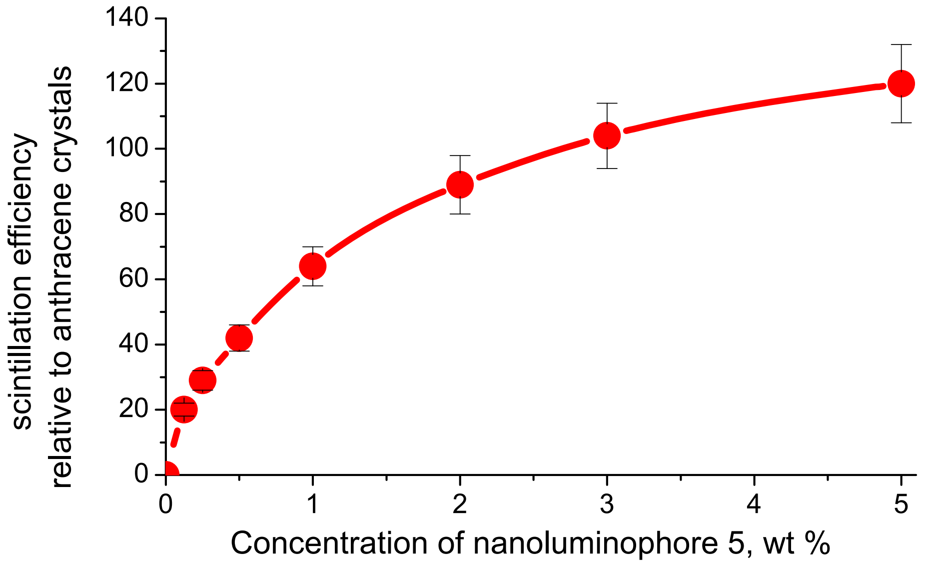




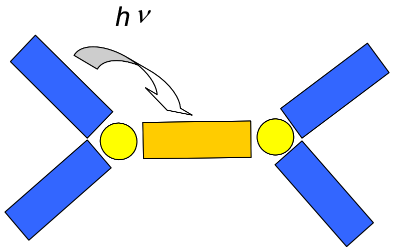
5

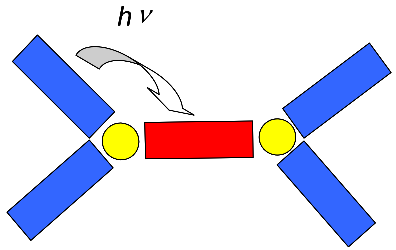
Q_{lum} **= 85+/-5%**

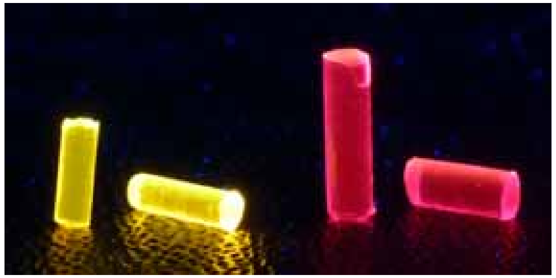
$E_{transfer}$ **= 98 +/-2 %**

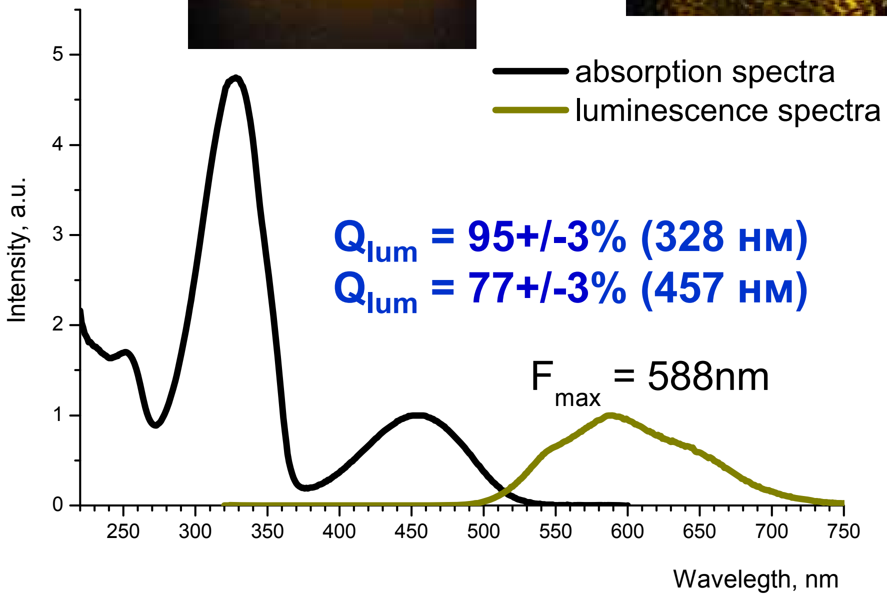


