Halbleitende Polymere für elektronische Anwendungen

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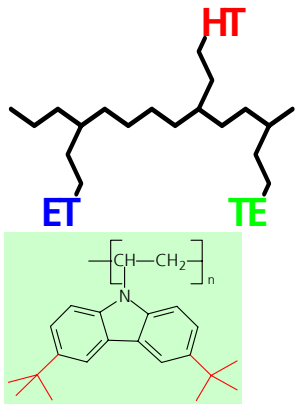
Development of polymer materials with semiconducting properties

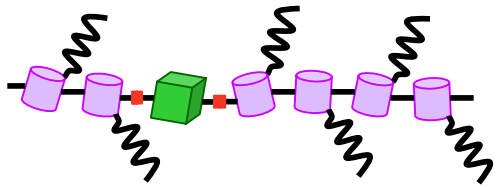
Preparation of functional polymers; polymerisation reaction with state of the art polymerisation technique

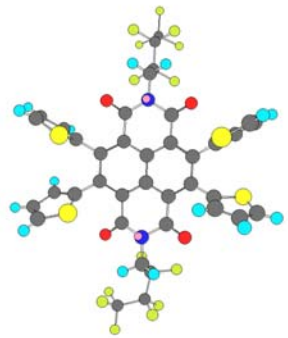
OLED
polymer triplett emitters
conjugated polymers

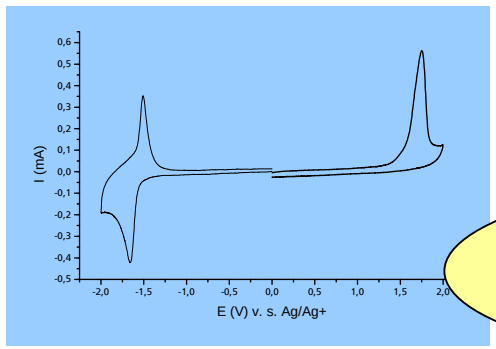
OFET
p- and n-type conjugated polymers

Photovoltaic
polymers with high EA,
low band gap materials









challange
no structure defects,
ion-free, analytics

Electronic properties
spectroscopy
cyclovoltammetry

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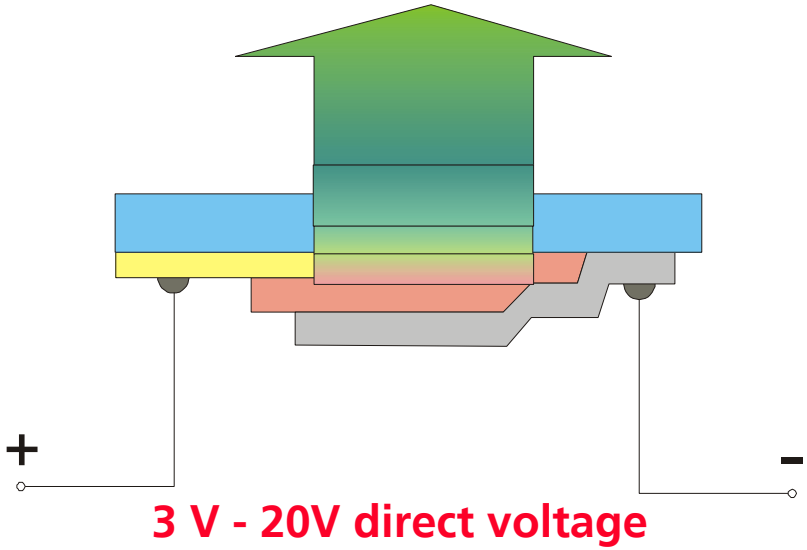
soluble polymers

the innovation – polymer substance

Basic structure of PLEDs and processing



3 V - 20V direct voltage

Glass substrate

Transparent anode 100 nm (ITO)
PEDOT-PSS-layer 80 nm

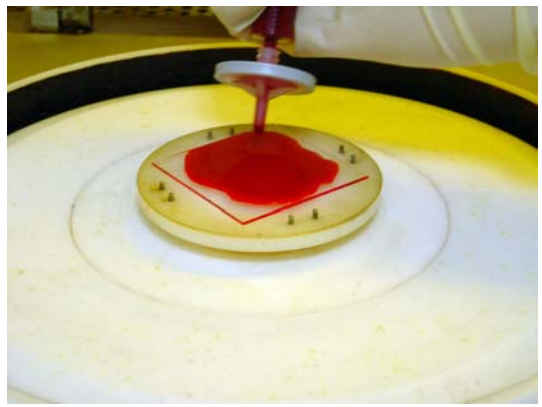
Emissive layer 70-130 nm

LiF interface layer (5 nm)
Reflective electrode (Ca 50 nm/Al 150 nm)

Vakuum deposition of metal electrodes

Solution processing

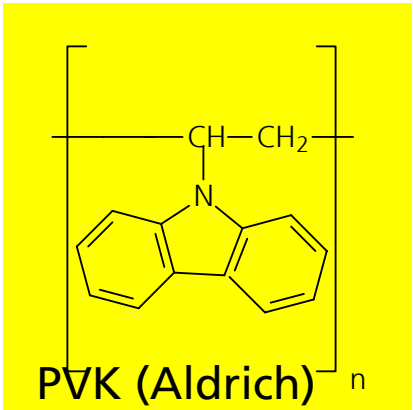
Spin coating or printing



Blend systems - max. 100% luminous efficiency possible

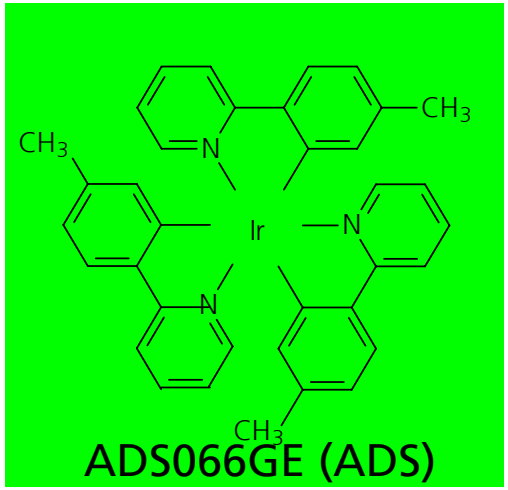
polymer triplett emitting systems as guest-host system

matrixpolymer



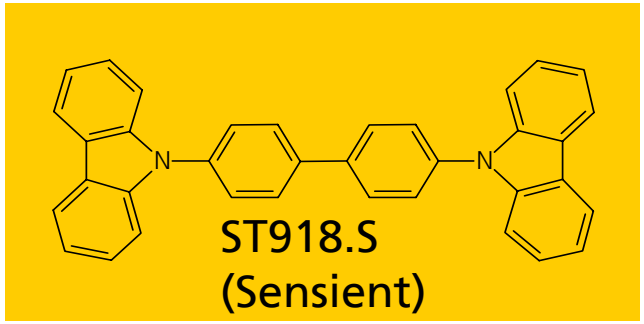
PVK (Aldrich)

phosphorescent complex



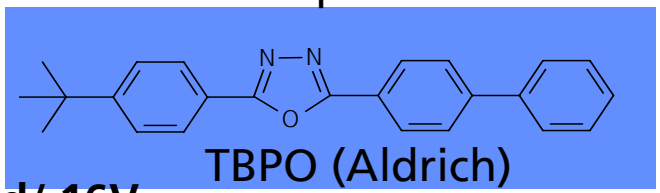
ADS066GE (ADS)

hole transport-material



ST918.S
(Sensient)

electron transport-material



TBPO (Aldrich)

achieved parameters: efficiency: **30 cd/A /8V,**
high clour purity, brightness: **1000 cd/ 16V**

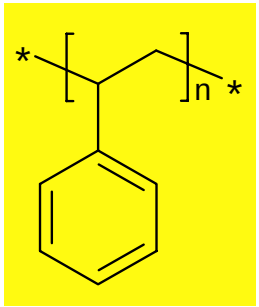
problems:
- high onset voltages (8-10 V)
- stability to low (only few hours)
- low lifetime because of migration, aggregation and recristallisation

Design of fixed polymer systems on the base of styrene building blocks

PLED

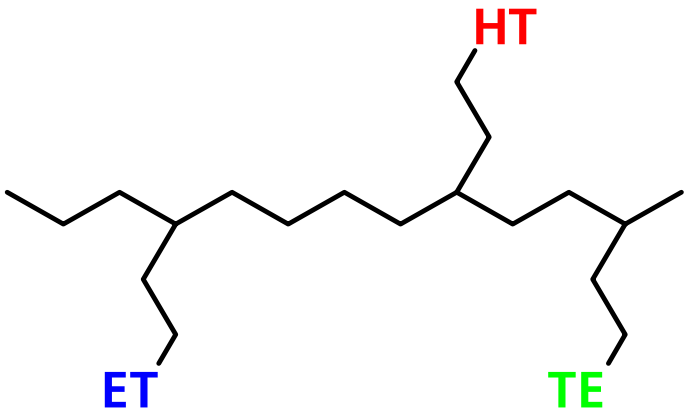
matrix polymer

blendsystems: high efficiency, pure emission of the Triplett emitters; chemical inert,

