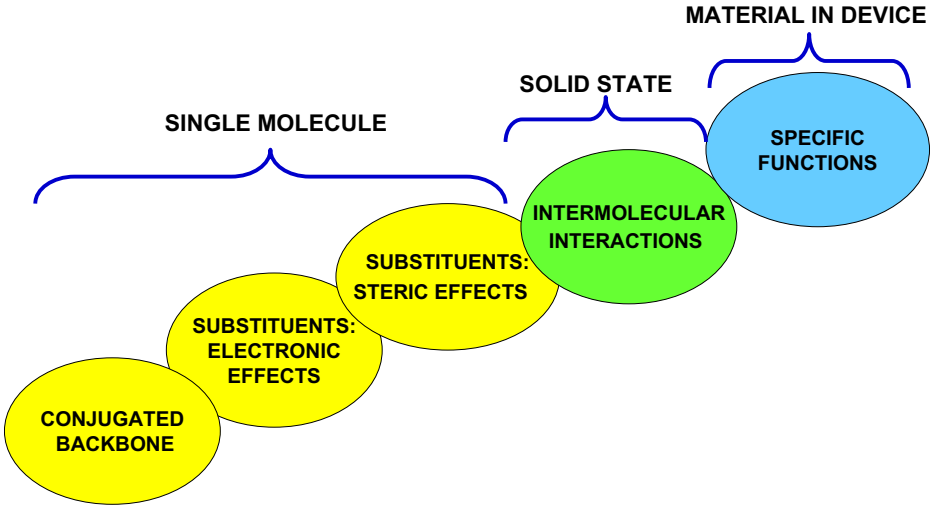
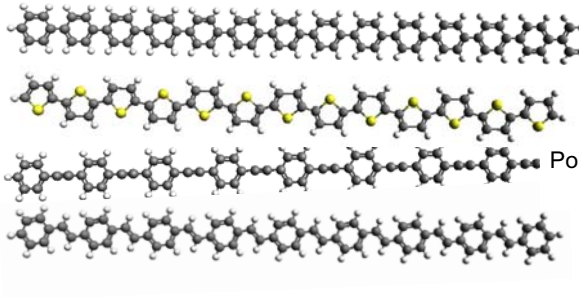
From molecules to materials

The logic of materials design and synthesis



π-Conjugated oligomers and polymers



Poly(*p*-phenylene) **PPP**

Polythiophene **PT**

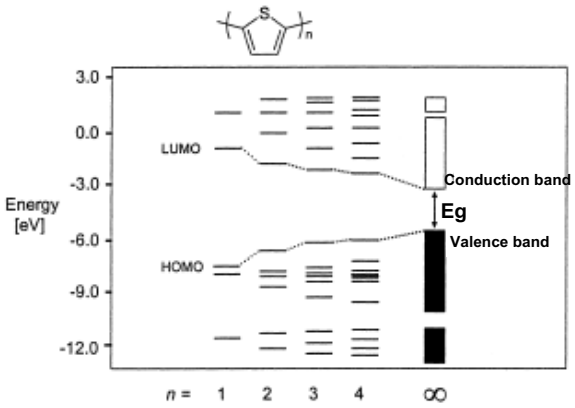
Poly(*p*-phenyleneethynylene) **PPE**

Poly(*p*-phenylenevinylene) **PPV**

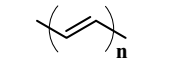
Organic compounds with optical and electrical properties of semiconductors

- ***Light absorption and emission***
- ***Charge transport***

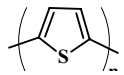
π-Conjugated polymers as semiconductors



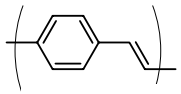
H.A.M. van Mullekom, J.A.J.M. Vekemans, E.E. Havinga, E.V.Meijer
Materials Science and Engineering 32, **2001**,1



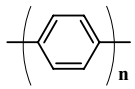
Eg = 1.5 eV



Eg = 2.0 eV



Eg = 2.3 eV



Eg = 3.0 eV

OUTLOOK

Materials for…

Light emission

Fluorinated electroluminescent polymers

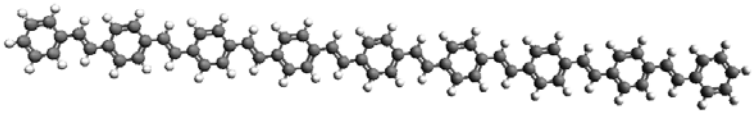
Light absorption

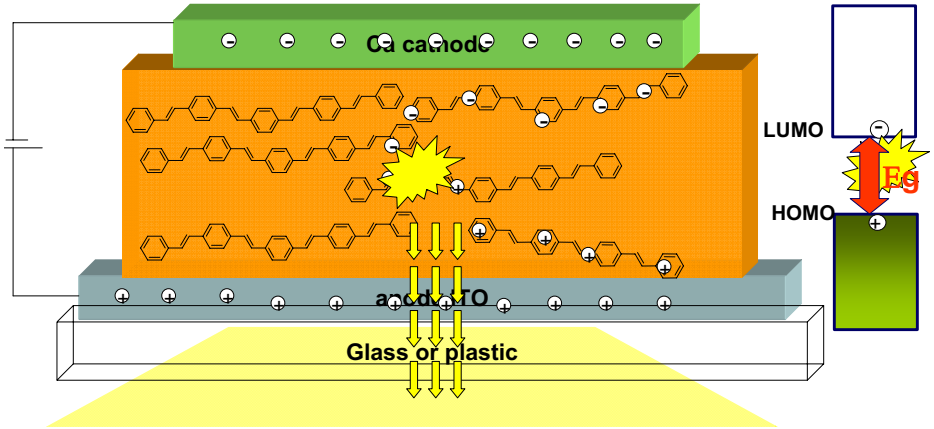
Conjugated polymers for photovoltaics

Charge transport

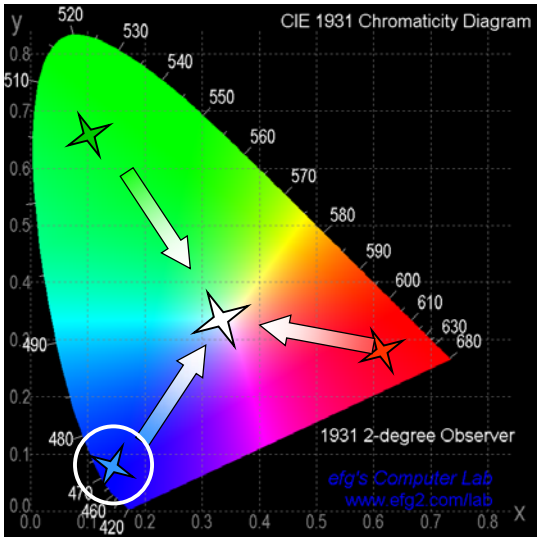
Bio-functionalized organic semiconductors for chiral sensing

Organic light emitting diode (OLED)





Materials for white OLEDs:
Combining emitters of different colors



Focusing on blue emitters

LED'S BE HONEST

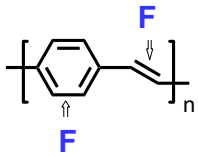
Dr. Doer D. Koek, ***VSL, Dutch Metrology Institute***
Greenlighting Event, Frankfurth, March 24th 2009

OPEN ISSUES:
- ☆ Short lifetimes
- ☆ Efficiencies lower than inorganic LEDs
- ☆ High prices

RESEARCH EFFORTS TO IMPROVE MATERIALS ARE STILL NECESSARY

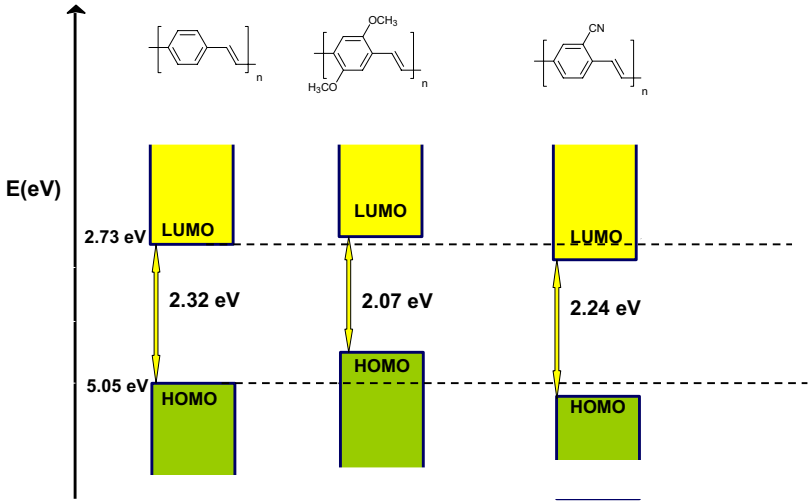
Fluorinated poly(*p*-phenylenevinylene)s (PPVs) for OLEDs

- ☆ Blue-shifted emission
- ☆ Increased stability
- ☆ Improved processability



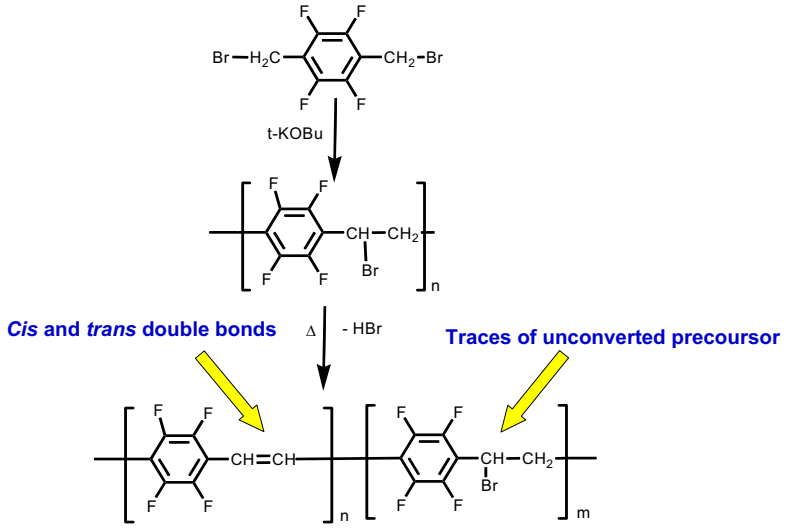
Chem. Commun. **2007**, 1003

Electronic effects of substituents on PPV



Bredas, J.L.; Heeger, A.J. *Chem. Phys Lett.* **1994**, *217*, 507

Fluorinated PPV *via* the bromine precursor route



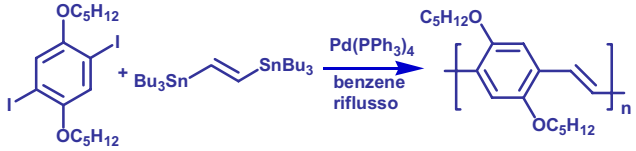
Gan, L.H.; Wang, Y. M.; Xu, Y.; Goh, N.K.; Gan, Y.Y. *Macromolecules* **2001**, *34*, 6117