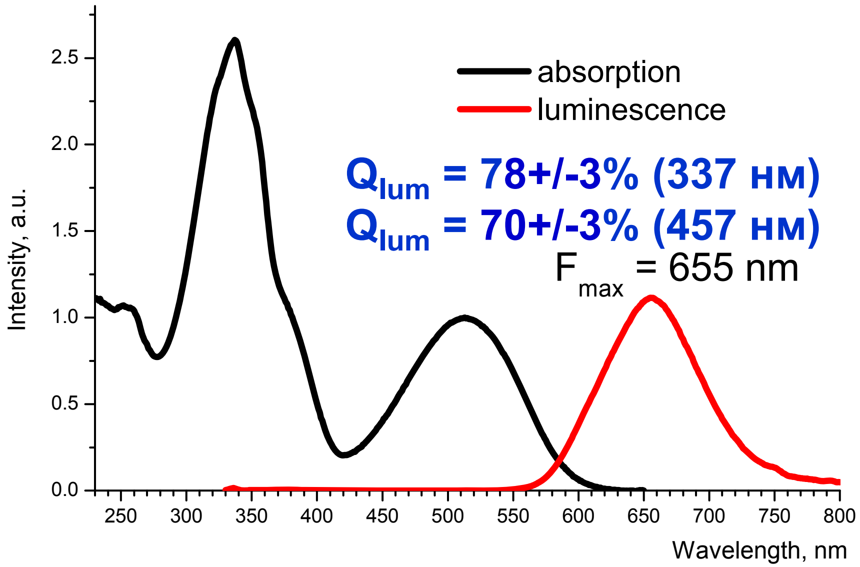
Novel organosilicon wavelength shifters











Efficient yellow and red wavelength shifters have been created

VUV Wavelength sifters for noble gas detectors

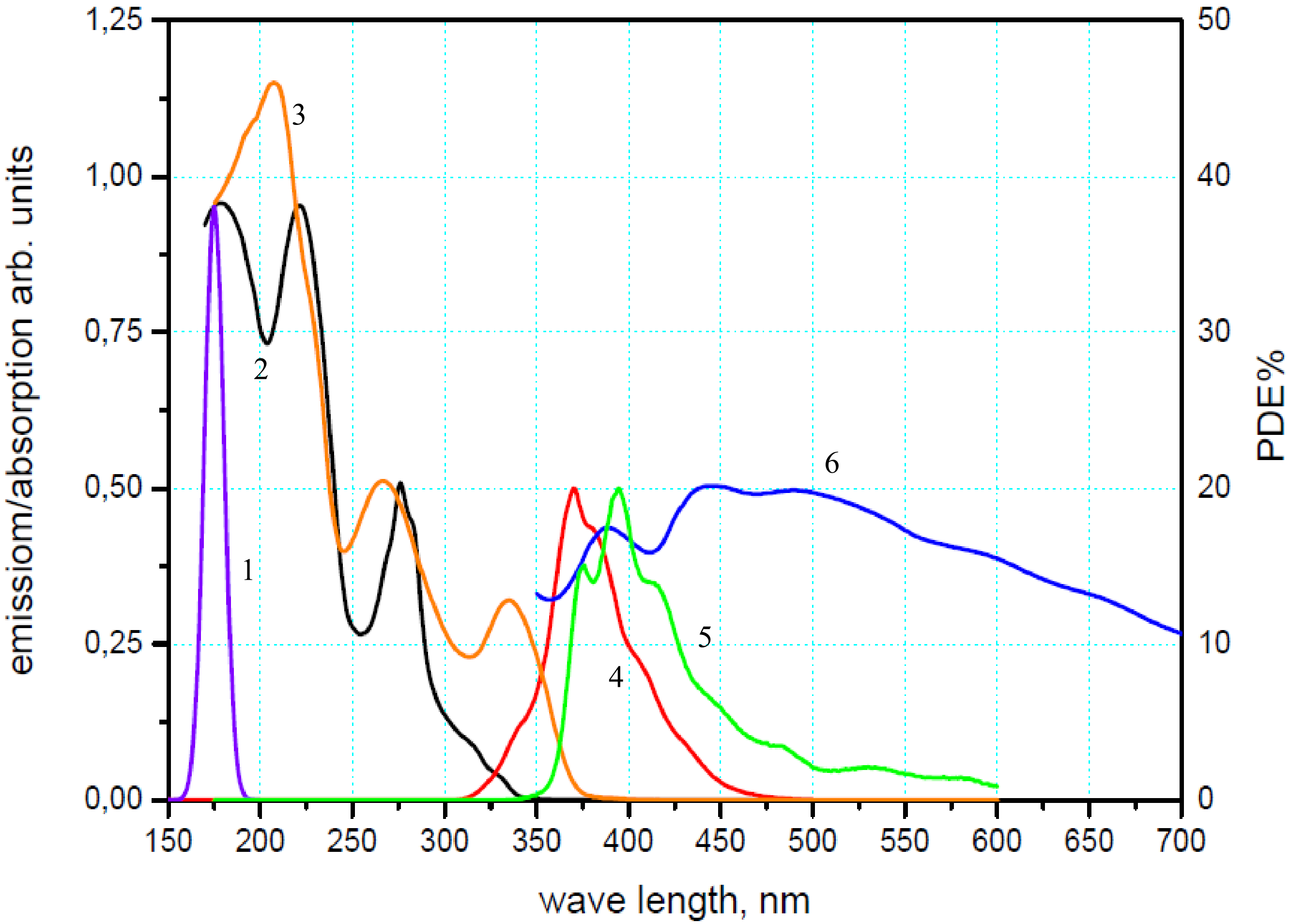
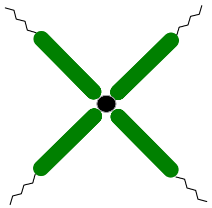


