Design and Synthesis of Conjugated Polymers towards Organic Solar Cell Applications

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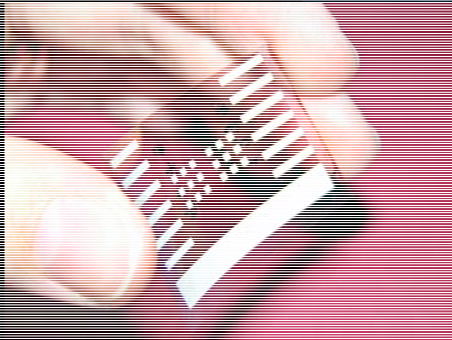
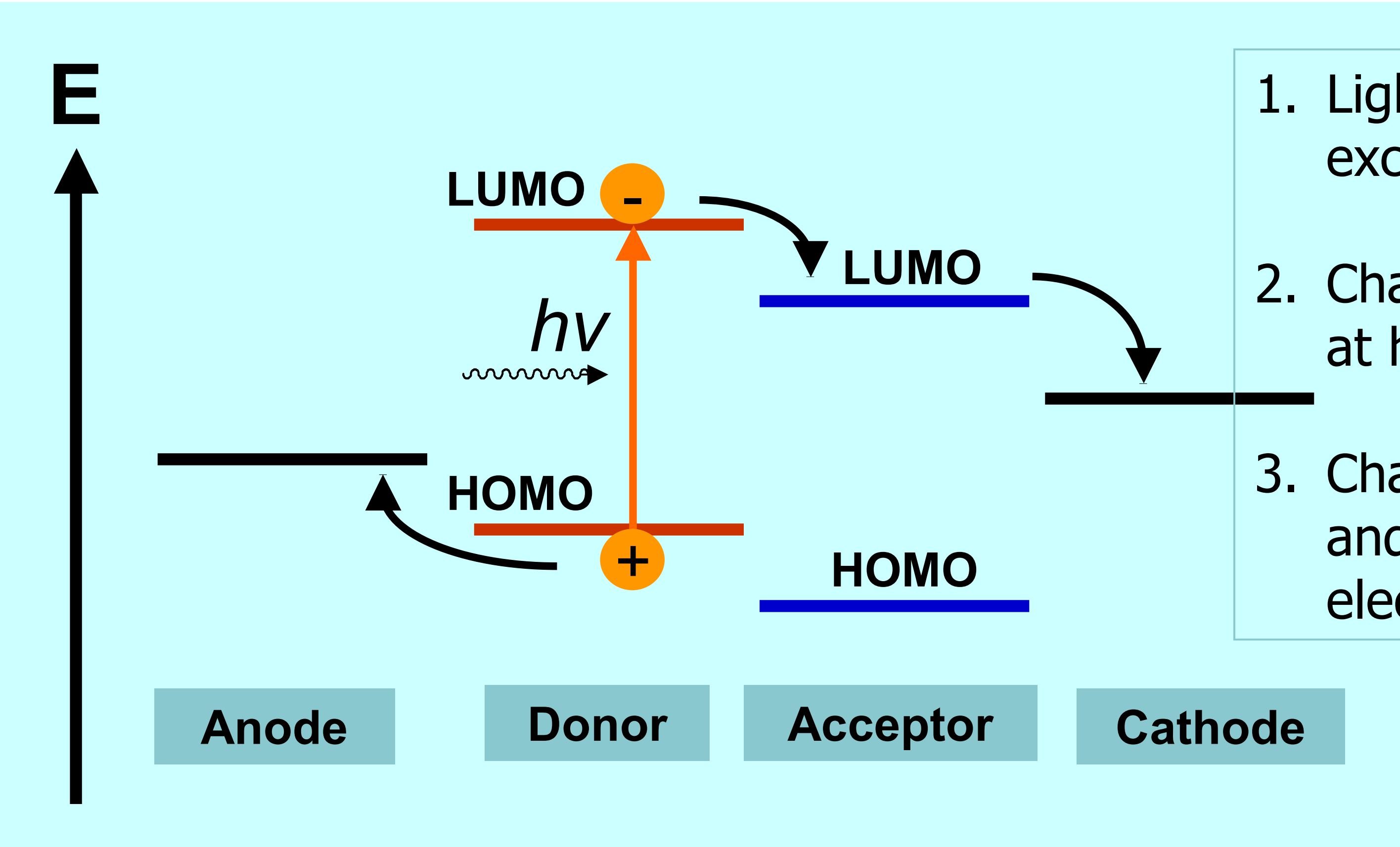
Organic Photovoltaics (OPV)