Organometallic methodologies for the synthesis of π-conjugated polymers

- **Medium/low molecular weight – high yields**
- **High regio- and stereoselectivity**
- **Absence of conjugation defects**
- **Mild experimental conditions, many groups are tolerated**

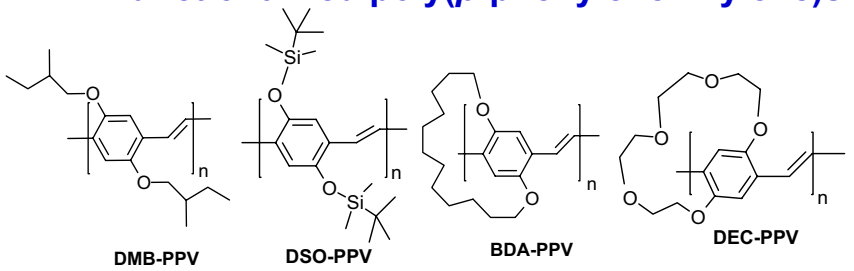
J. Mater. Chem. **2004**, *14*, 11

Stille cross-coupling for synthesis of PPVs



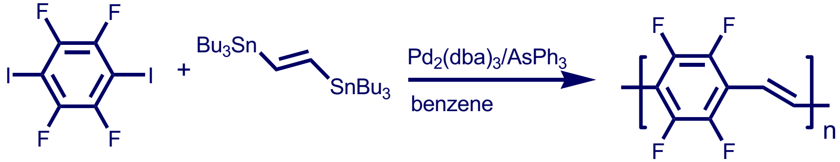
Macromol. Rapid Commun., **1996**, *17*, 905

Functionalized poly(*p*-phenylenevinylene)s



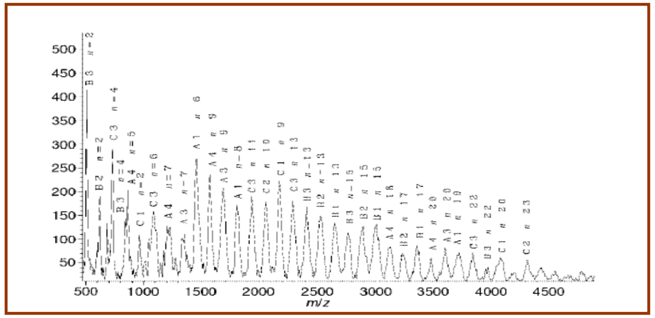
J. Mater. Chem. **2000**, *10*, 1573; *Phys Rev B* **2001**, *64*, 205205 1-8

PPV with fluorinated aromatic rings

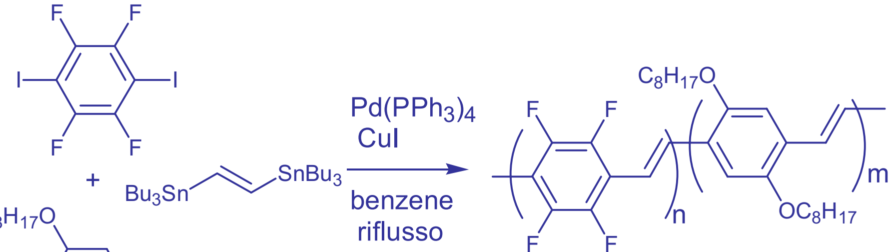


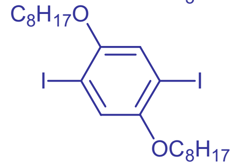
Chem. Commun. **2001**, 1940

Mw = 2400, Mn = 1700
PD = 17-20



Fluorinated PPV copolymers



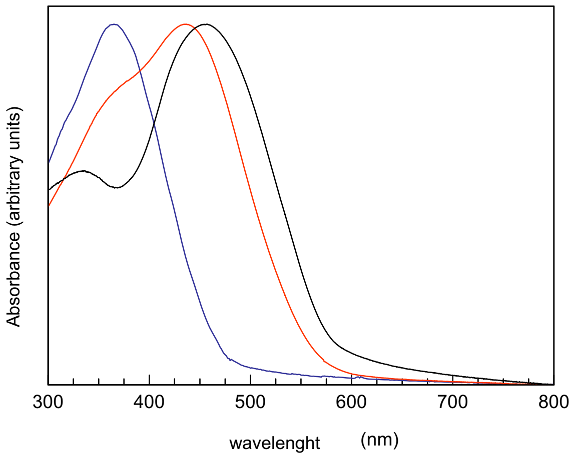


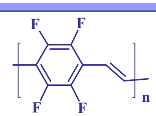
Monomers ratio (F : OR)
20 : 80
50 : 50
65 : 35

Incorporated monomers ratio (F : OR)
25 : 75
60 : 40
65 :35

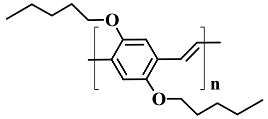
Macromol. Chem. Phys., **2003**, *204*, 1621