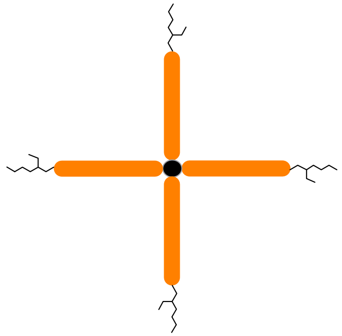
Fig 1. Emission spectrum of LXe (1), absorption spectrum of p-terphenyl (2), absorption spectrum of new WLS (3), emission spectrum of p-terphenyl (4), emission spectrum of new WLS (5), photon detection efficiency (PDE) of the CPTA "blue-sensitive" photodiode (6), right axis.

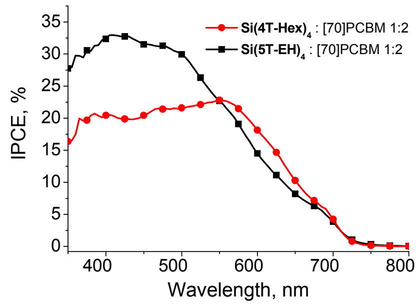
***Nuclear Instruments and Methods in Physics Research A* (in press), doi:10.1016/j.nima.2011.12.036.**

Conclusions

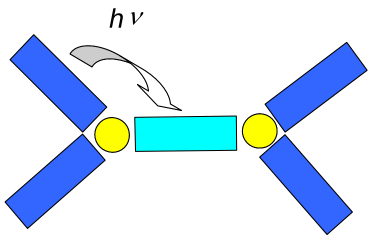
• Soluble oligothiophenesilane multipods are promising materials for organic BHJ solar cells and photodetectors with the response time of 20 - 30 ns .

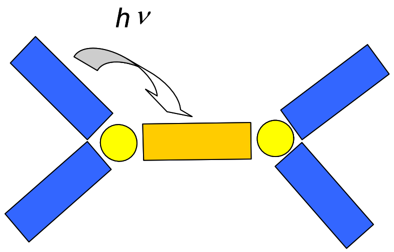


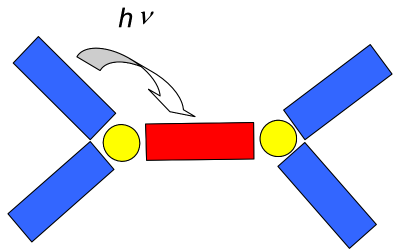




• Silicon atoms brake the conjugation between the adjacent luminophores that allows creation of organosilicon nanostuctured luminophores, which can be used in highly efficient and fast plastic scintillators and wavelength shifters.







• Light output of the “plastic nanoscintillators” can exceed those of the standard BC408 more then 1,6 times and even exceed the efficiency of anthracene crystals.

Acknowledgements

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Thank you for your attention!