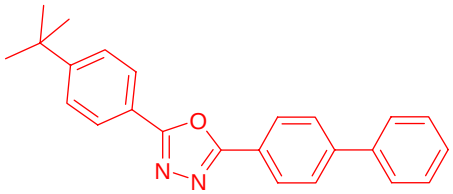


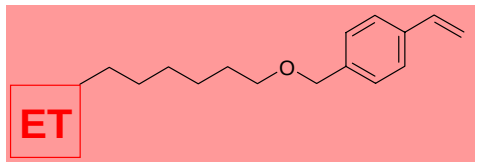
polystyrene (PS)

goal: chemical connection of the HT-, ET- and the TE on a matrix

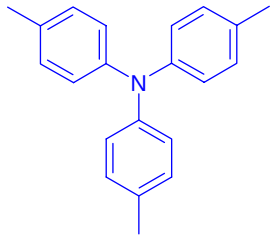


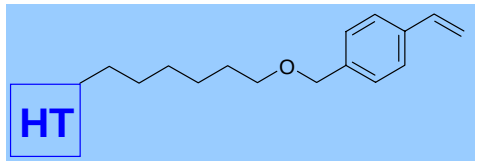
ET



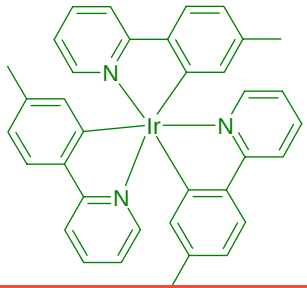


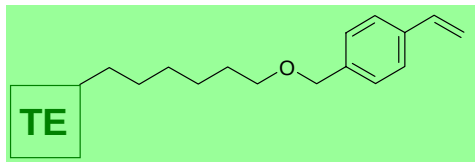
HT





TE





Terpolymerisation of different styrene monomers, variation of the composition

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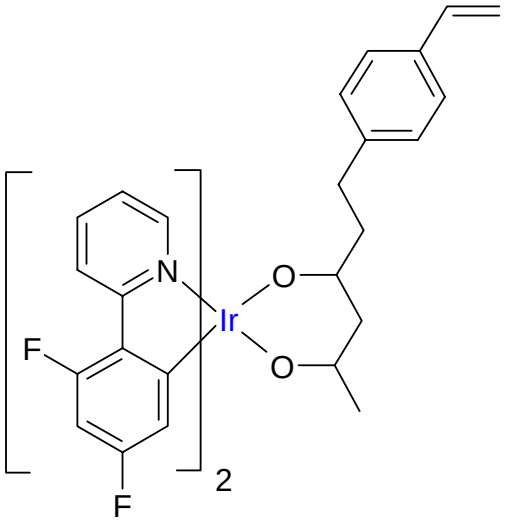
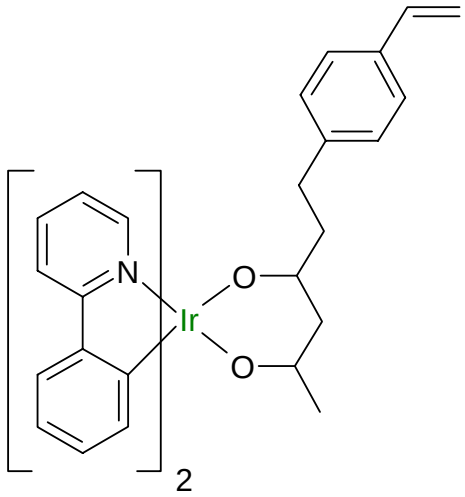
IAP

Monomer synthesis

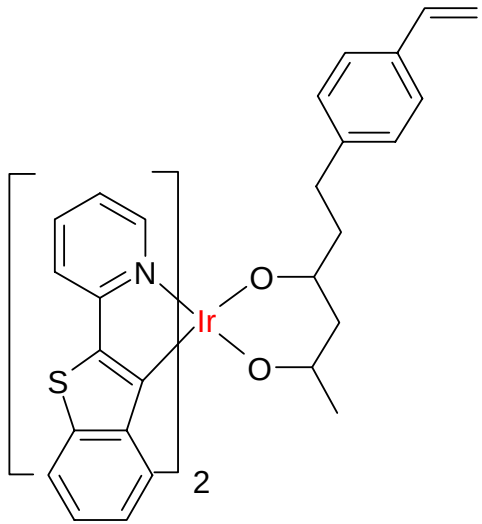
Triplet emitter monomer (TE)



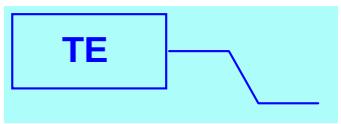
blue

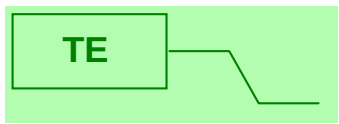


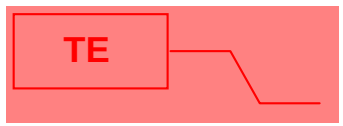
green



red

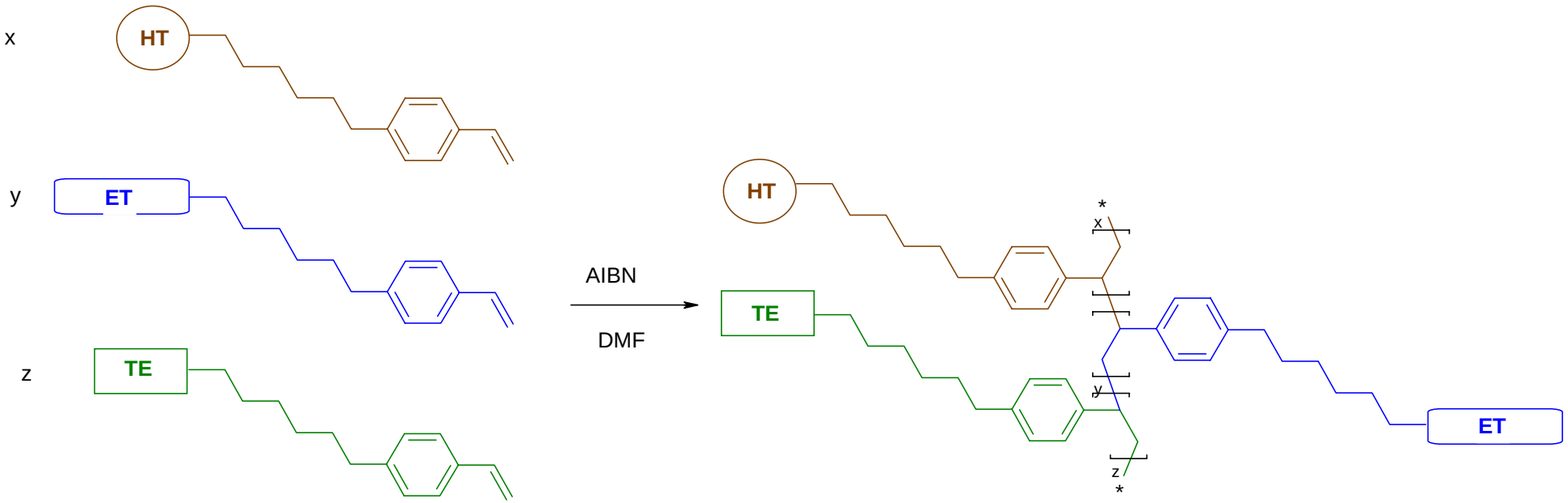




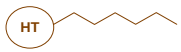
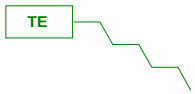
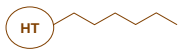
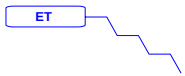
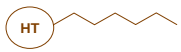


Polymerization process

- Radical polymerization of homo-, co- and terpolymers
- Best ratio between HT, ET und TE was determined by blend system
- Statistical arrangement of comonomers
- AIBN, DMF, 60 °C



Terpolymers HT/ET/TE

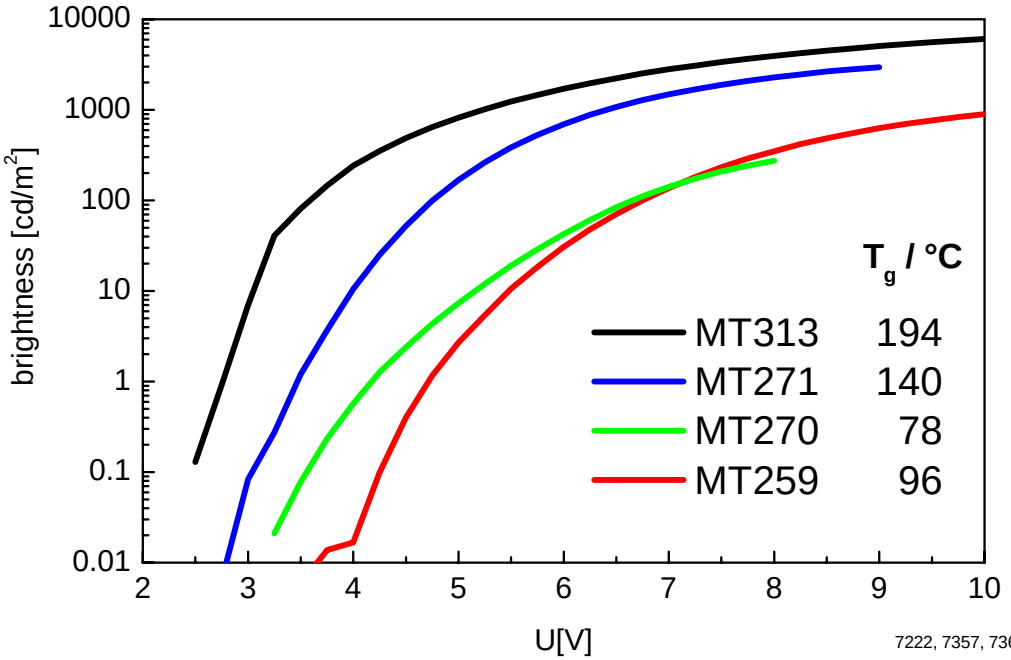
Terpo-lymer	HT	ET	TE	M_w g/mole	T_g °C
MT259				35.600	96
MT270				40.900	78
MT271				57.600	140
MT313				61.300	194

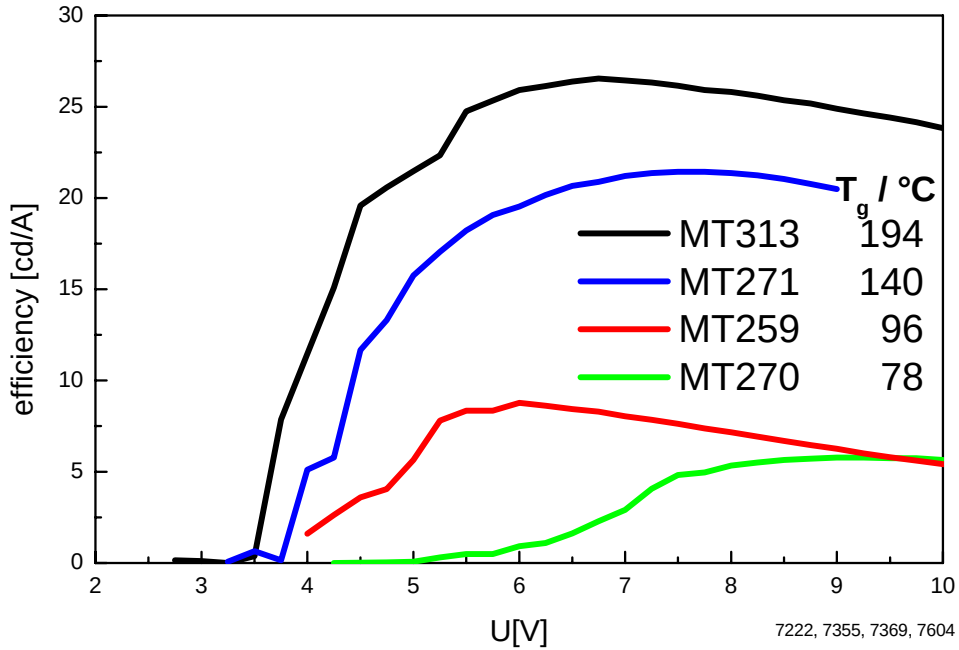
T_g depends on spacer length of comonomers