Thin film absorption spectra

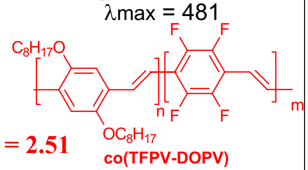




E_g = 2.95 eV
λmax = 347

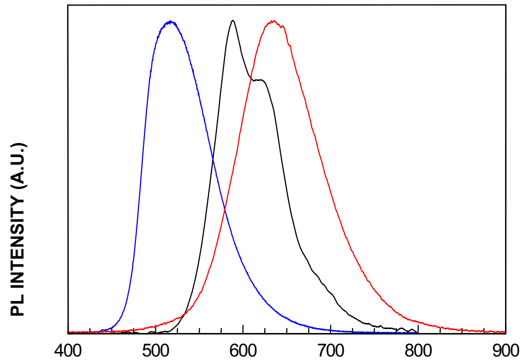


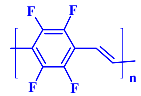
E_g = 2.32 eV
λmax = 481



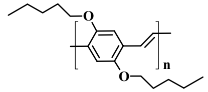
E_g = 2.51
λmax = 466

Thin film emission spectra

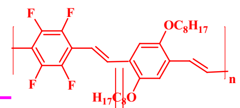




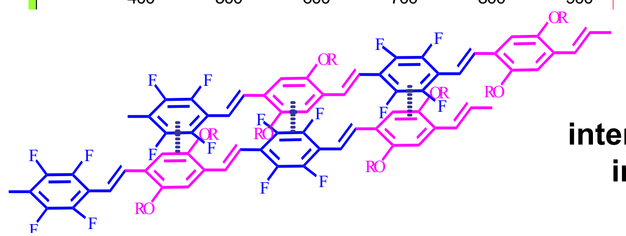
λmax = 520 nm



λmax = 580 nm

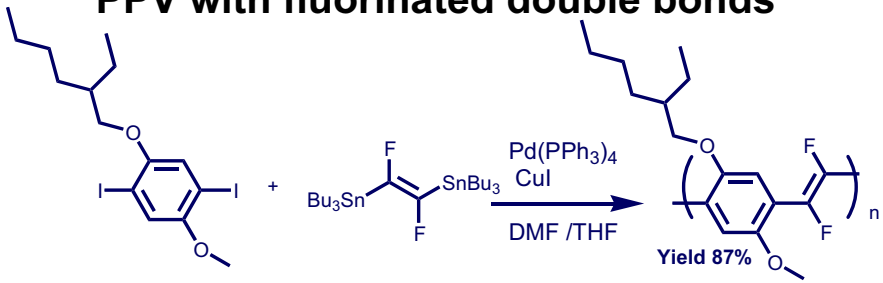


λmax = 645 nm



Strong interchain interactions in the solid state

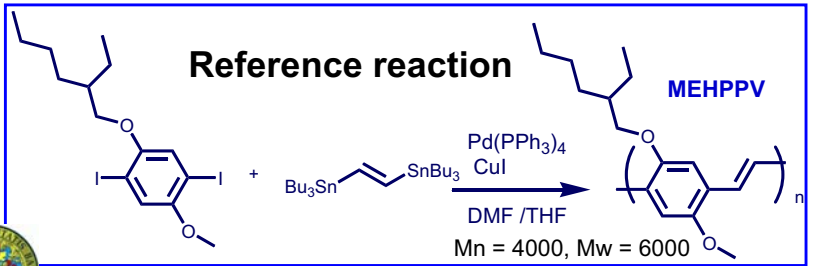
PPV with fluorinated double bonds



Eur. J. Org. Chem. **2008**, 1977

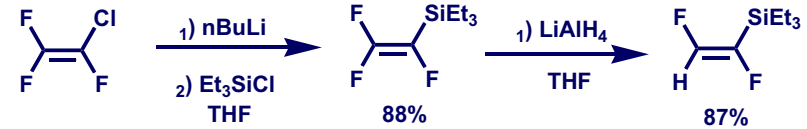
Mn = 28000, Mw = 47000

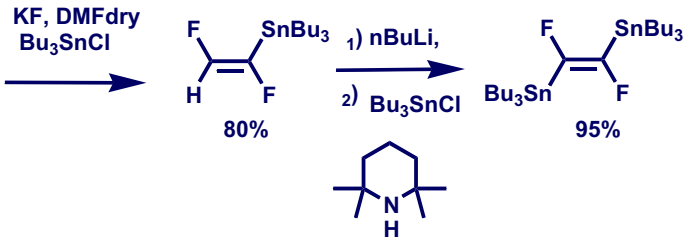
Reference reaction



Mn = 4000, Mw = 6000

Synthesis of the fluorinated organotin monomer

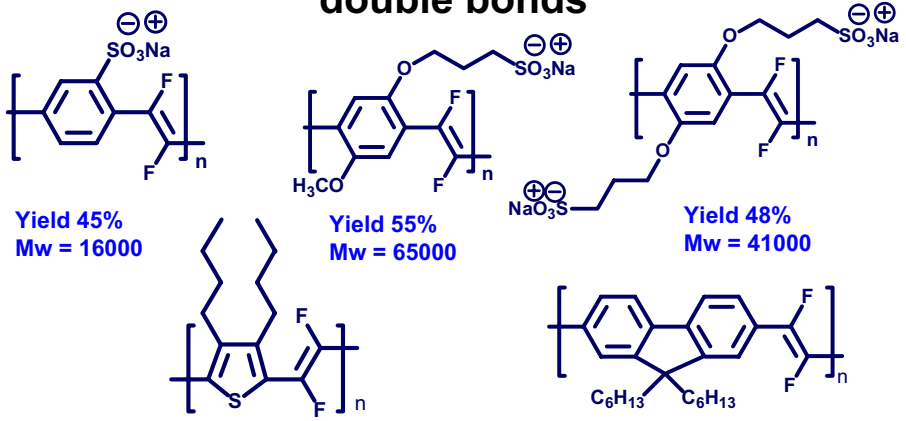




D.J. Burton, Q. Liu, *Org. Lett.* **2002**, *4*, 1483

Eur. J. Org. Chem. **2008**, 1977

Poly(arylenevinylene)s with fluorinated double bonds



Yield 45%
Mw = 16000

Yield 55%
Mw = 65000

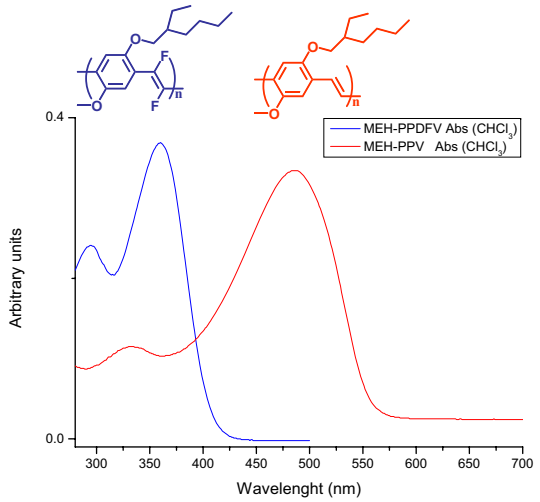
Yield 48%
Mw = 41000

Yield 50%
Mn = 17000, Mw = 47000

Yield 82%
Mn = 23000, Mw = 45600

Eur. J. Org. Chem. **2008**, 1977

Absorption spectra in solution

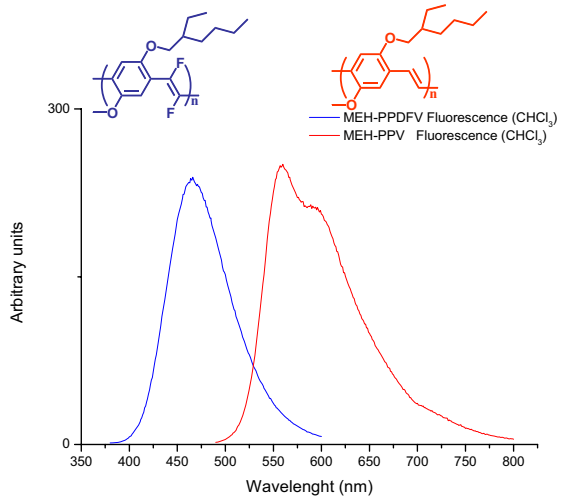


Absorption maximum: 360 nm

Absorption maximum: 480 nm

BLUE SHIFT 120 nm

Emission spectra in solution

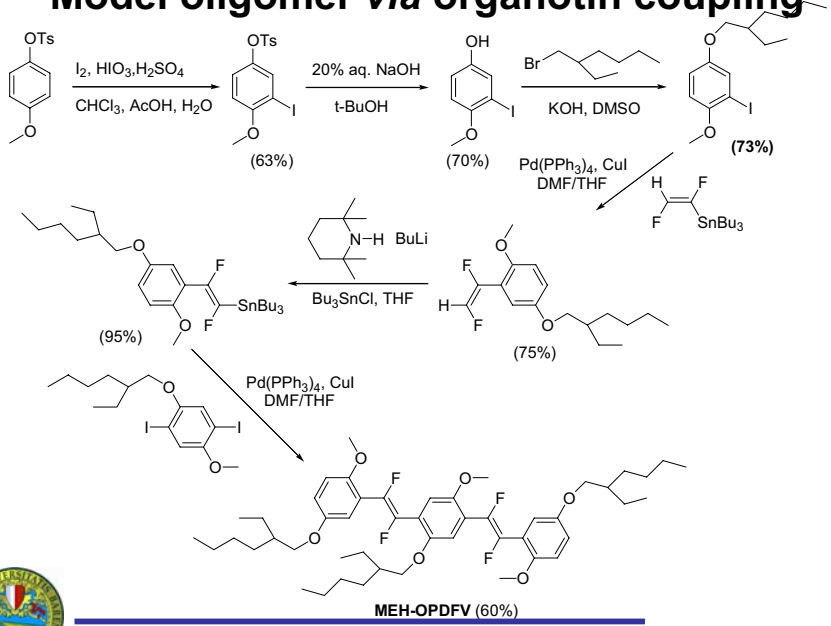


Emission Max: 466 nm

Emission Max: 555, 580 nm

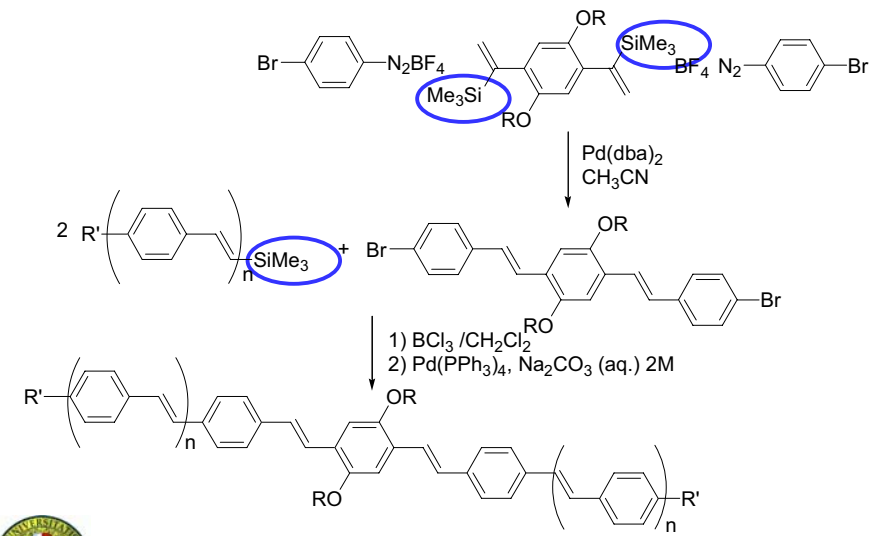
BLUE SHIFT 89 nm

Model oligomer *via* organotin coupling



MEH-OPDFV (60%)

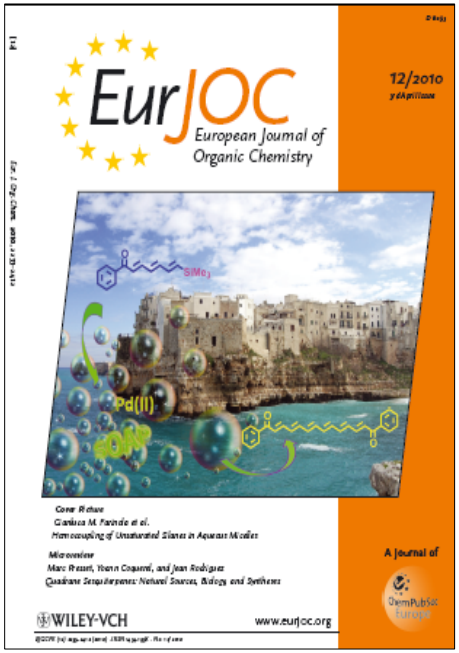
Model oligomers *via* organosilicon coupling



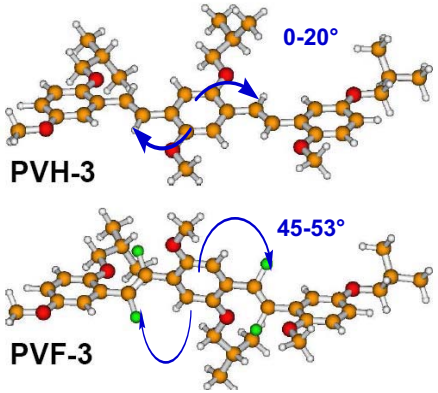
Chem. Commun. **1995**, 2523; *J. Org. Chem.* **2001**, 66, 3878

Synthesis of π-conjugated molecules *via* coupling of organosilicon compounds in aqueous micelles

Eur. J. Org. Chem **2010**, *12*, 2275



Modeling



Only moderately twisted
Phenyl rings almost coplanar

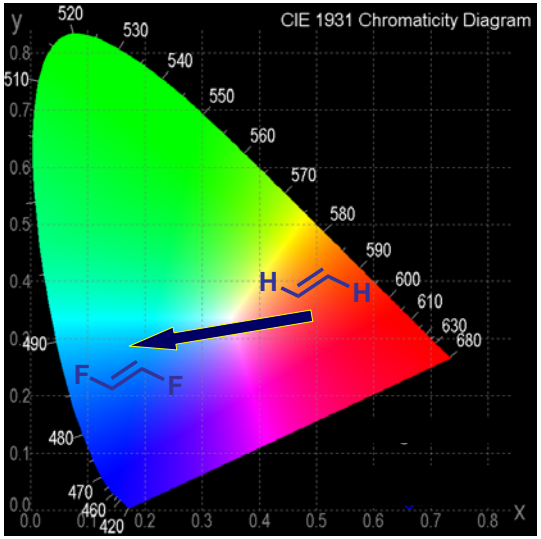
Strongly twisted
Phenyl rings in an approximate perpendicular orientation

Repulsive interactions of the fluorine atoms with the neighboring alkoxy groups

J. Phys. Chem. B **2008**, *112*, 2996
ChemPhysChem **2009**, *10,* 1284

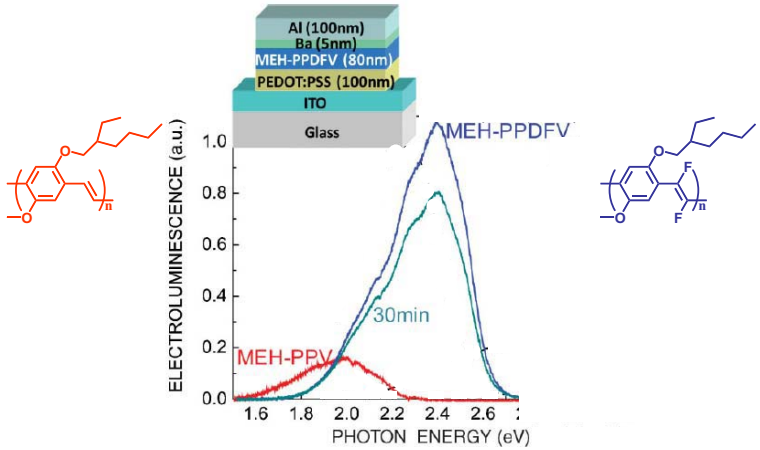
Time Dependent Density Functional Theory (TD-DFT)
Collaboration with Dr. F. Della Sala, University of Salento