- Solar energy – plentiful and free
- Organic vs inorganic
  - Low cost
  - High-speed production (solution, roll-to-roll processing)
  - Mountable on flexible substrates
  - Chemical flexibility for modifications via synthetic methods
  - *Downside: low efficiency, instability*



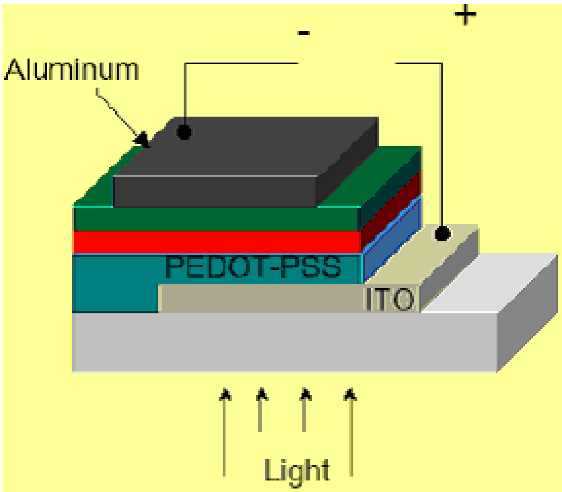
Photovoltaic energy conversion



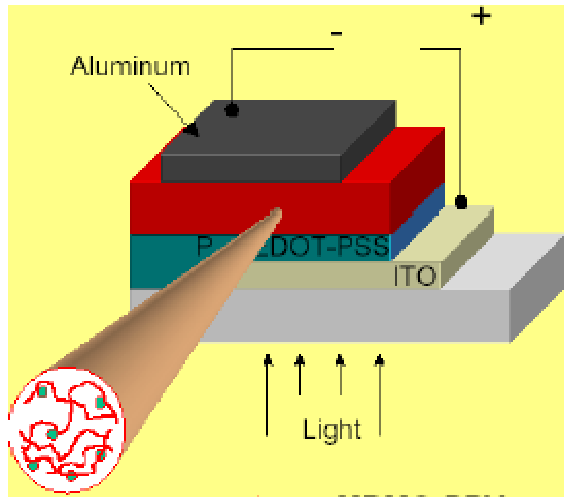
1. Light absorption and exciton formation.
2. Charge dissociation at heterojunction.
3. Charge transport and collection at electrodes.