OLED performance of terpolymers HT/ET/TE

PLED

ITO/CH8000/MTXXX/CsF/Ca/Ag





Brightness-voltage characteristic improved with higher T_g

Efficiency increases with higher T_g

strong dependence of brightness and efficiency from the spacer length

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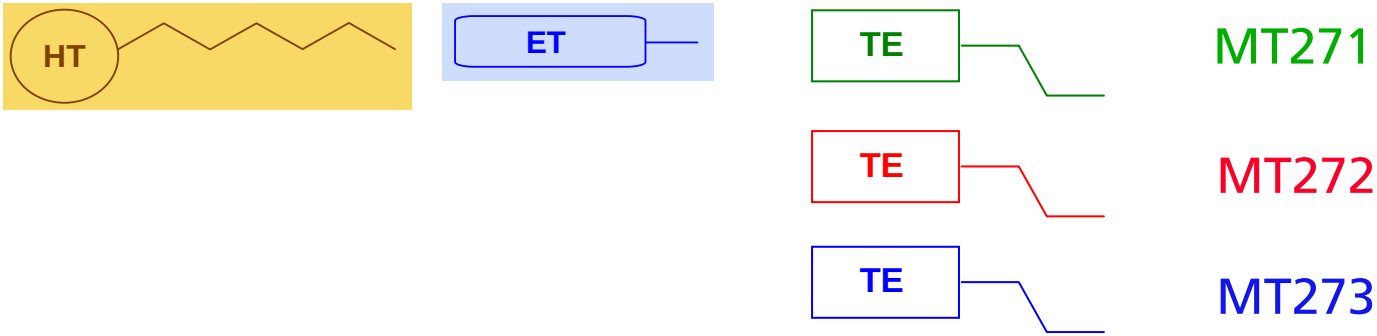
Comparison for terpolymers with RGB-Ir-emitter

PLED

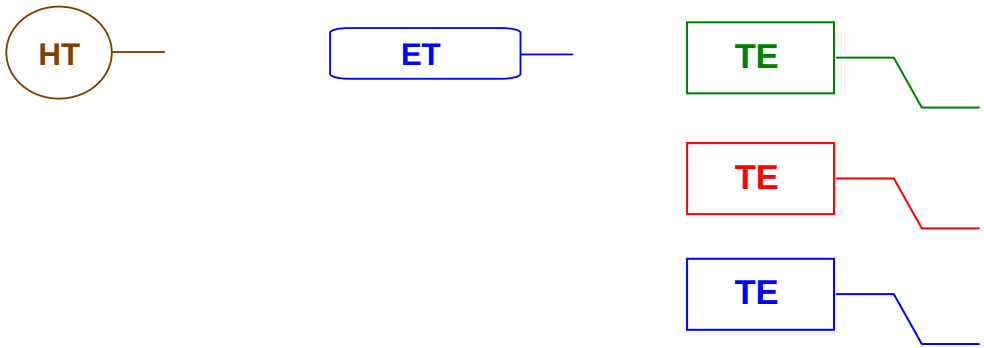


Terpo-lymer	M_w g/mole	T_g °C	brightness cd/m²	efficiency cd/A
MT271	57.600	140	3000 @ 9V	21 @ 8 V
MT272	60.700	137	450 @ 8 V	4 @ 7 V
MT273	55.500	125	250 @ 9 V	2,2 @ 8 V

Improvement assumed for HT without spacer as for green
5000 cd/m² @ 9 V
28 cd/A @ 8 V

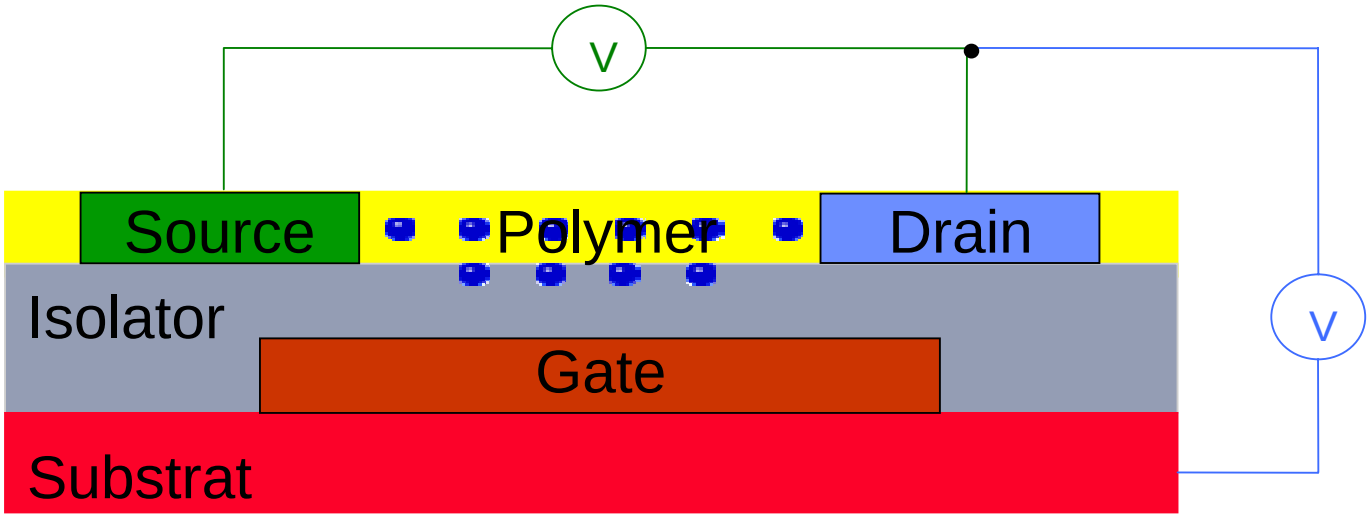
Comparison for terpolymers with RGB-Ir-emitter

PLED

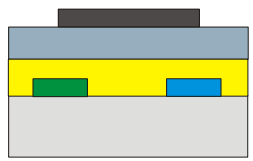


Terpo-lymer	M_w g/mole	T_g °C	brightness cd/m²	efficiency cd/A	HT/ET/TE Mol%
MT313	61.300	194	5000 @ 9V	28 @ 8 V	27,4/70,3/2,3
MT317	74.700	196	700 @ 8V	6,5 @ 8V	32,5/65,2/2,3
MT318	67.800	197	650 @ 9V	4,5 @ 6V	32,6/65,1/2,3

Model of an organic field effect transistor OFET



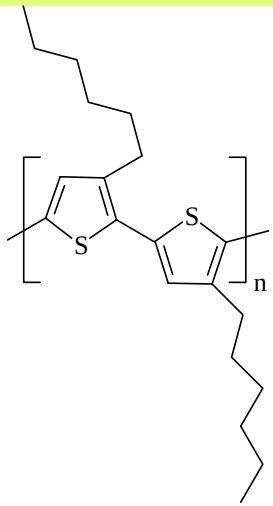
- Semiconducting polymers are able to conduct and switch the current
- From semiconducting polymers could be realized electronic circuits
- OFET is an essential component for integrated circuits

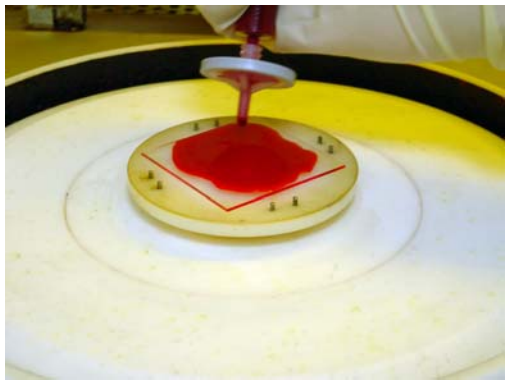


Semiconducting polymers for OFETs

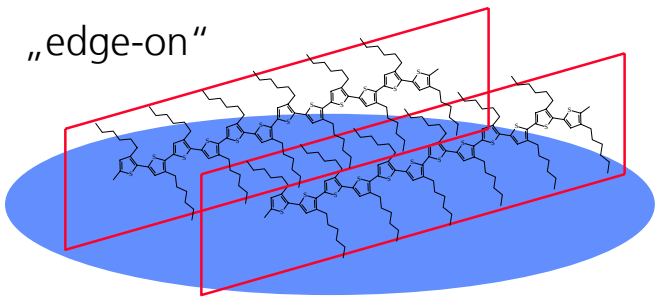
Active organic layer fabricated by spin coating or printing-technologies