Blue-shift due to double bond fluorination



Polymer 2008, *49*, 4133

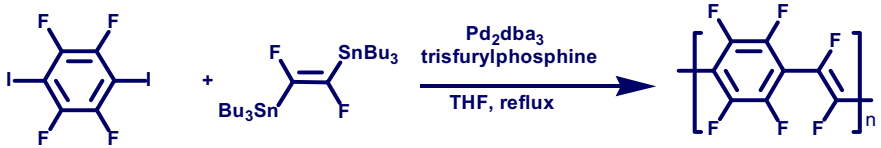
Blue electroluminescence



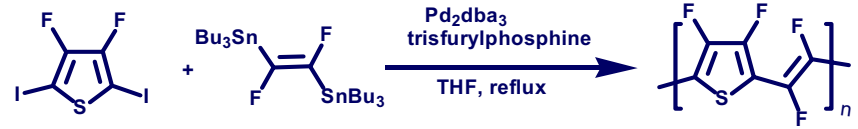
Electroluminescence measurements (Philips Research, Aachen)

Adv. Mater. 2009, *21*, 1115

Perfluorinated poly(arylenevinylene)s



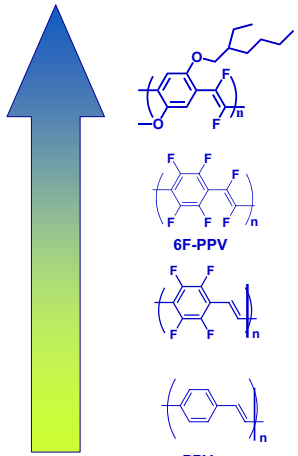
Yield 55%
Mn = 2000



Yield 60%
Mn = 2400

J. Polym. Sci. Polym. Chem. **2010**, *48*, 285

Tuning PPV emission in the blue by fluorination



Eg = 3.68 eV

Eg = 3.34 eV

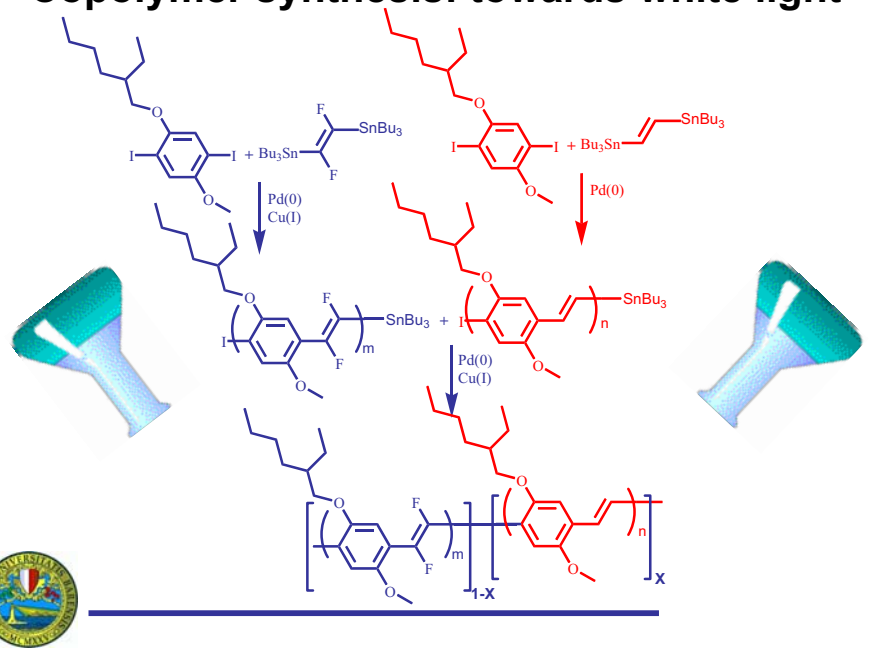
6F-PPV

Eg = 2.95 eV

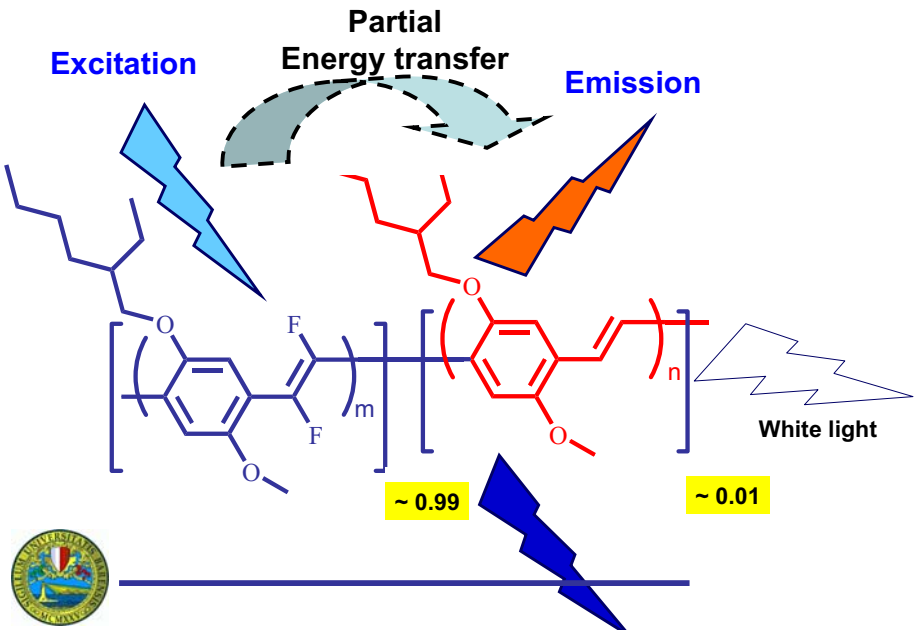
Eg = 2.4 eV

PPV

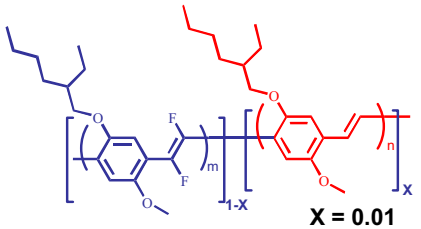
Copolymer synthesis: towards white light



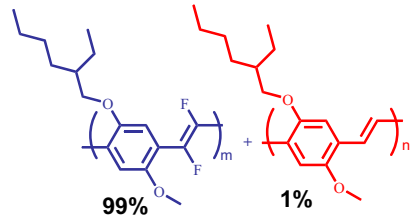
Copolymer light emission



Copolymer emission: towards white light

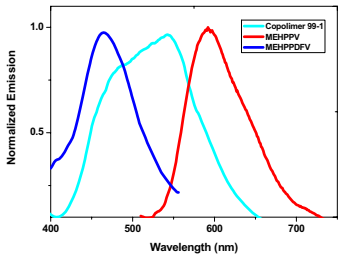


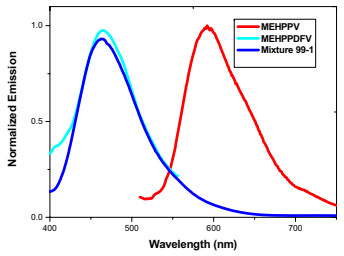
X = 0.01



99%

1%





Emission of copolymer thin film

Emission of blend thin film

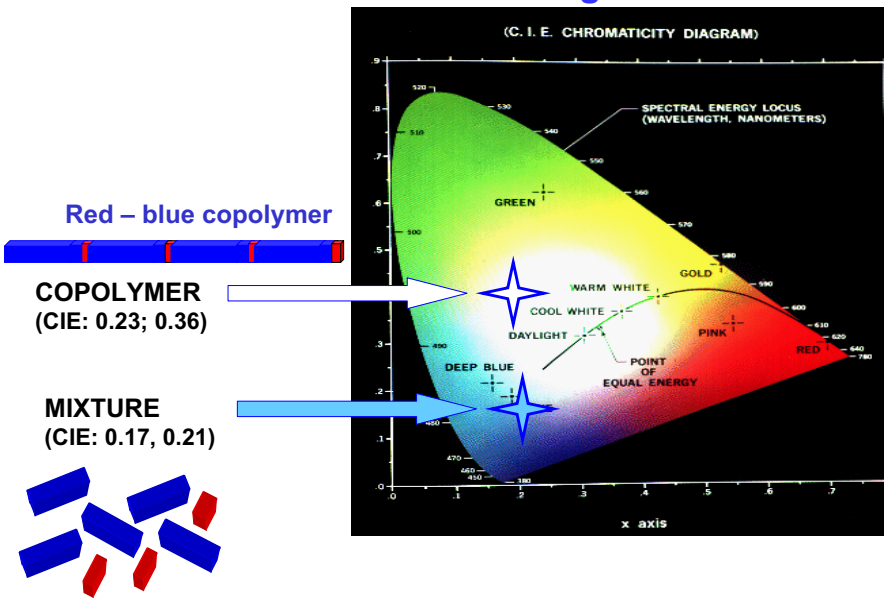
Copolymer emission color

Towards white light

Red – blue copolymer

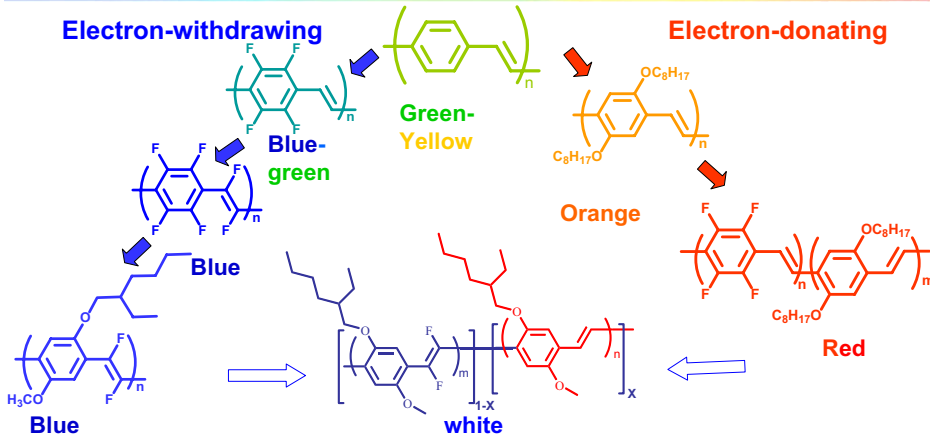
COPOLYMER
(CIE: 0.23; 0.36)

