

# Synthesis and Physical Properties of Donor Copolymers for All-Polymer Solar Cells

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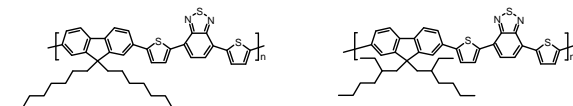
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## Introduction

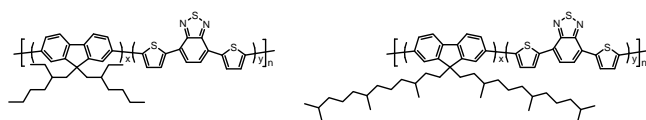
Our project aims at the understanding and the advancement of the photovoltaic properties of organic solar cells with all-polymer active layers. A novel NIR absorbing "low-bandgap" CPDT-based copolymer has been synthesized and its electronic properties have been investigated by UPS. For the investigation of the influence of increasing electronic disorder on the photovoltaic behaviour we have synthesized alternating and random fluorene/dithienyl benzothiadiazole copolymers. The copolymers have been characterized by UV-Vis spectroscopy. First all-polymer solar cells have been prepared.

## Fluorene-based and CPDT-based copolymers

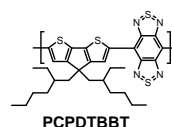
### Alternating fluorene/dithienylbenzodithiazole copolymers



### Random fluorene/dithienylbenzodithiazole copolymers



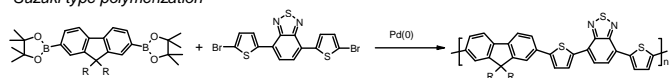
### CPDT-based "low-bandgap" copolymer



## Synthesis of the alternating and random fluorene copolymers PFTBT

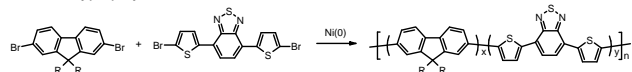
### Alternating copolymers

#### Suzuki type polymerization



### Random copolymers

#### Yamamoto type polymerization



### Molecular weights of the

#### alternating copolymers

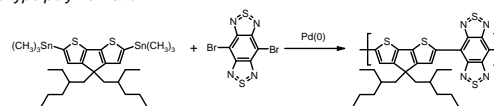
R	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)
Octyl	5.000	12.400
Ethylhexyl	4.000	6.600

#### random copolymers

R	TBTT (%)	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)
Ethylhexyl	32,00	10.000	20.000
Ethylhexyl	2,25	40.000	160.000
Farnesyl	17,00	10.000	15.000

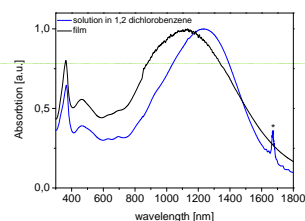
## Synthesis of the CPDT-based copolymer PCPDTBBT

### Stille type polymerization

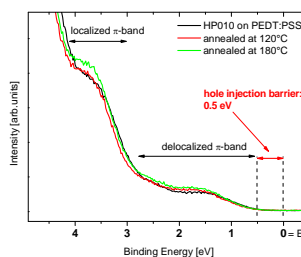


M<sub>n</sub> = 8.100 g/mol  
M<sub>w</sub> = 16.500 g/mol

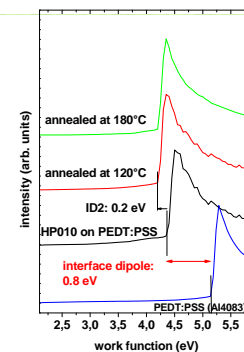
## Optical properties and UPS characterization of PCPDTBBT



UV-Vis spectra in solution (chlorobenzene; blue line) and in film (black line); \* solvent signal

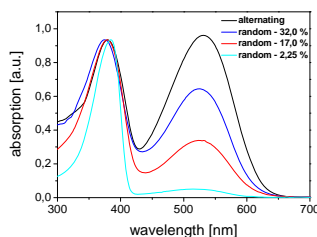


UPS valence band region of PCPDTBBT. Film thickness ca. 10 nm on PEDT:PSS (AI4083); annealing up to 180°C in vacuo; no energy shifts were detected, the hole injection barrier is 0.5 eV



UPS secondary electron cutoff region of PCPDTBBT, yielding the sample work function. Film thickness ca. 10 nm on PEDT:PSS (AI4083). Annealing up to 180°C in vacuo. The initial "interface dipole" of 0.8 eV between PEDT:PSS and PCPDTBBT (i.e., work function changes from ca. 5.1 eV to 4.3 eV). Upon initial annealing the sample work function is further reduced by 0.2 eV (work function is then 4.1 eV). This shift is not paralleled by the valence band region.

## Optical properties of the copolymers and performance of all-polymer solar cells based on P3HT/PFTBT

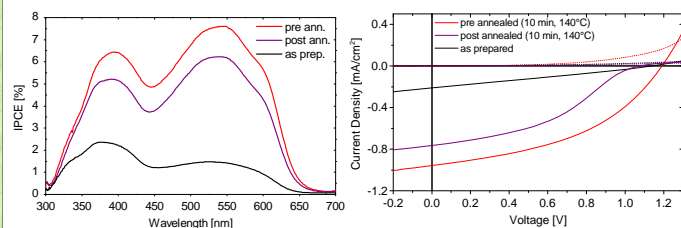


UV spectra of the copolymers: at 380 nm the absorption of the fluorene unit and at 530 nm the absorption of the TBTT unit occurs; from the ratio of the absorption maxima the composition of the copolymers can be estimated

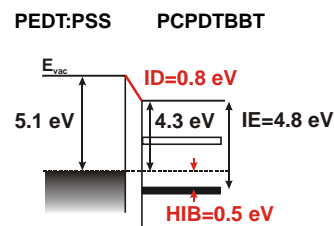
### Bilayer solar cell P3HT/alternating copolymer:

Sample setup: glass/ITO/PEDT:PSS(AI083)/P3HT-interlayer(3nm)/acceptor(40nm)/top electrode acceptor: alternating copolymer; top electrode: 20 nm Ca / 75 nm Al

pre-annealing: annealing before the evaporation of the electrode  
post-annealing: annealing after the evaporation of the electrode



sample	FF [%]	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	PCE [%]
pre ann.	43.6	1.2	1.0	0.5
post ann.	38.8	1.1	0.8	0.3
as prep.	27.3	1.1	0.2	0.06



Schematic energy level diagram for PCPDTBBT on PEDT:PSS derived from UPS experiments