$$\eta_{TOTAL} = \eta_{ABS} \times \eta_{DISS} \times \eta_{COLL}$$

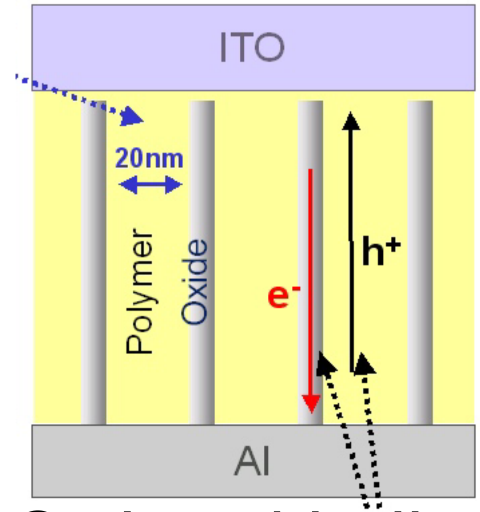
Organic Heterojunction Solar Cells



Double-layer heterojunction

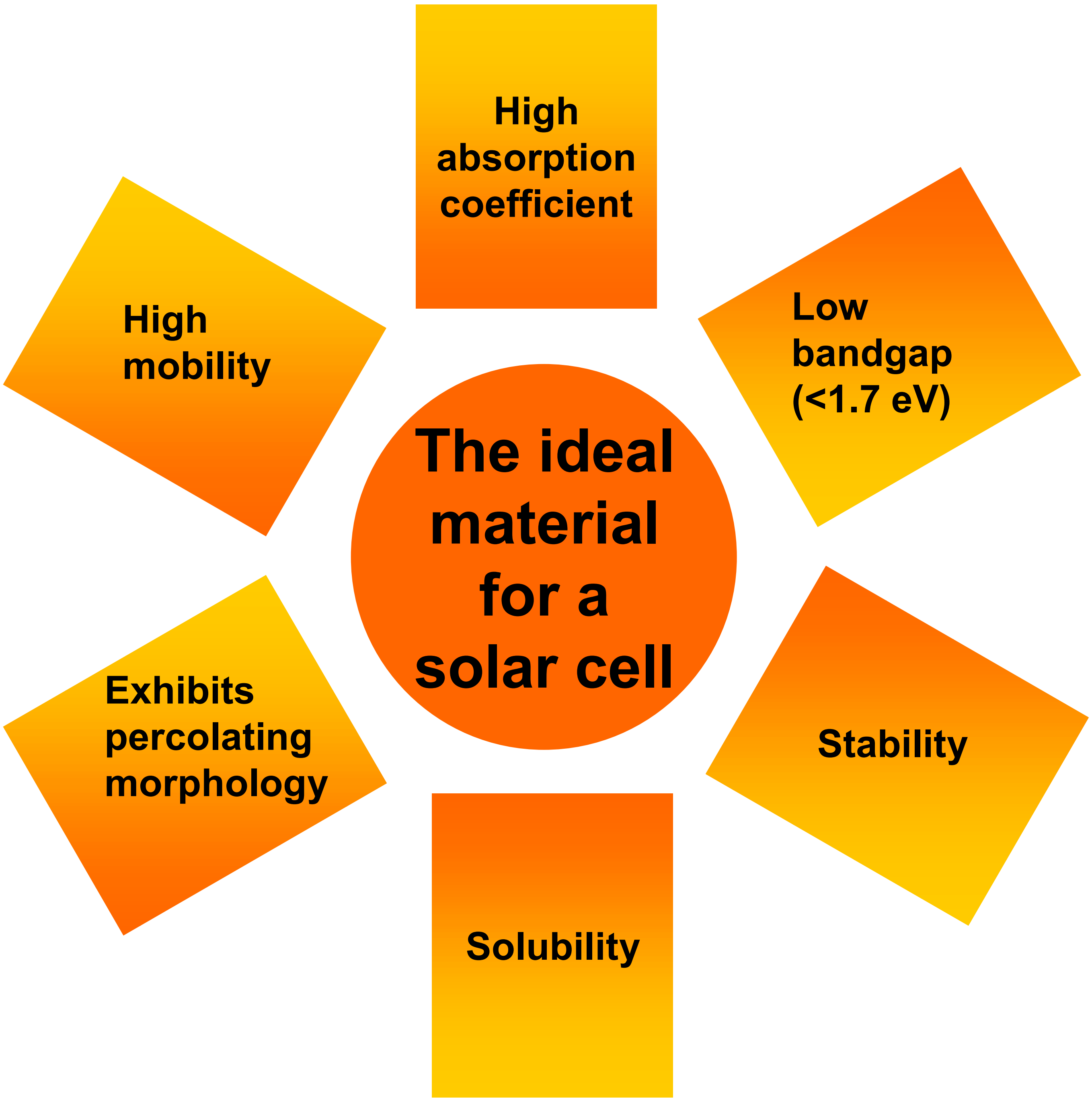


Bulk heterojunction

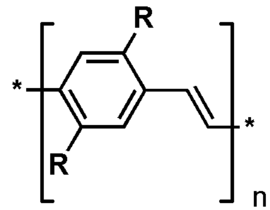
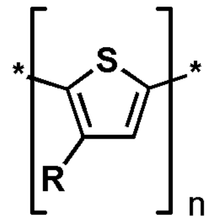
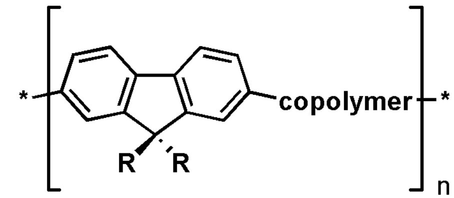