MIXTURE
(CIE: 0.17, 0.21)



Tuning PPV emission over the visible spectrum

Blue — Green — Red



Materials **2010**, *3*, 3077

Adv. Mater. **2009**, *21*, 1115

OUTLOOK

Materials for…

Light emission

Fluorinated electroluminescent polymers

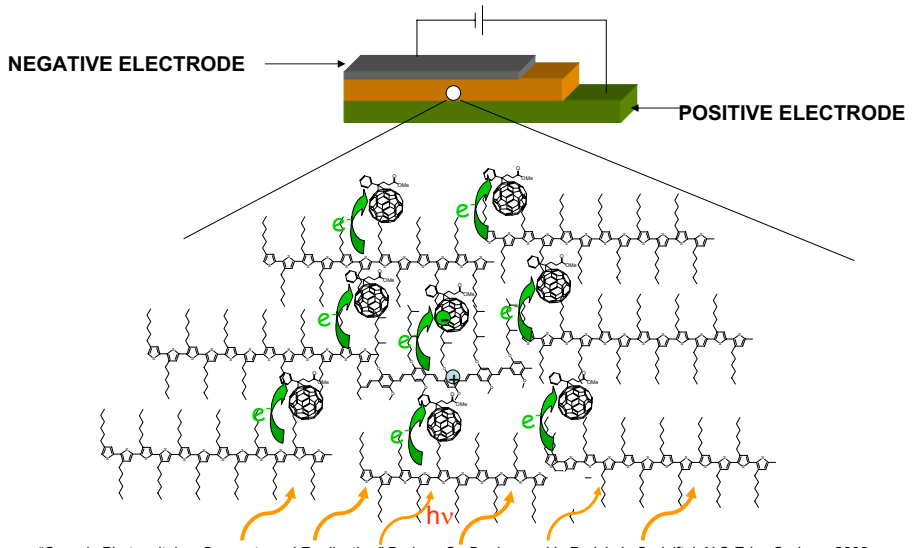
Light absorption

Conjugated polymers for photovoltaics

Charge transport

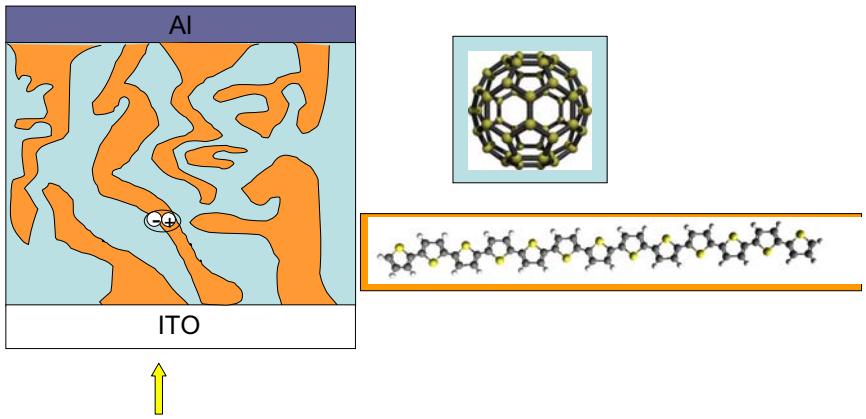
Bio-functionalized organic semiconductors for chiral sensing

Polymer solar cells



"Organic Photovoltaics. Concepts and Realization" *Brabec, C.; Dyakonov, V.; Parisi, J.; Sariciftci, N.S.Eds., Springer* **2002**

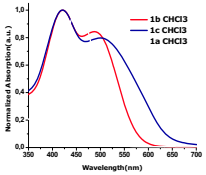
The bulk heterojunction concept



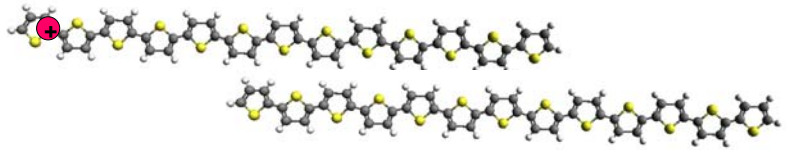
Halls, J.J.M.; Walsh, C.A.; Greenham, N.C.; Marseglia, R.H.; Friend, R.H.; Moratti, S.C.; Holmes, A.B. *Nature,* **1995**, *376,* 498