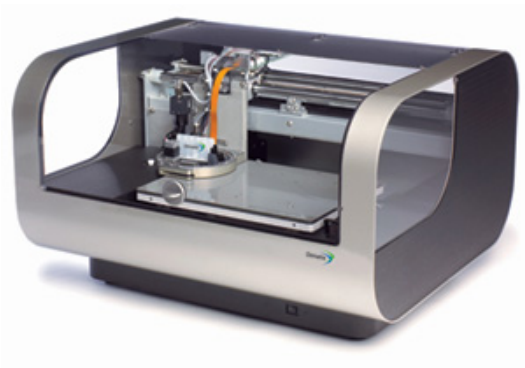
Semicrystalline polymers





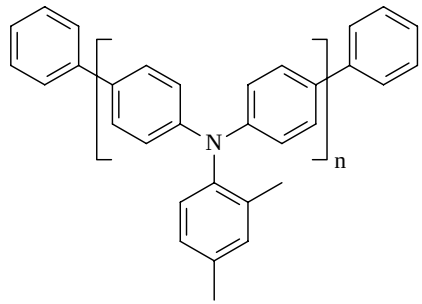
„edge-on“





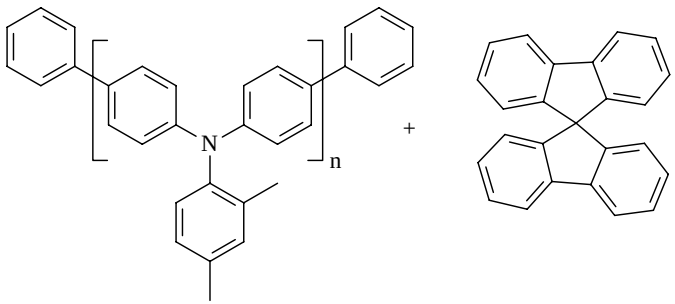
Mobilities up to ~ **0,2 cm²/Vs**

Amorphous polymers



Mobilities up to ~ **8 x 10^{-3} cm²/Vs**

Mixtures of PTAA polymers an low molecular weight additives



Mobilities up to ~ **1 x 10^{-2} cm²/Vs**

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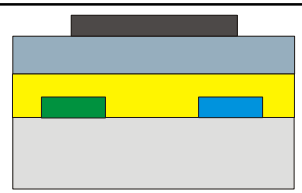
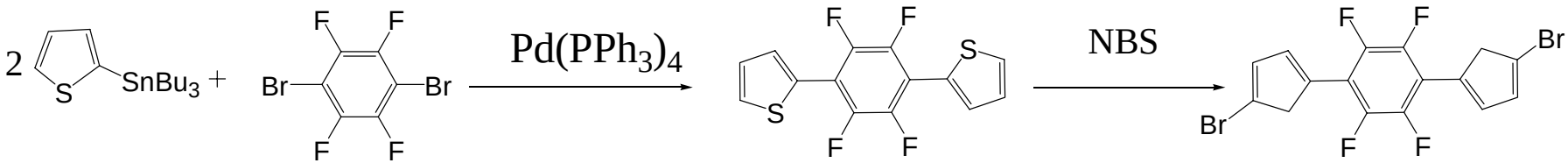


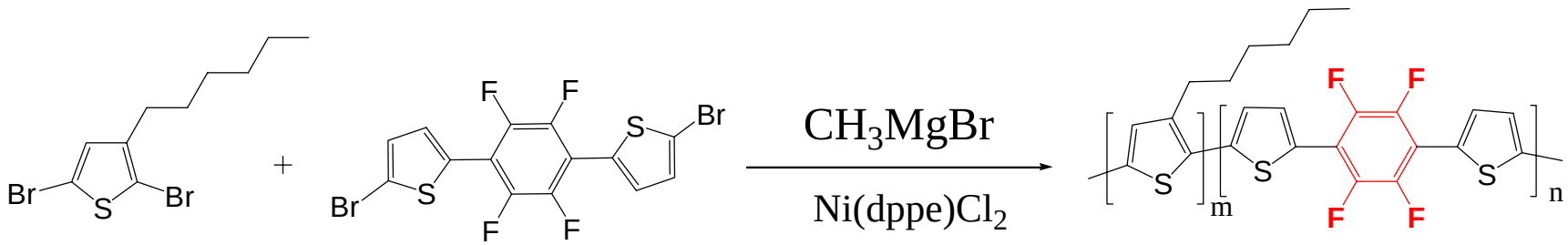
New copoly(3-hexylthiophene) with covalent attached acceptors

synthesis of the Dibromo-functionalized monomer



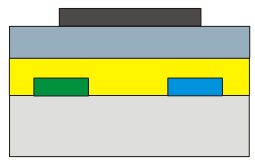
2 **3**

McCullogh Grignard Metathese method



3 **4**

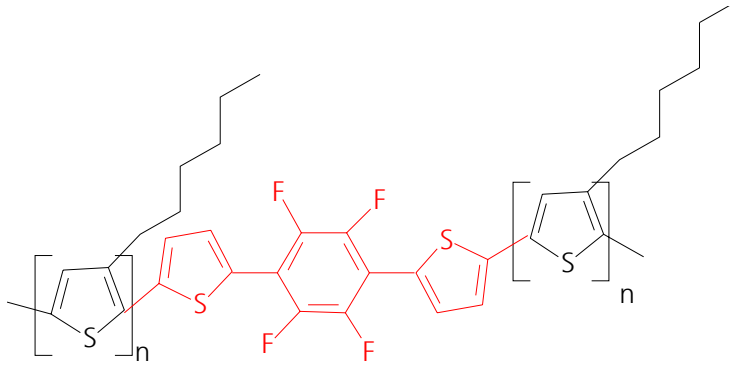
Statistical copolymers with different content of acceptor units were synthesized



Poly(3-hexylthiophene, acceptor) - Results

Acceptor molecule: 1,4-Bis(5-bromothienyl)-2,3,5,6-tetrafluorobenzene

✓ Varied acceptor amount in the P3HT-chain



Polymer	M_n [g/mol]	M_W [g/mol]	PD	Acceptor [mol%]
P3HT	19 200	28 800	1.5	-
P(3HT, TFT_**1**)	15 700	28 900	1.6	1.1
P(3HT, TFT_**3**)	19 800	28 700	1.4	3.0
P(3HT, TFT_**5**)	14 800	22 300	1.5	5.1
P(3HT, TFT_**10**)	14 500	21 100	1.5	9.5

IAP
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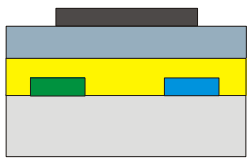
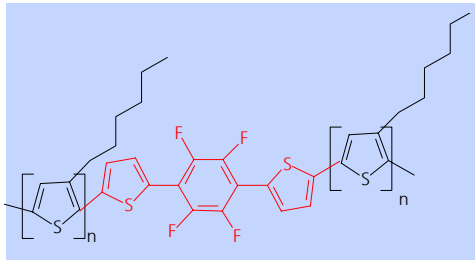
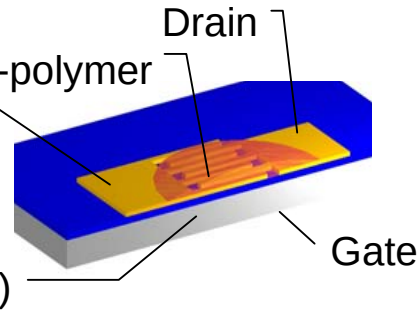


OFET Characterisation – P(3HT, acceptor)

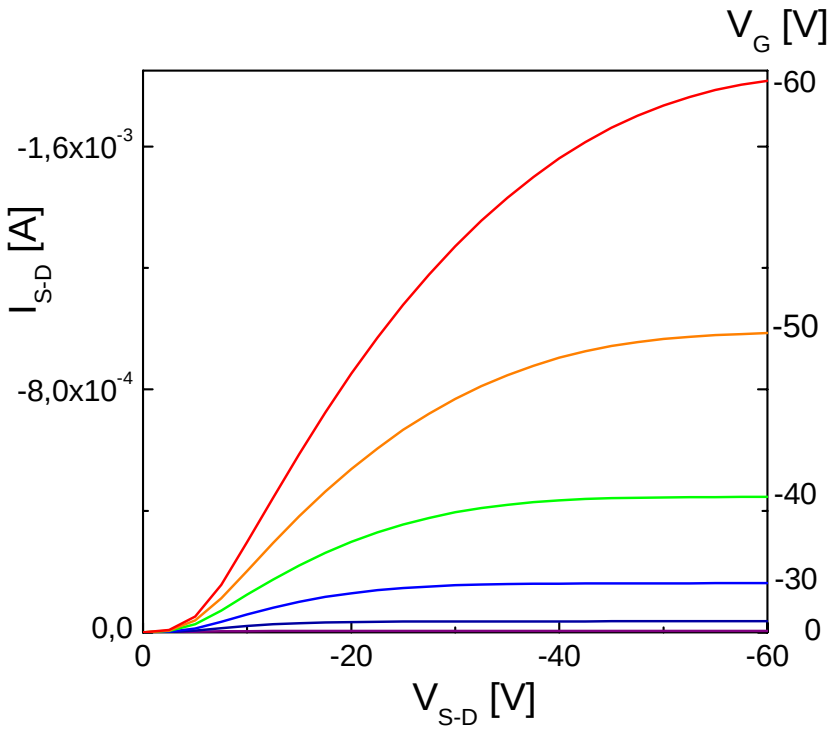
OFET

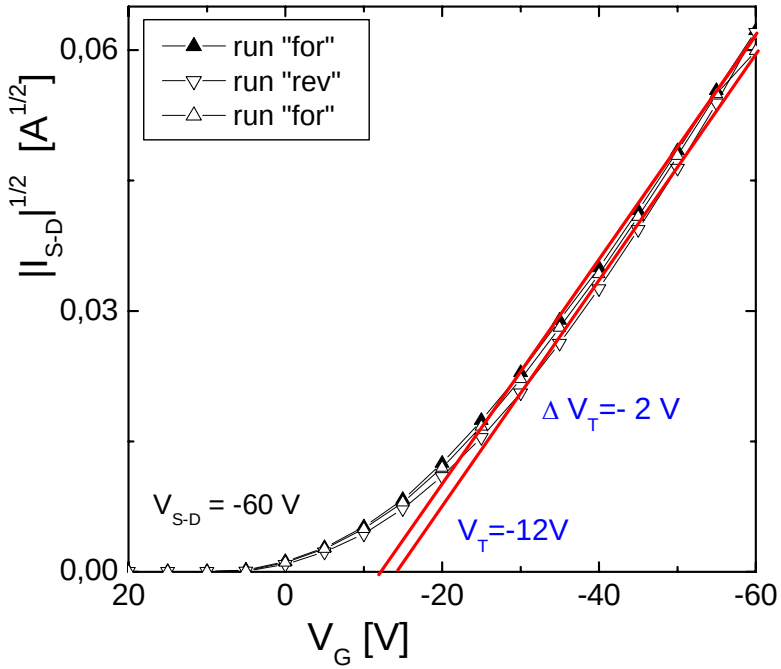
ON/OFF: 10^4, μ_{sat}: 1.2 x 10^{-2} cm^2/Vs
Example: P(3HT, TFT_3)





W = 195 mm
L = 10 µm
SiO_2 (d=235 nm)