Ordered bulk heterojunction

Type of Device	Efficiency (%)
Bulk heterojunction	5.5
Inorganic solar cell	> 30
Target for OPV	15 – 20


High absorption coefficient
High mobility
Low bandgap (<1.7 eV)
The ideal material for a solar cell
Exhibits percolating morphology
Stability
Solubility

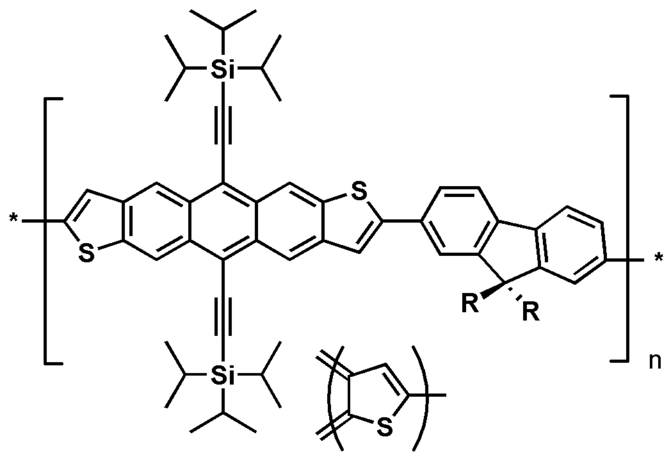
Representative/Promising classes of materials to-date

Material		PPVs	P3HTs	Fluorene copolymers
Structure				
HOMO-LUMO gap (eV)		2.0 – 2.2	~1.9 – 2.2[5]	1.6
Mobility (cm^2/V s)		~10^{-7}[3]	~0.01-0.1	~10^{-6} – 10^{-4}
Best performance reported	**I_{SC} (mA/cm^2)**	5.4	12.5	8.9
	V_{OC} (V)	0.80	0.65	0.59
	FF	0.56	0.65	0.42
	PCE (%)	**3.0**[1]	**4.6**[2]	**2.2**[4]

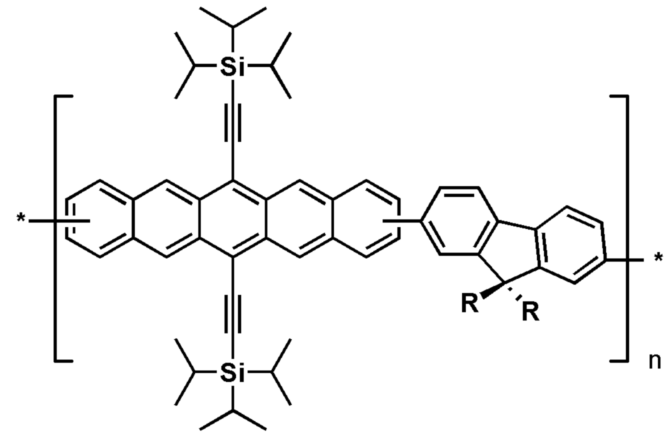
Desirable bandgap: < 1.7 eV, mobility > 0.01cm^2/Vs

1. Chem. Commun., 2003, 2116–2118; 2. *Solar Energy Materials & Solar Cells* 91 (2007) 1187–1193; 3. *J. Phys. Chem. B* **2004,** *108,* 5235-5242; 4. *Adv Mater* 2006, 18, 2169-2173; 5. *Adv. Funct. Mater.* 2007, 17, 1071-1078

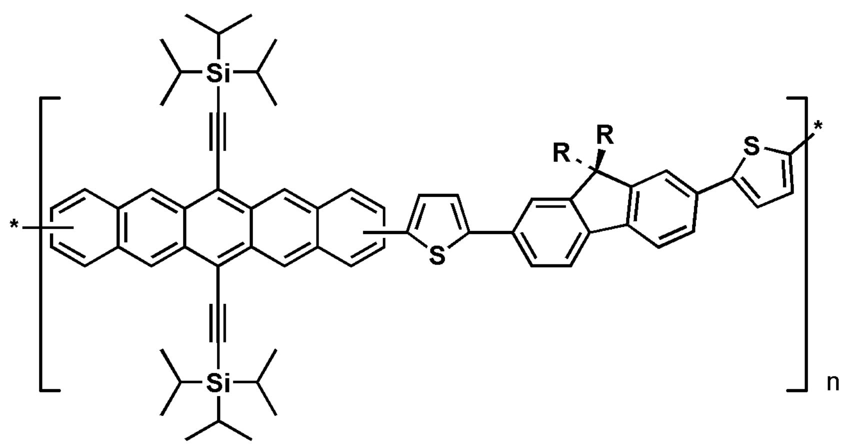
Our approach: acene-containing conjugated polymers