Organic semiconductors for solar cells

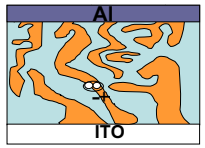
- **ABSORPTION IN THE SOLAR SPECTRUM**



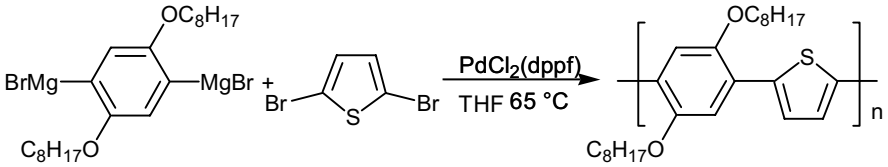
- **GOOD CHARGE TRANSPORT PROPERTIES**



- **BULK HETEROJUNCTION MORPHOLOGY**

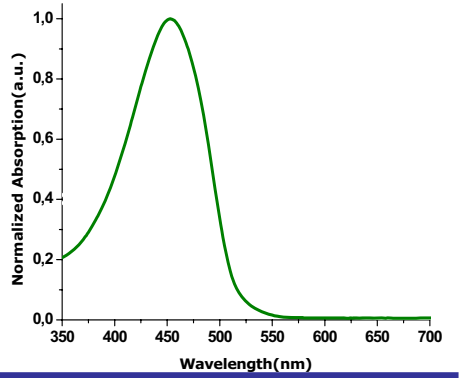


Phenylene thienylene polymer

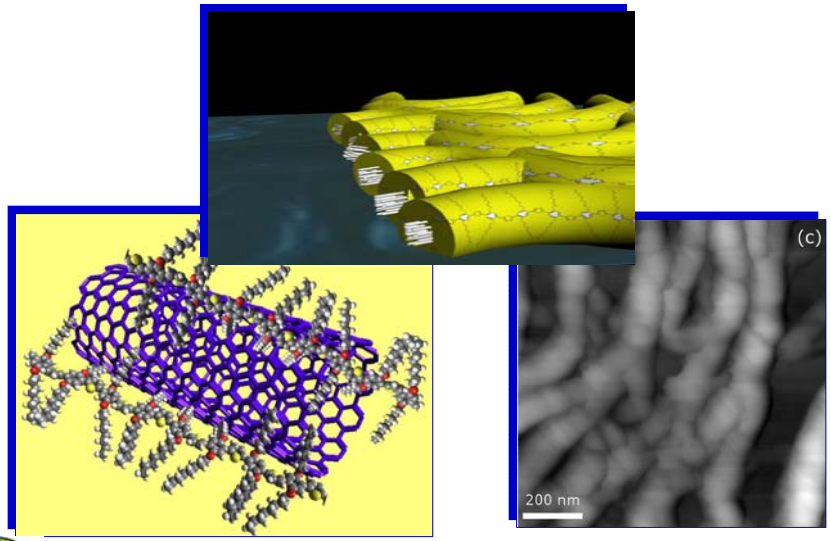


Eur. J. Org. Chem. **2002**, 2785

Mn = 4300, Mw = 7100

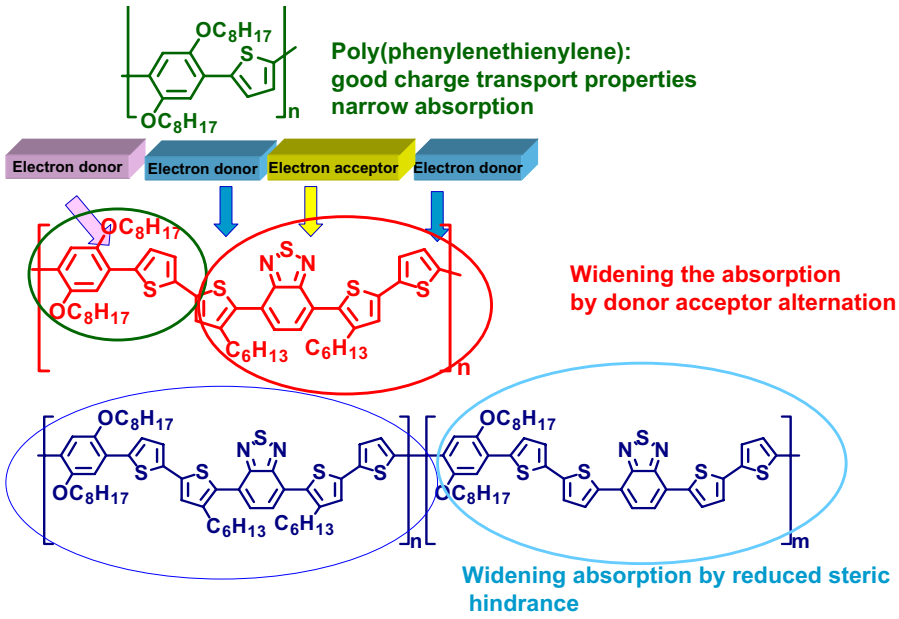


Interactions with carbon nanotubes



Adv. Funct. Mater. **2010** , *20, in press*

Thiophene benzothiadiazole copolymers

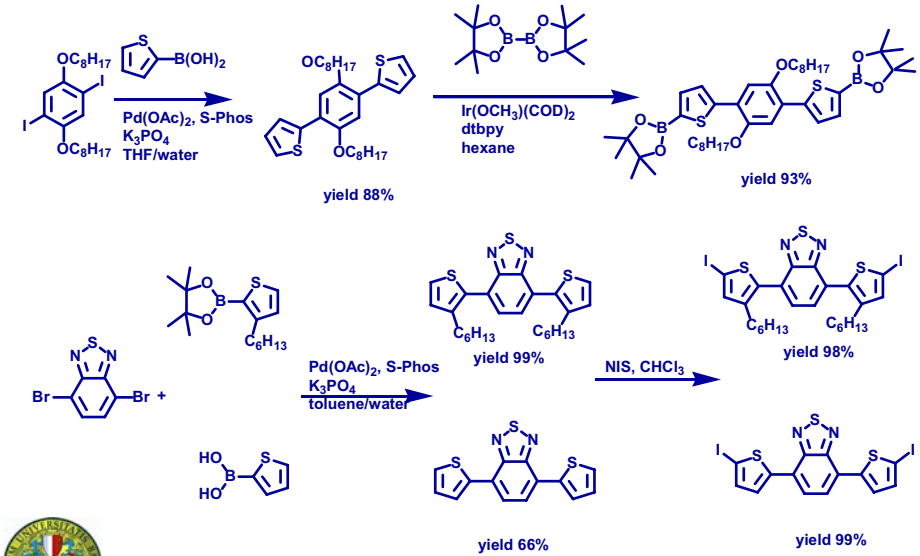


Poly(phenylenethienylene):
good charge transport properties
narrow absorption

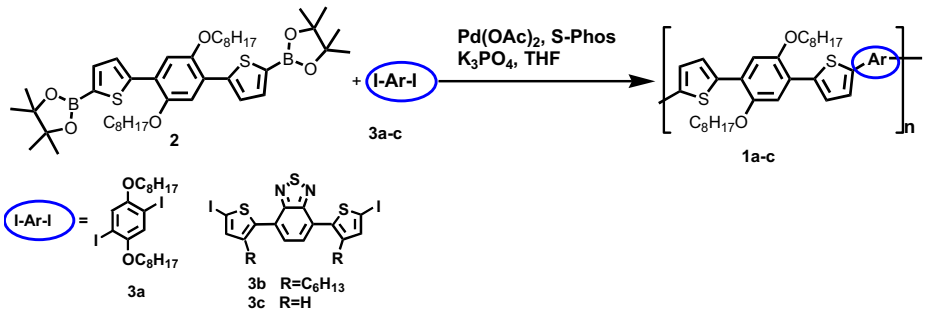
Widening the absorption
by donor acceptor alternation

Widening absorption by reduced steric
hindrance

Synthesis of the monomers



Polymerization

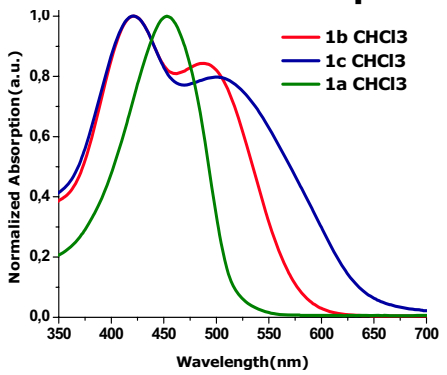


Yield= 91%
Mn = 3600
Mw = 4400

Yield= 88%
Mn = 17900
Mw = 30000

Yield 63%
Mn = 5700
Mw = 9500

Absorption spectra



1a

1b

1c

OUTLOOK

Materials for…

Light emission

Fluorinated electroluminescent polymers

Light absorption

Conjugated polymers for photovoltaics

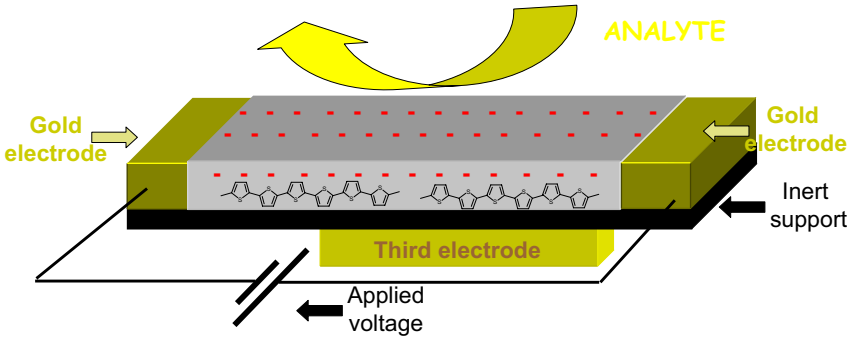
Charge transport

Bio-functionalized organic semiconductors for chiral sensing

Organic semiconductors for electronic sensors

$C \propto \Delta I$

The change in current depends on analyte concentration



Organic semiconductors for advanced electronic sensors

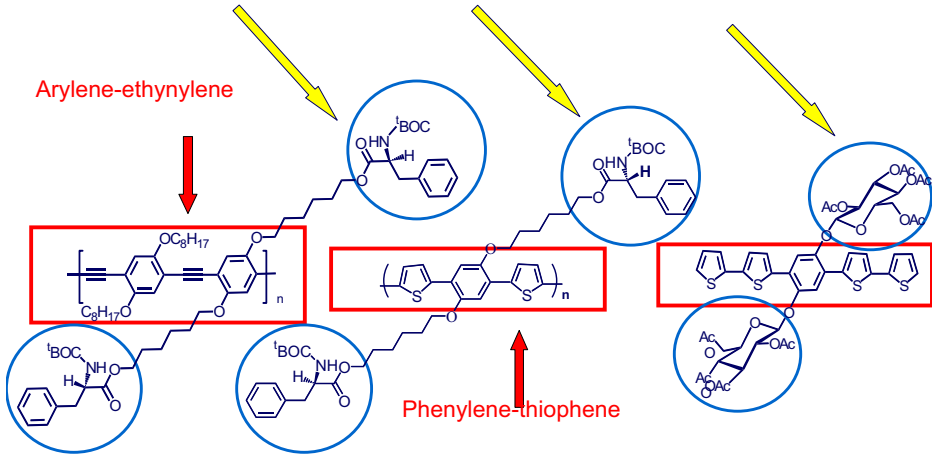
Conjugated polymers functionalized with bio-molecules