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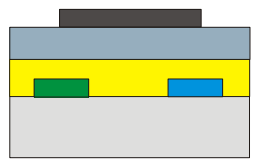
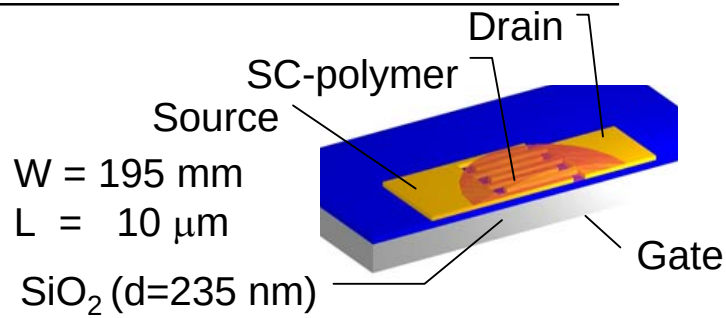


OFET Characterisation - Summary

OFET



Polymer	µ [cm^2/Vs]	ON/OFF	V_T [V]	Δ V_T [V]
P3HT	3.7 x 10^{-2}	1 x 10^4	-10	-4 to -6
P(3HT, TFT_**1**)	3.2 x 10^{-2}	1 x 10^4	-10	-1 to -2
P(3HT, TFT_**3**)	1.2 x 10^{-2}	3 x 10^4	-12	-1 to -2
P(3HT, TFT_**5**)	4.8 x 10^{-3}	2 x 10^5	-14	-1 to -2
P(3HT, TFT_**10**)	1.2 x 10^{-3}	2 x 10^5	-16	-1 to -2

±15 % device parameter deviation

➢ Favourable combination of the OFET-parameters: µ, ON/OFF & operational stability

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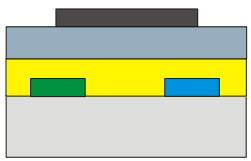
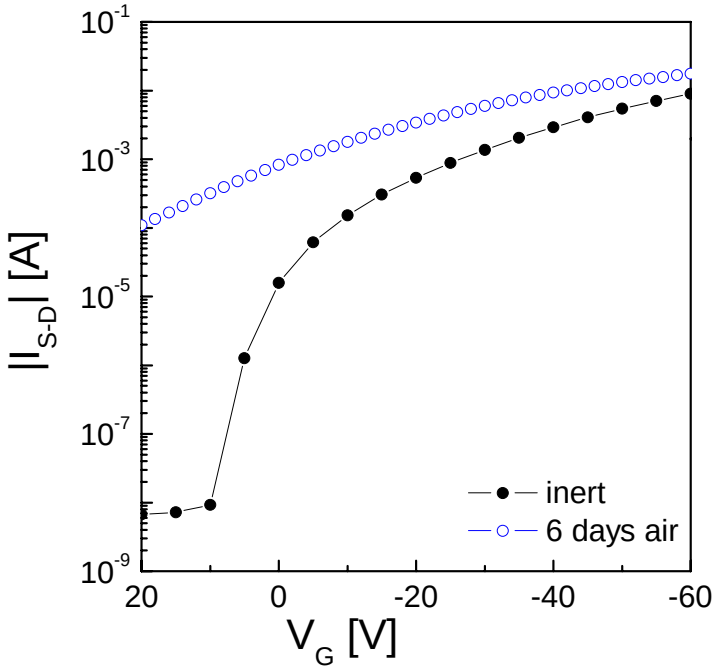


Transfer characteristics – air exposure test

Comparison of the transfer characteristics:

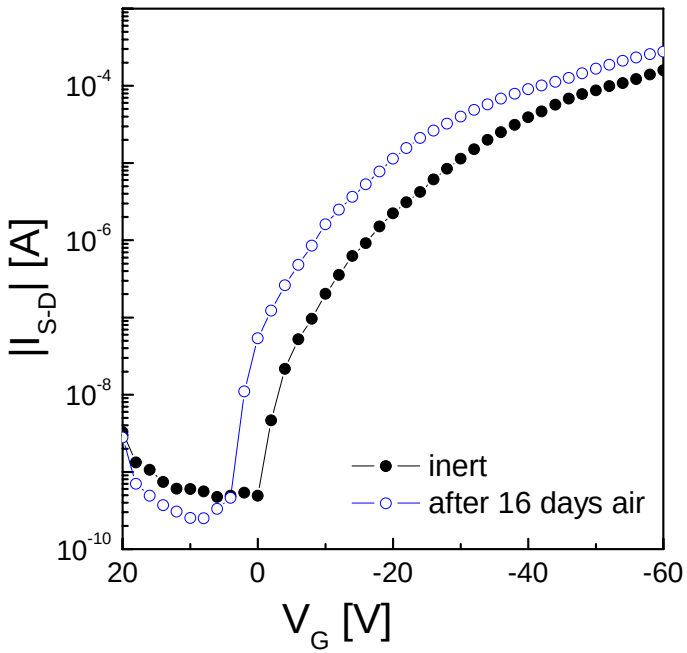
✓ P3HT



- fast „OFF"-current increase (~10^4)

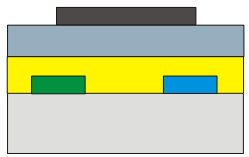
➢ significant performance decrease

✓ P(3HT, TFT_**10**)

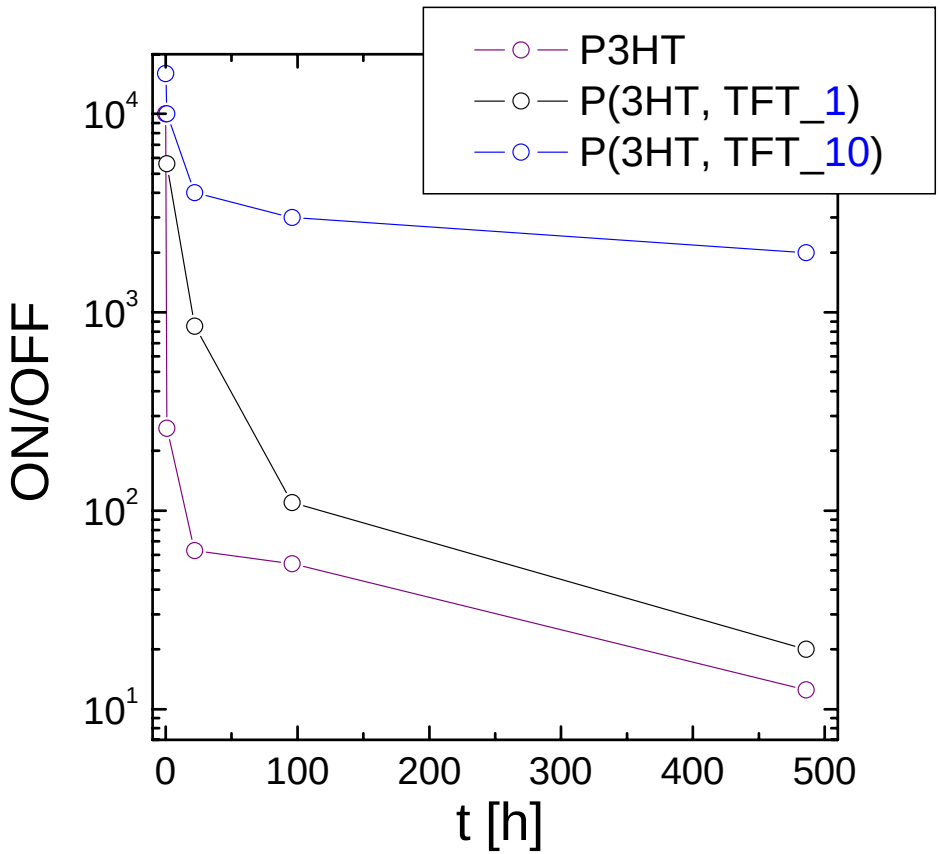


- positive V_{onset}-shift (~ 5 V)

➢ distinctly improved ambience-stability



ON/OFF ratio - air exposure test – further results



P3HT

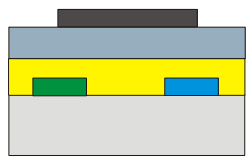
- rapid performance decrease
- saturation at prolonged air exposure

➢ pronounced oxidative doping tendency

P(3HT, acceptor)

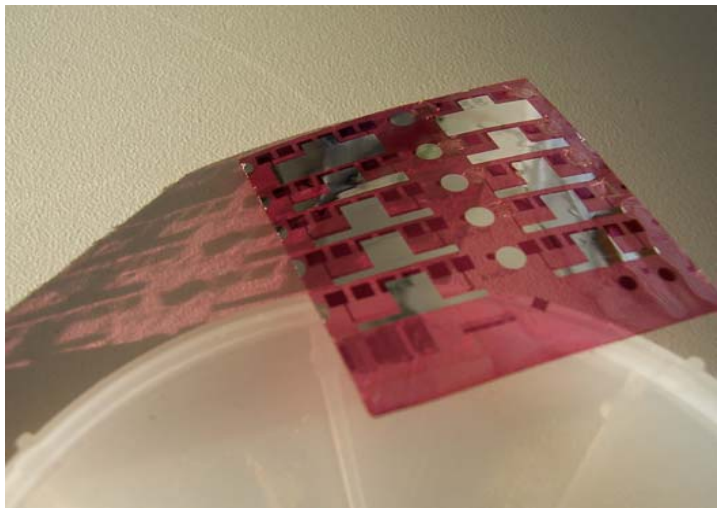
- distinct air stability improvement
- stronger effect at high acceptor content

➢ supressed oxidation effect



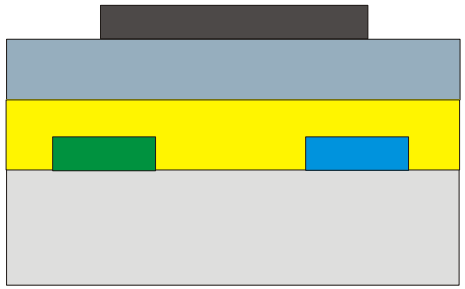
P3HT_TFT1 on flexible substrate

Flexible substrate PET foil with copper S-D contacts (supported from IZM Munich)