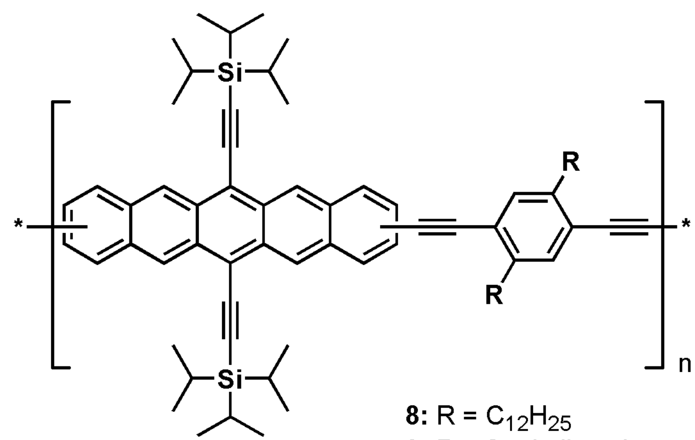
1: R = C_8H_{17}
2: R = 2-ethylhexyl
3: R = $C_{12}H_{25}$



4: R = C_8H_{17}
5: R = 2-ethylhexyl
6: R = $C_{12}H_{25}$



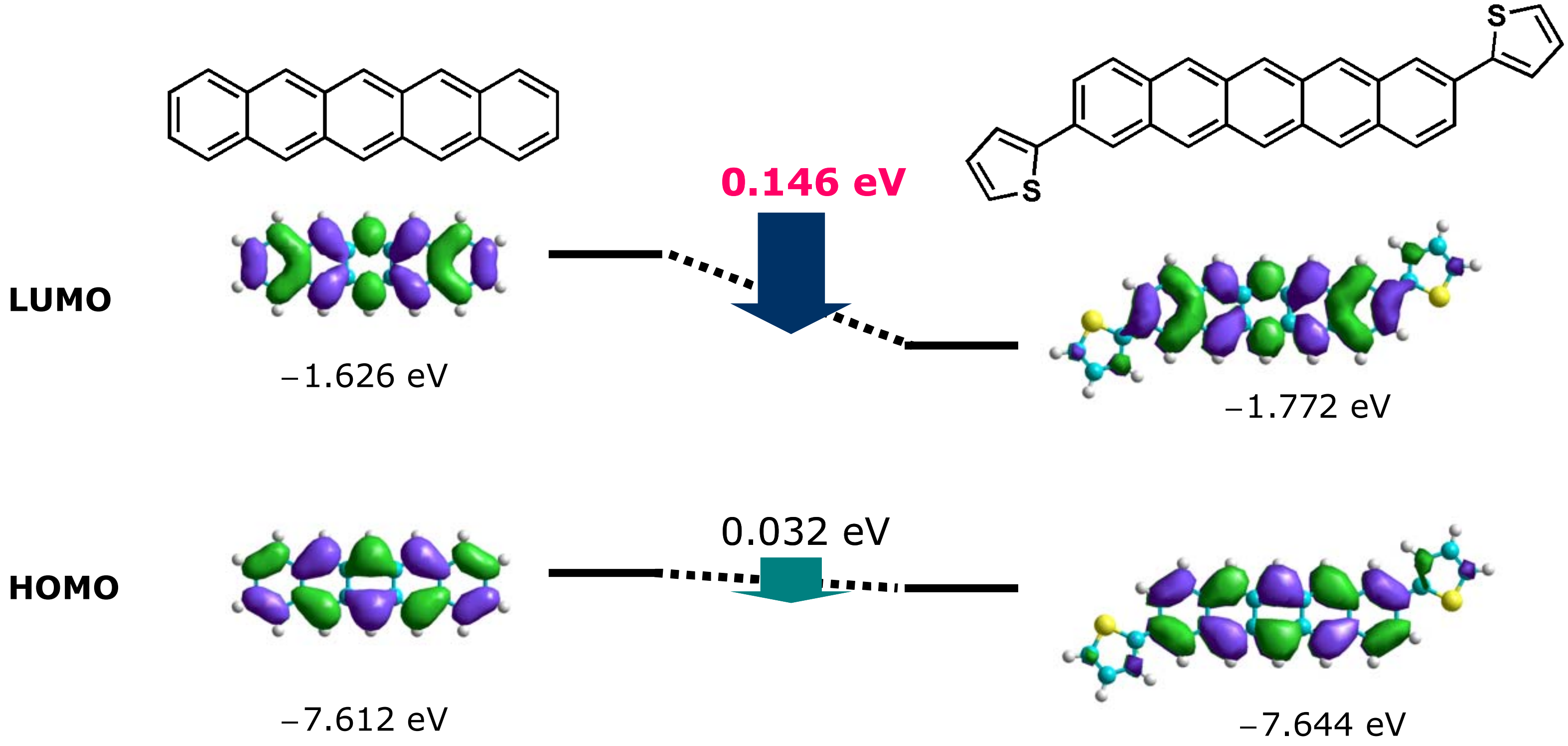
7: R = $C_{12}H_{25}$