Conjugated backbone → **Semiconducting properties**

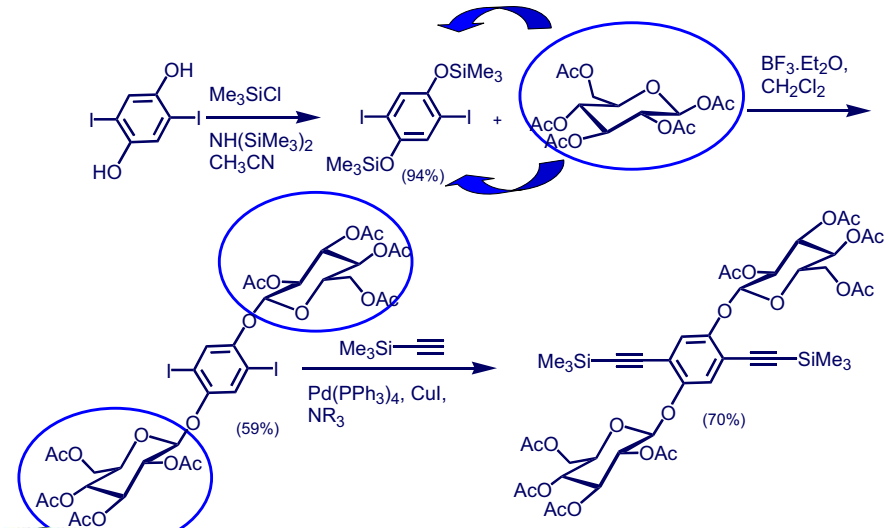
Bio-molecules → **Recognition ability**

Combining semiconducting properties with recognition ability

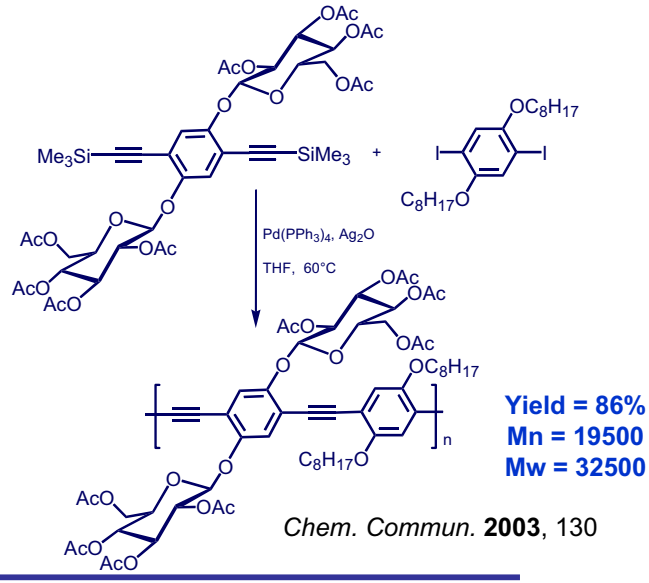
Bio-molecules as chiral side groups



(D)-Glucose-substituted PPE

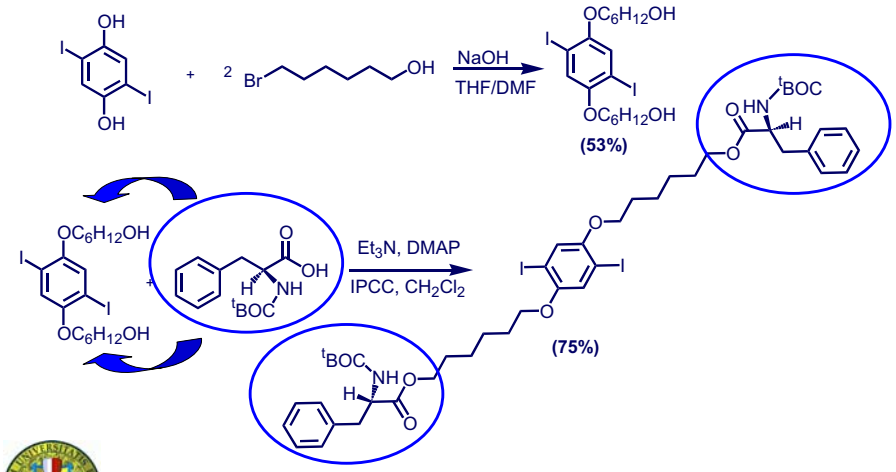


(D)-Glucose-substituted PPE

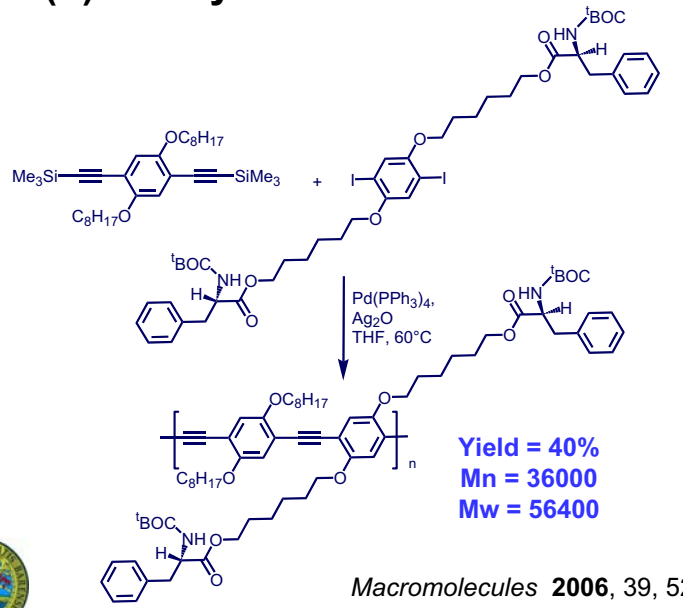


Chem. Commun. **2003**, 130

(L)-Phenylalanine-substituted PPE

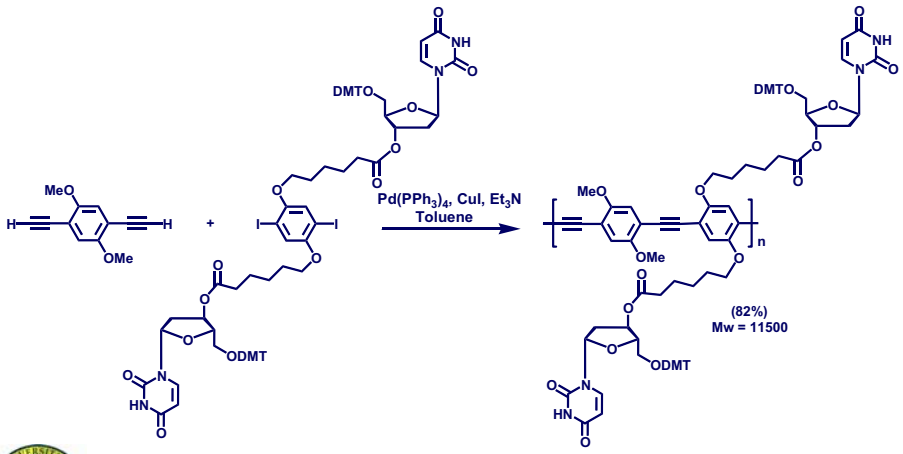


(L)-Phenylalanine-substituted PPE

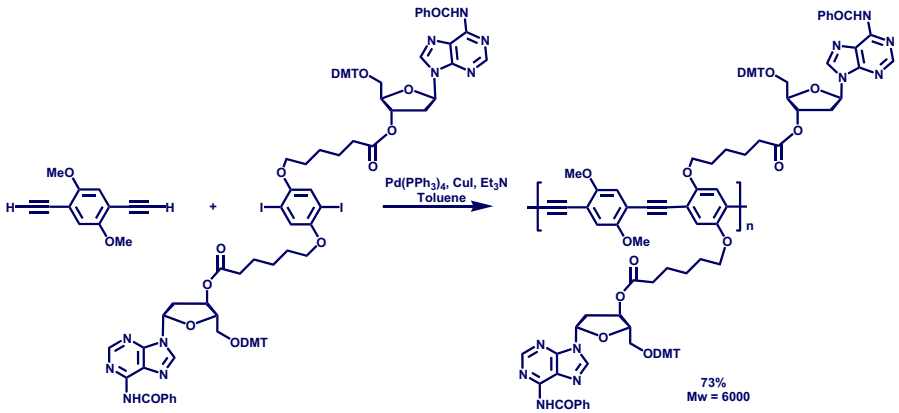


Macromolecules **2006**, 39, 5206

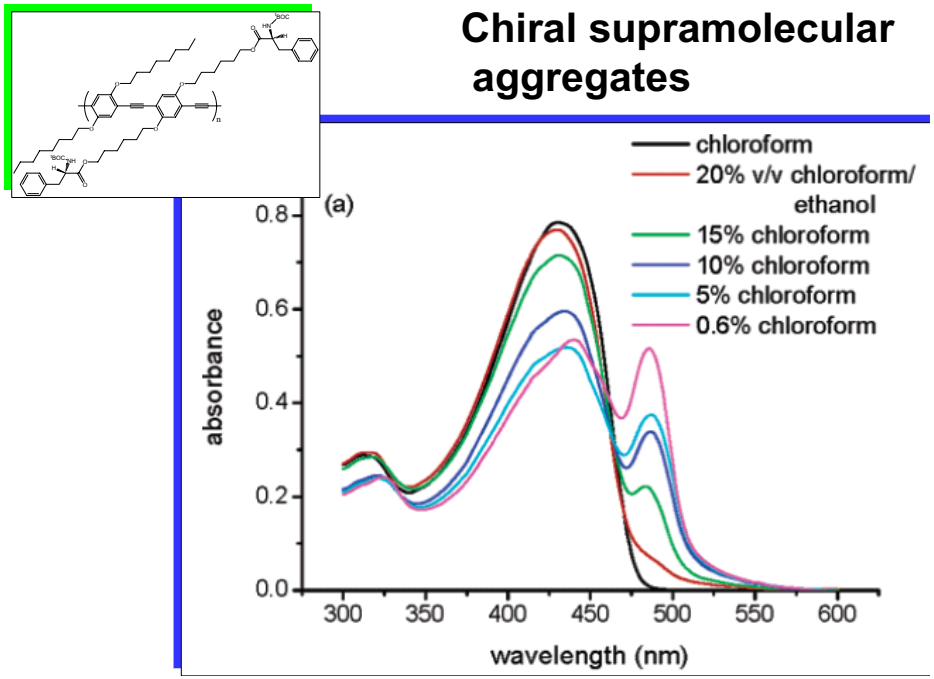
Deoxyuridine-substituted PPE



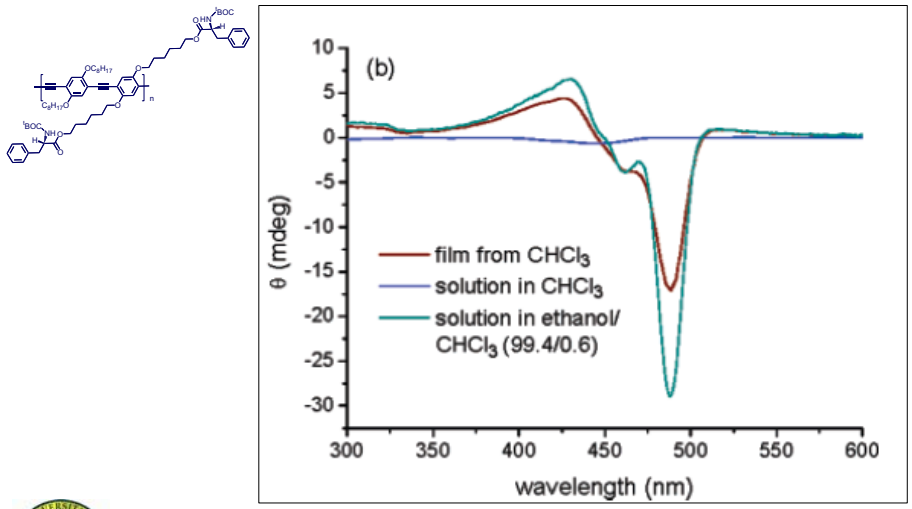
Deoxyadenosine-substituted PPE



Chiral supramolecular aggregates

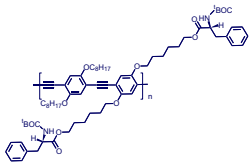


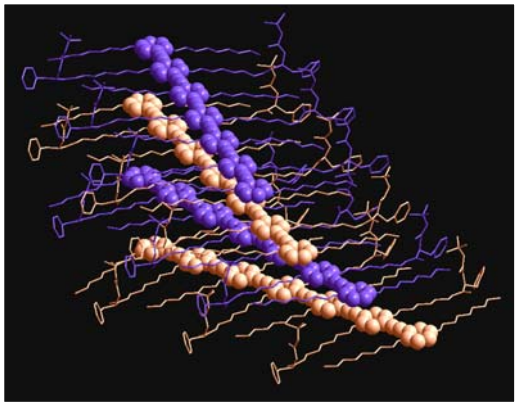
Chiral supramolecular aggregates



Collaboration with Proff. L. Di Bari and G. Pescitelli , University of Pisa

Chiral supramolecular aggregates

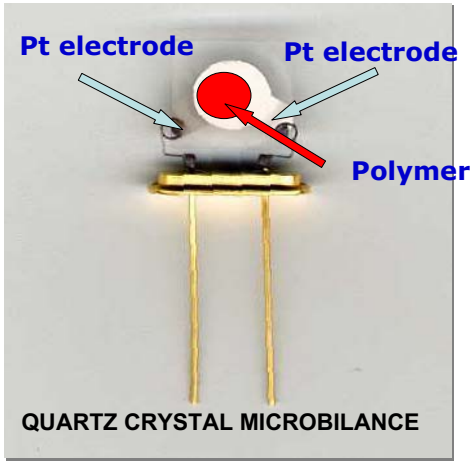


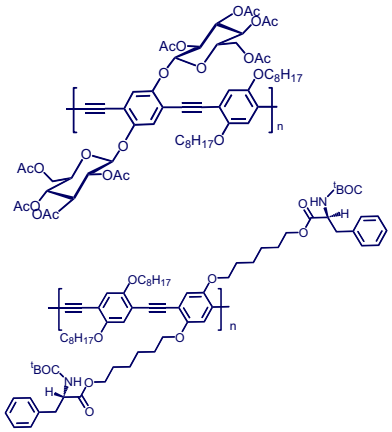


A pictorial model of aggregated chains evidencing supramolecular chirality adopted by the polymer backbones

Macromolecules **2006**, *39*, 5206

Chiral discrimination

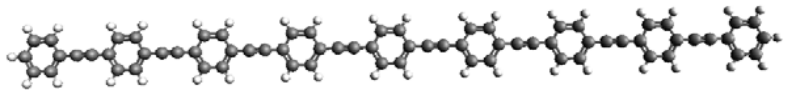




Sensors and Actuators B **2004**, 17

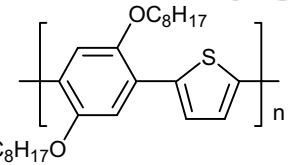
Chiral discrimination

Electrical characteristics of PPE polymers are not suitable for electronic sensors