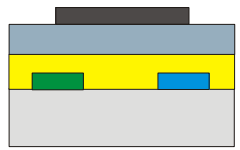


Picture of the self-prepared flexible OFET devices

Top gate structure
gate electrode (aluminum) by IAP Potsdam



processing of P(3HT, TFT_**1**) on flexible substrate
Solution of dielectric polymer P121 (9%) from Merck KG



Summary: P3HT_TFT1

Device	$\mu_{saturated} \pm 10\%$ [cm^2/Vs]	ON/OFF	V_T [V]
standard	3.2×10^{-2}	1.1×10^{4}	-10 to -15
on flexible	1×10^{-2}	up to 10^{3}	-18 to -22

Acceptor-modified P3HTs are suitable semiconductors for different OFET applications

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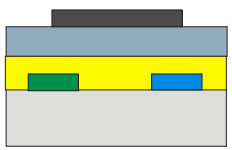
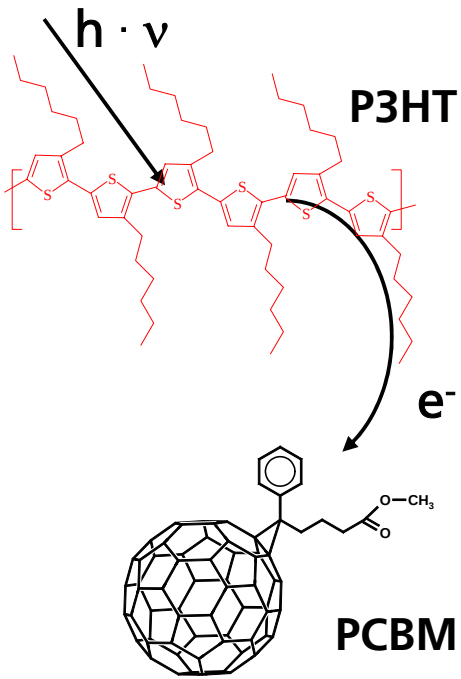
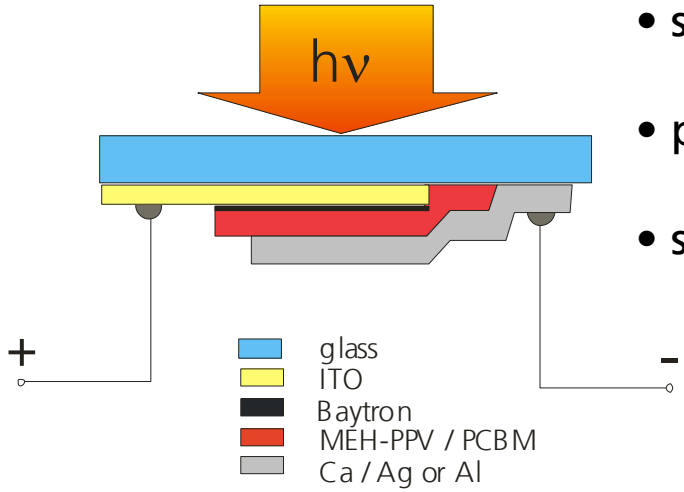


Heterojunction cell - (Linz)

PSC



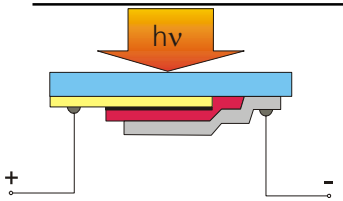


- P3HT / PCBM 1:4
- spin-coated from chlorobenzene
- prepared in glove-box
- sealed

EFF: ~ 3 – 5 %

➢ **substitution of the fullerene by polymer materials with high electron affinity**

➢ **development of new low bang gap polymers**



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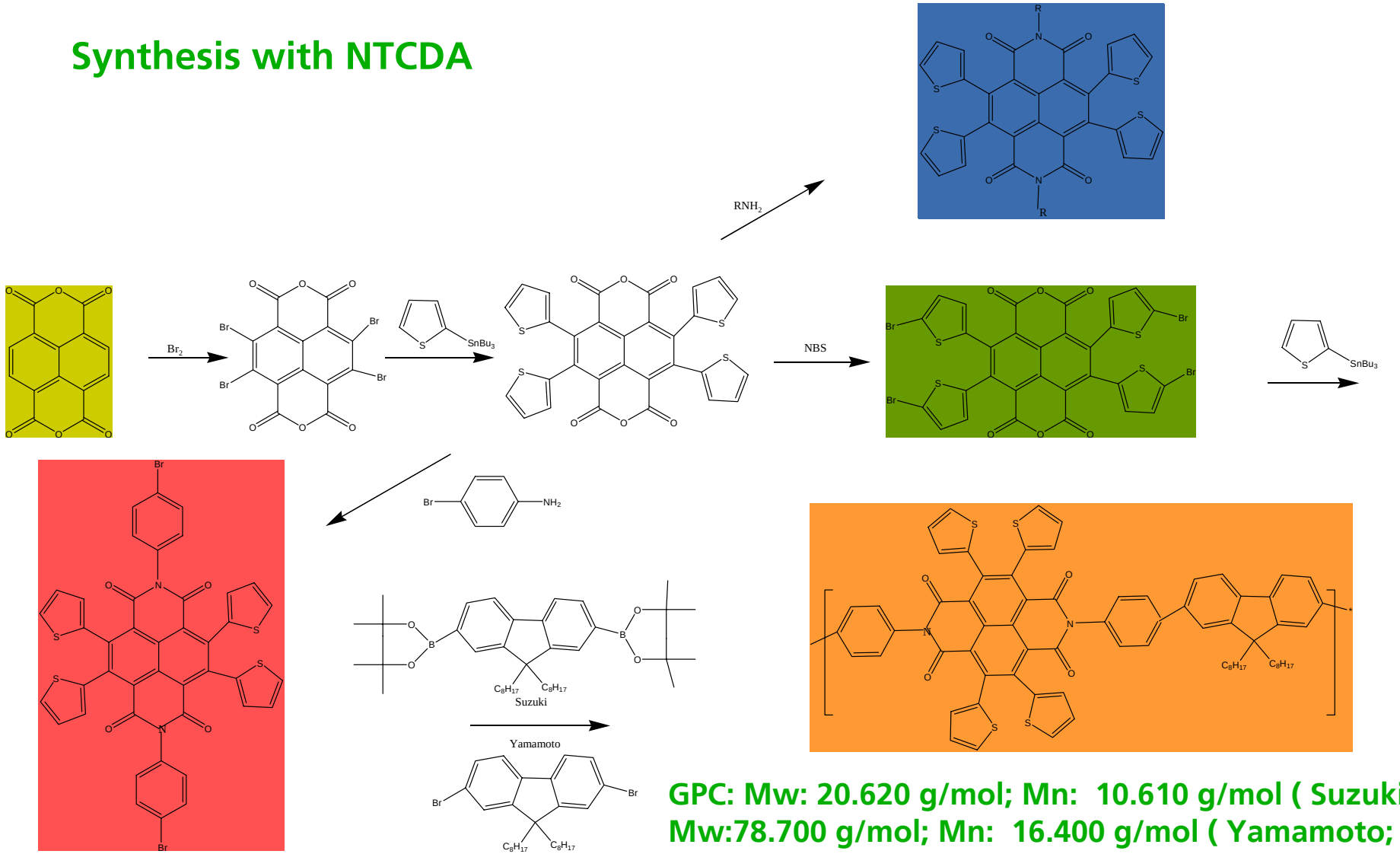
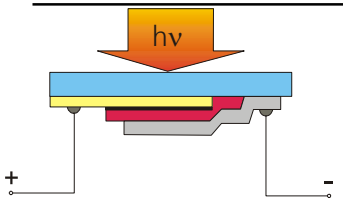
Substitution of the fullerene by polymer materials with high electron affinity

PSC

Synthesis with NTCDA



GPC: Mw: 20.620 g/mol; Mn: 10.610 g/mol (Suzuki; MT177)
Mw:78.700 g/mol; Mn: 16.400 g/mol (Yamamoto; MT203)



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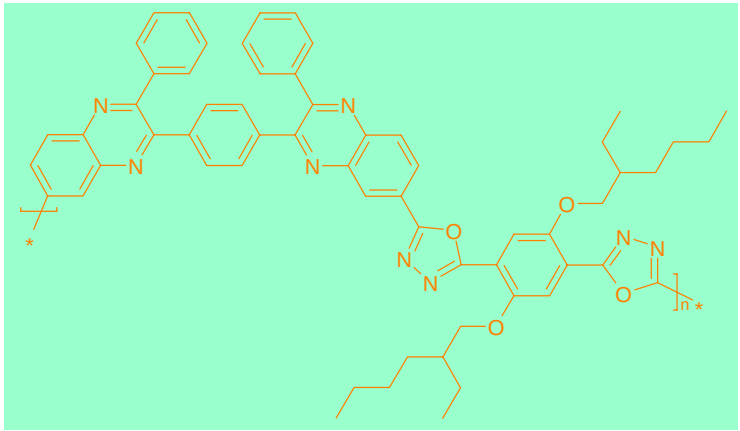
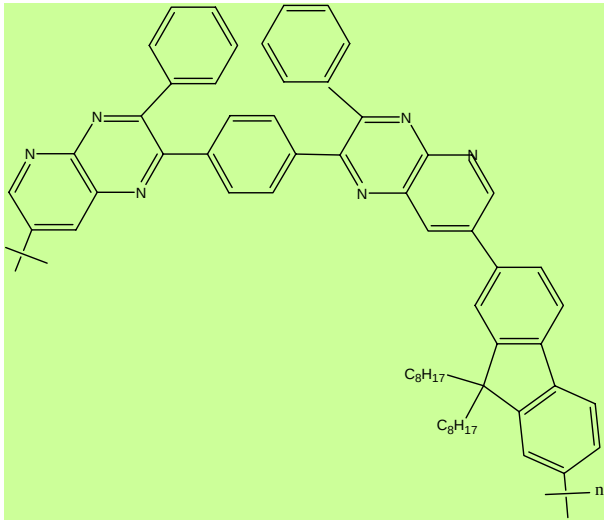
Substitution of the fullerene by polymer materials with high electron affinity