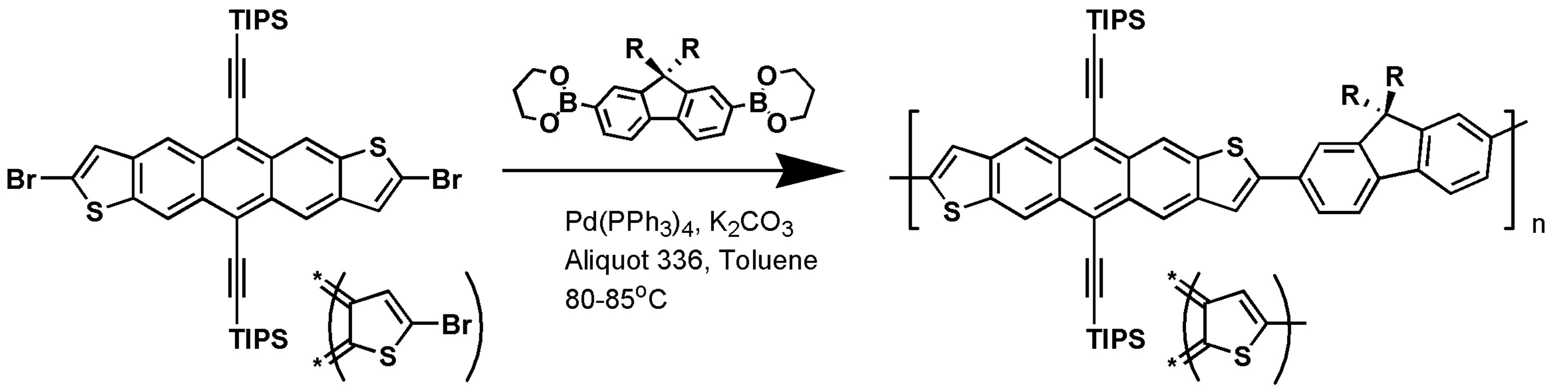
8: R = $C_{12}H_{25}$
9: R = 2-ethylhexyl

Low bandgap conjugated pentacene derivatives

- **Pentacene**
  - Optical band gap 2.1 eV in solution, 1.77 eV in thin film
  - Further reduction in band gap by extending conjugation