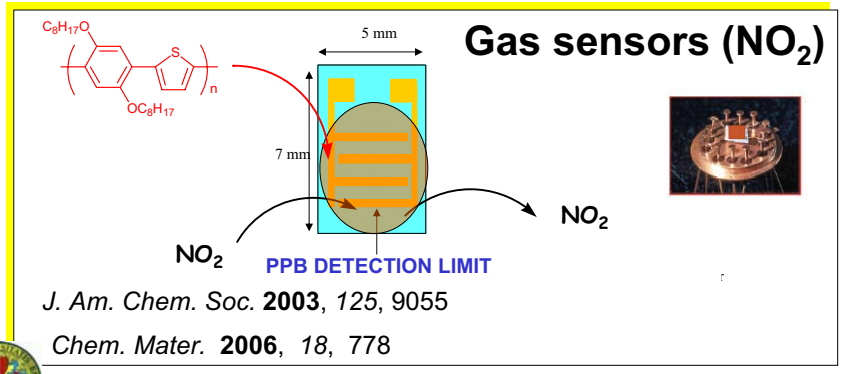


The conjugated backbone must be changed

Switching to a different conjugated polymer



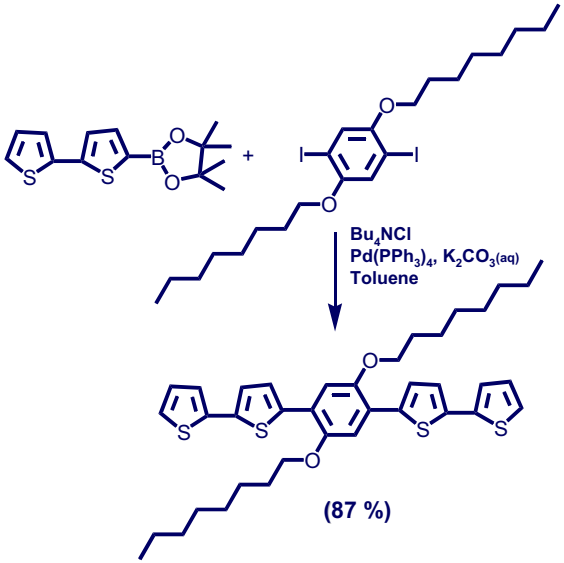
Eur. J. Org. Chem. **2002**, 2785



J. Am. Chem. Soc. **2003**, *125*, 9055

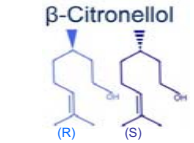
Chem. Mater. **2006**, *18*, 778

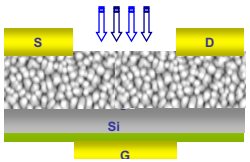
Synthesis of a phenylene-thiophene oligomer

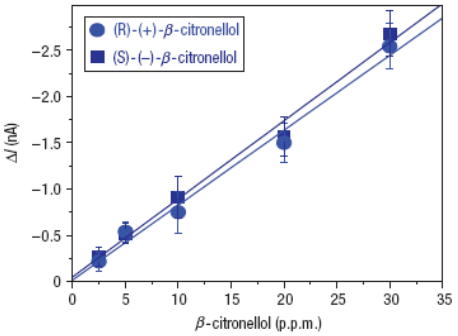


Sensing measurements

30 ppm of (-) citronellol



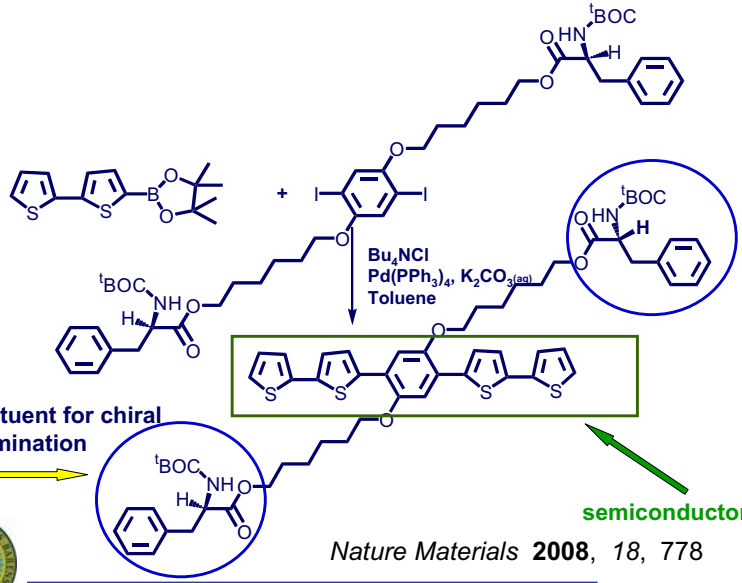




LoD =3.6 ± 1.5 pm

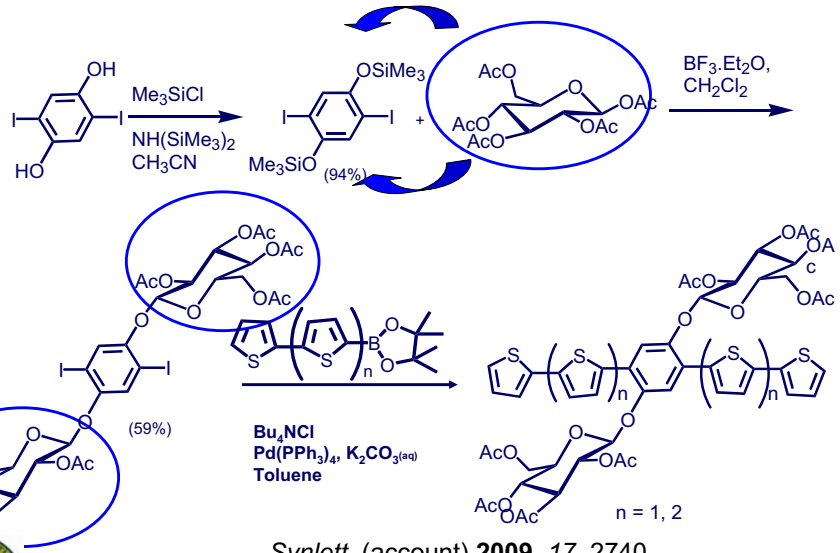
Collaboration with Prof. L. Torsi Univ. of Bari and Prof. L. Valli Univ. of Salento

Molecular semiconductor for chiral sensing



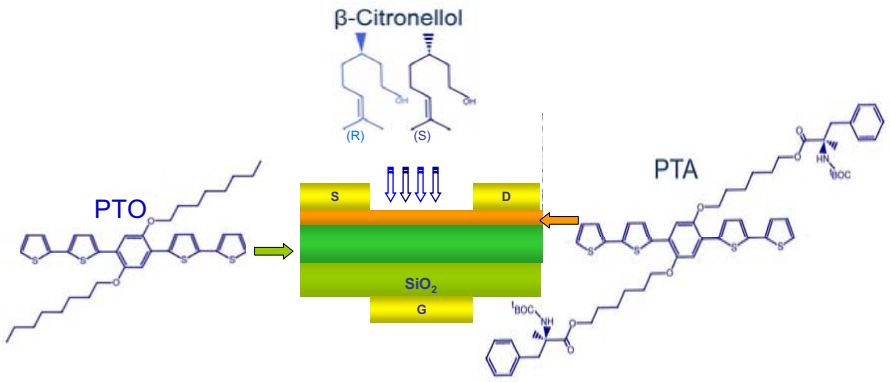
Nature Materials **2008**, *18*, 778

Molecular semiconductors for chiral sensing



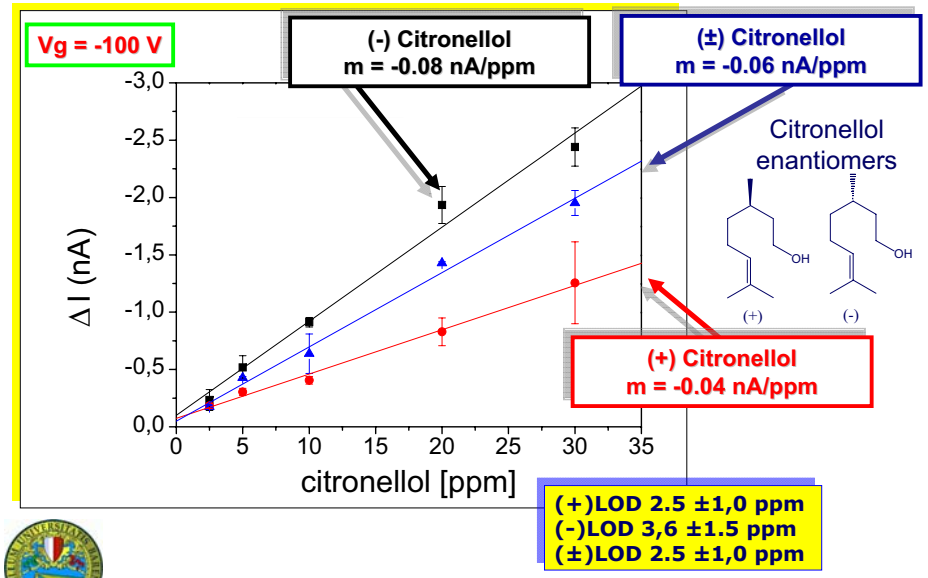
Synlett (account) **2009**, *17*, 2740

Chiral sensor



Nature Materials **2008**, *18*, 778

Enantioselective sensing



BETTER THAN LITERATURE

K. Bodendhofer, A. Hierlemann, J. Seemann, G. Gauglitz, B. Koppenhoefer, W. Gopel *Nature,* **1997**,*387*, 577.
E.J.Severin, R.D. Sanner, B.J. Doleman, N.S. Lewis *Anal. Chem.* **1998**, *70,* 1440.
B.P. de Lacy Costello, N.M. Ratcliffe, P.S. Sivanand, *Synth. Met.* **2003**, 139, 43.

PPTH DETECTION THRESHOLD

BETTER THAN UMAN NOSE

(S)-(-)-citronellol – floral, rose-like odour, reminiscent of geranium oil;
described as very **fresh light and clean rosy-leafy, petal-like** **LoD 40-50 ppm**
(R)-(+)-citronellol- citronella oli-like; described as slightly
oily light rosy-leafy, **petal like odour with irritating top note** **LoD 50 ppm**

Molecular diversity as key feature of organic electronics

- ***CHALLENGING MOLECULAR DESIGN AND SYNTHESIS***
- ***CONCEIVING AND CREATING NEW MULTIFUNCTIONAL MATERIALS***
- ***FINE TUNING OF PROPERTIES***

iasoc