PSC

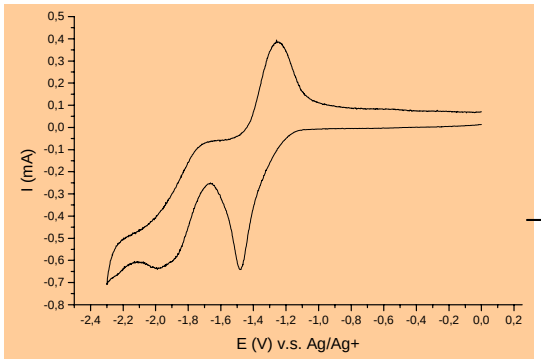


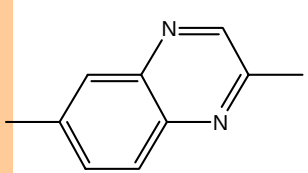
Copolyquinoxalines

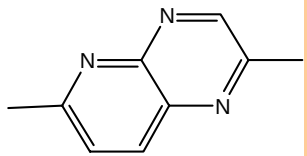


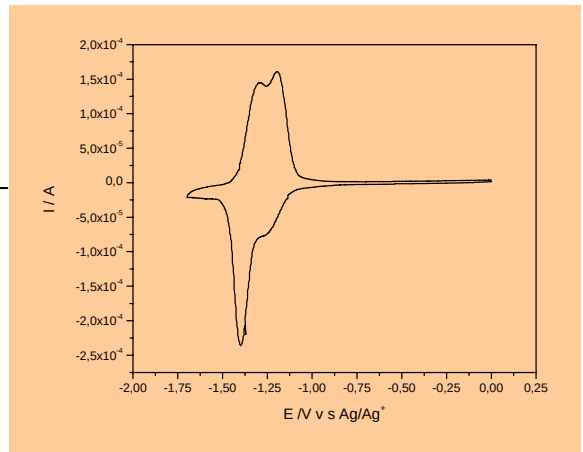
M_n = 2.5 10^4 g/mole;
Mw = 1.2 105 g/mole

Mn = 110.200 g/mole
Mw = 579.400 g/mole,(aggregation in chloroform)



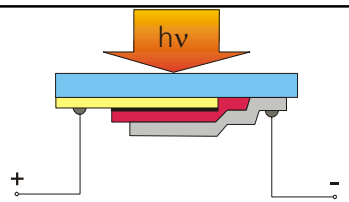






HOMO: > -6,4 eV; LUMO -3.1 eV

HOMO: > 6,0 eV; LUMO -3.3 eV



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Substitution of the fullerene by polymer materials with high electron affinity

PSC

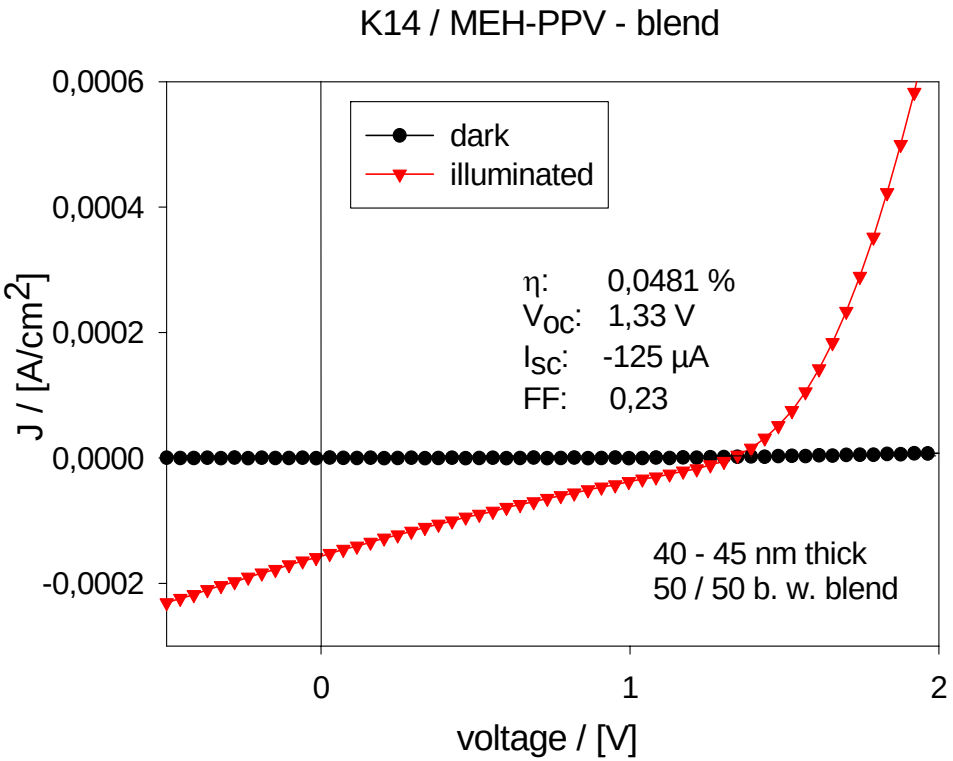
polymer / polymer-solar-cells

Substitution of the fullerene through polymer materials with high electron affinity

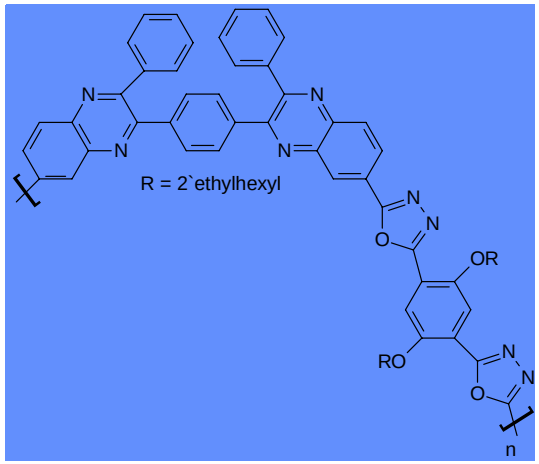
Chinoxaline / Oxadiazol-CP MEH-PPV

2 : 1

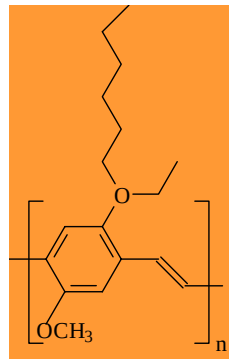
solar cell-characterisation



Eff.: 0,1 %



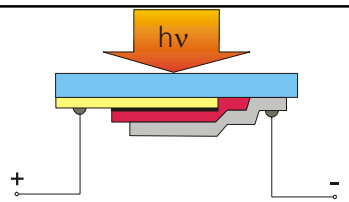
LUMO: ~3.1 eV



HOMO: ~5.3 eV

positive: open circuit voltage : 1.3V → high

to improve: - electron mobility
- blend morphology



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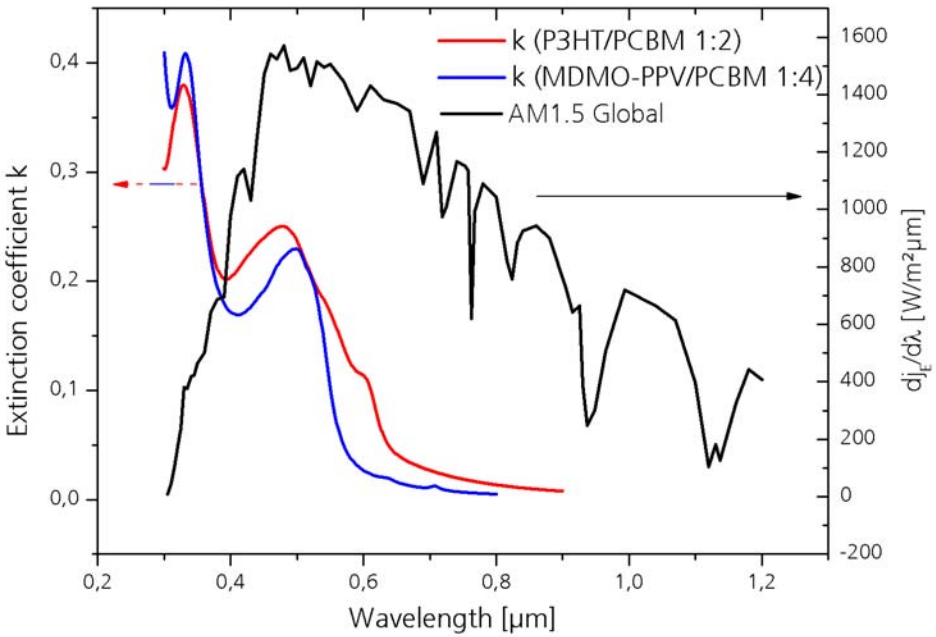
Development of new low bang gap polymers

Why development of long wave absorbing polymers?



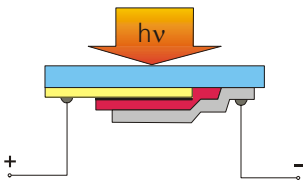
spectral mismatch between solar spectrum and absorption trough P3HT or MDMO-PPV

goal:

- better utilization of the solar energy
- Development of processable, long wave absorbing polymers (low bandgap-polymers < 2 eV)

Assessment criteria:

- Improved absorption behaviour of the blendfilms
- Higher efficiency in comparison with P3HT / fulleren



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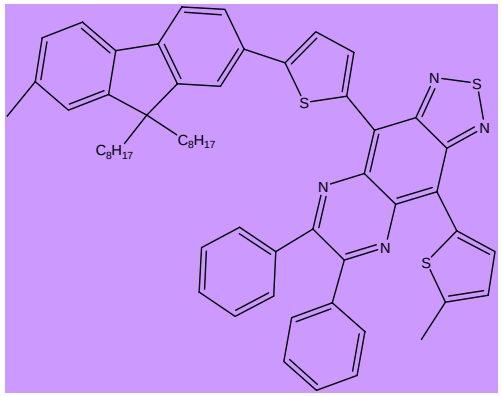
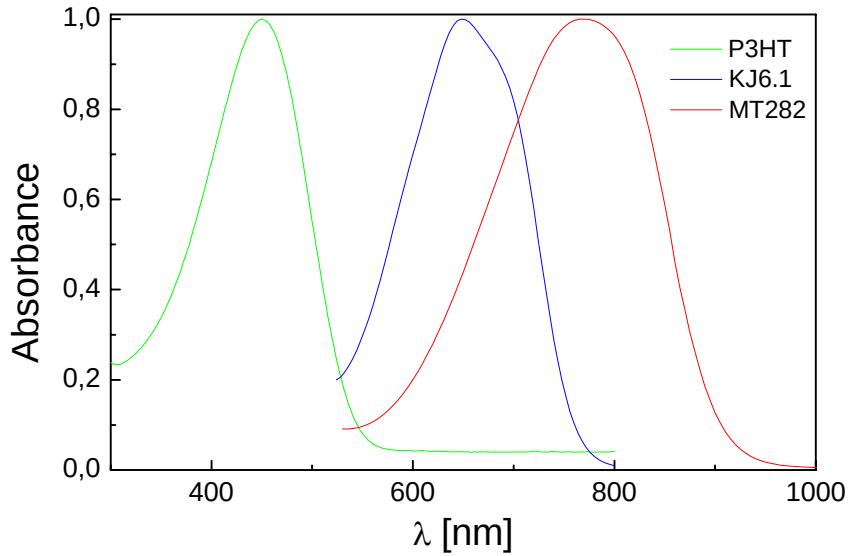
Development of new low bang gap polymers

PSC

polyfluoren with LBG-character



MT282

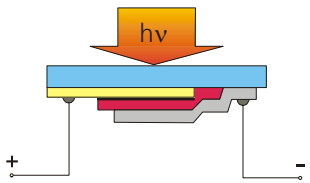


Mn – 2.800 g/mol; Mw – 4.800 g/mol

- molecular weight very small
- solubility problems

- absorptionsmaxima **770** nm (solution)
- optical band gape: **1,38** eV

improvement through copolymerisation



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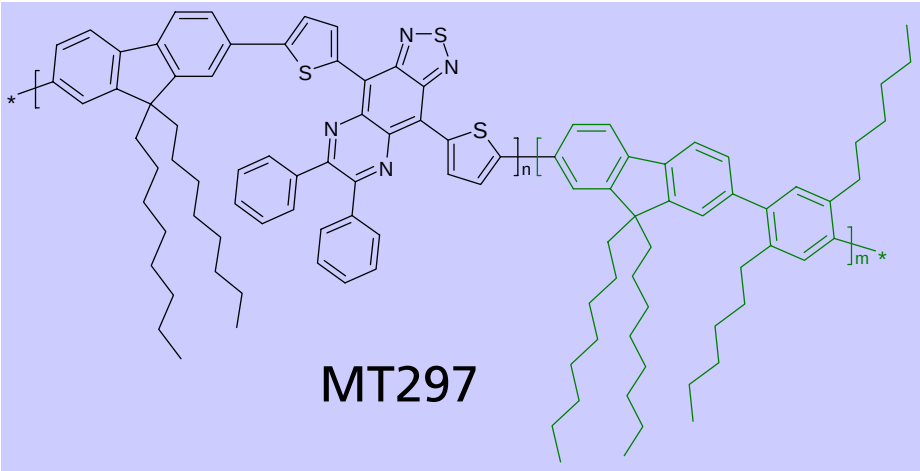
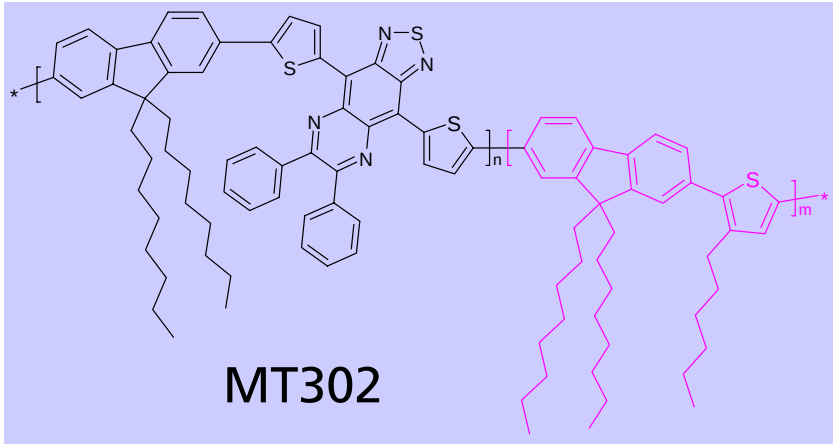
Development of new low bang gap polymers

PSC

Copolyfluorenes with LBG-character and improved solubility





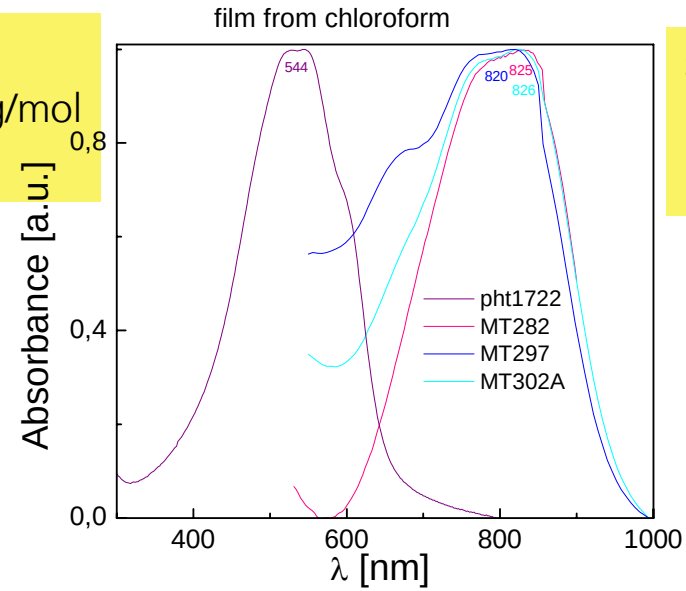
soluble in: THF, Chlorbenzol

M_n – 11.700 g/mol; M_w – 22.400 g/mol

n = 0,36; m = 0,64

LUMO: -3,7 eV

HOMO: -5,6 eV



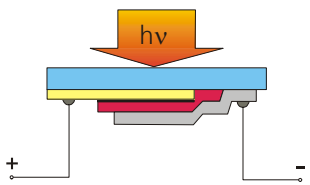
soluble in: THF, Chlorbenzol, ($CHCl_3$)

M_n – 5.400 g/mol; M_w – 7.900 g/mol

n = 0,44; m = 0,56

LUMO: -3,8 eV

HOMO: -5,4 eV



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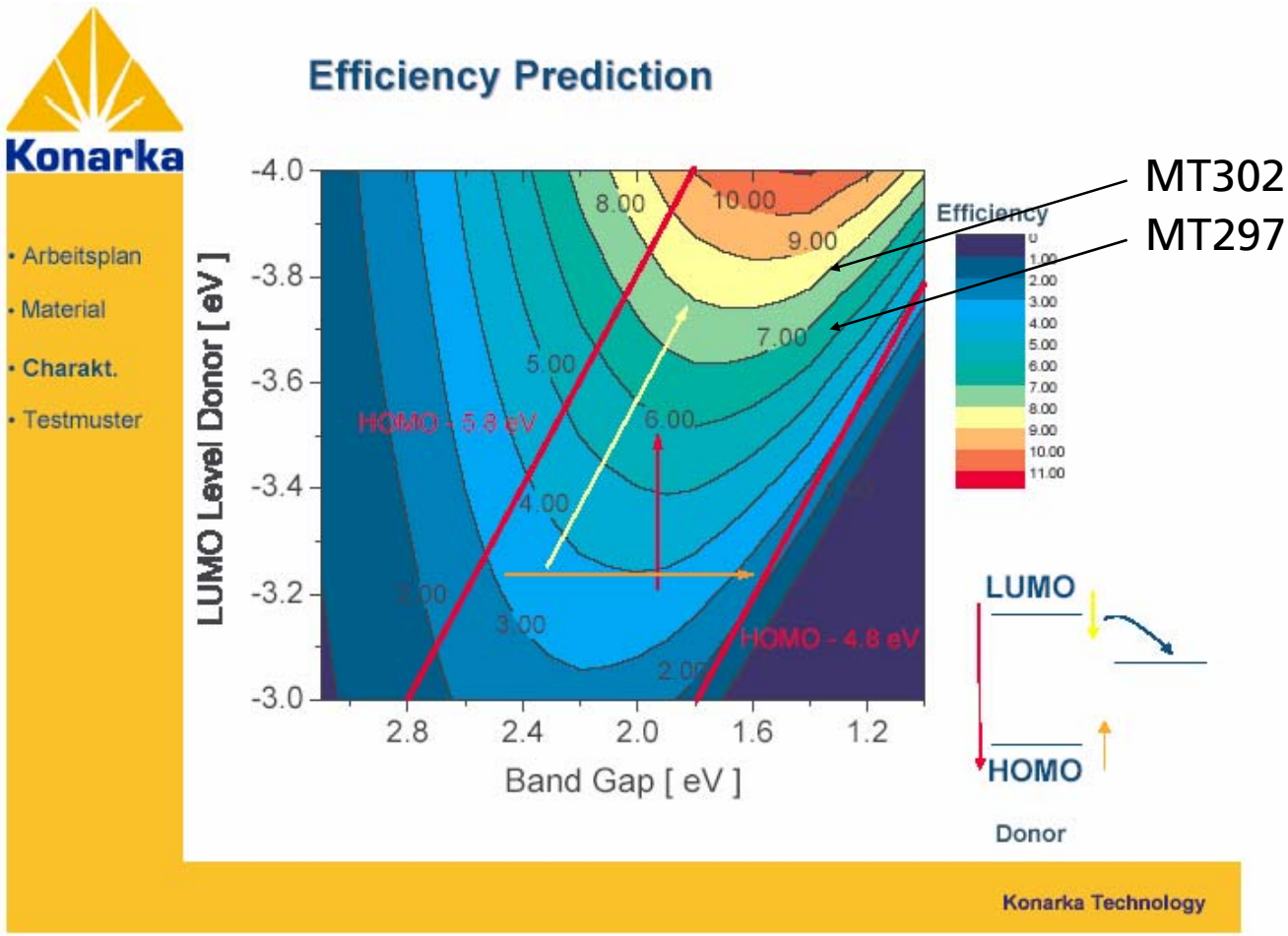
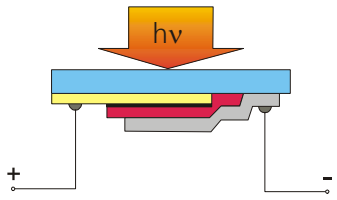
Connection between LUMO and band gap





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