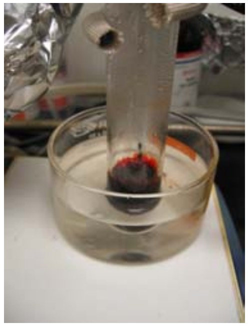
ADT-fluorene copolymer



1: R = C_8H_{17}
2: R = 2-ethylhexyl
3: R = $C_{12}H_{25}$

E_g = 2.2 eV;
More stable than pentacene

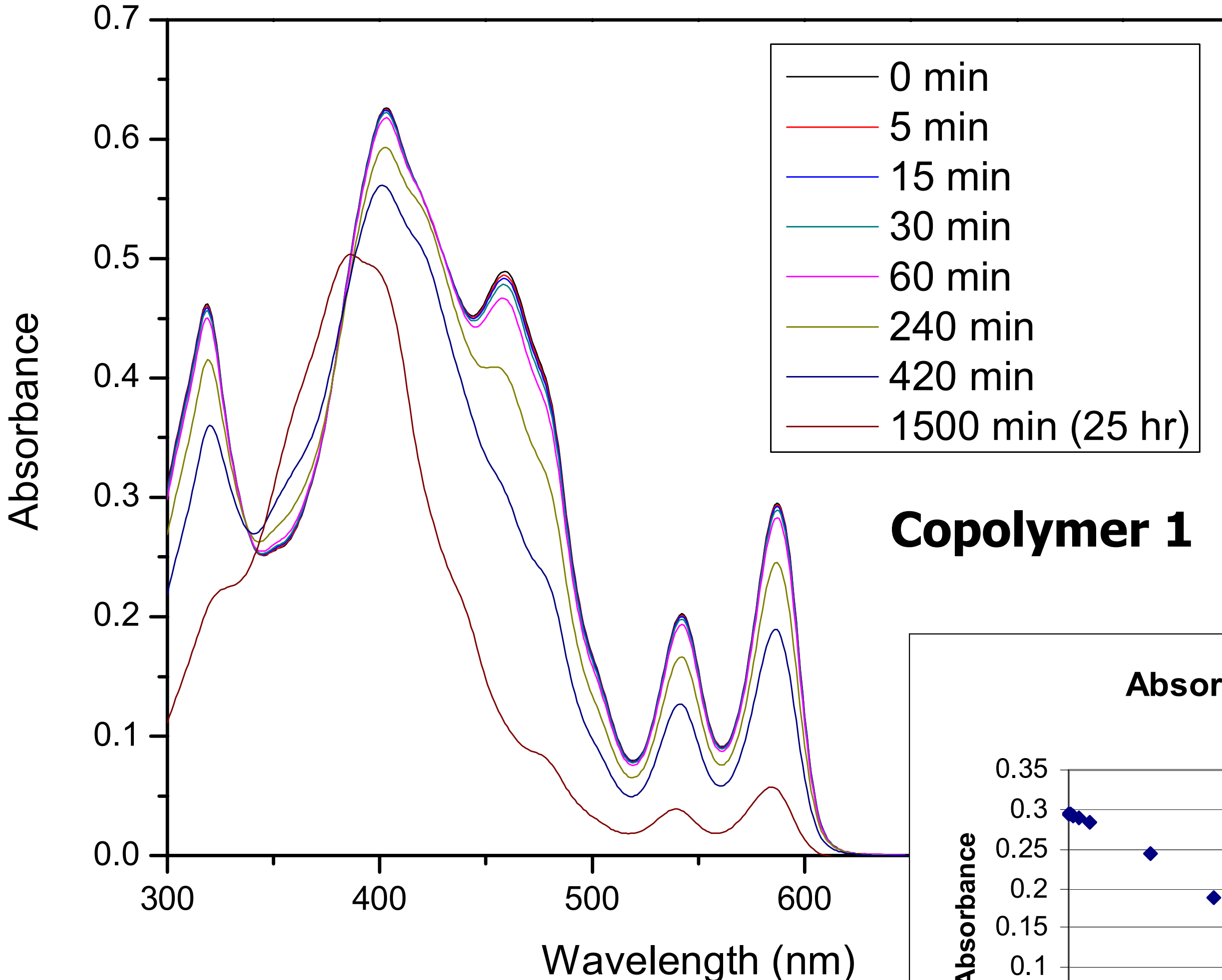
R	M_n	M_w	PDI	HOMO (eV)	Optical Band Gap (eV)
Octyl	46×10^3	131×10^3	3.8	-5.24	2.03
Dodecyl	8×10^3	23×10^3	2.9	-5.22	2.05
2-Ethylhexyl	10×10^3	24×10^3	2.4	-5.23	2.02



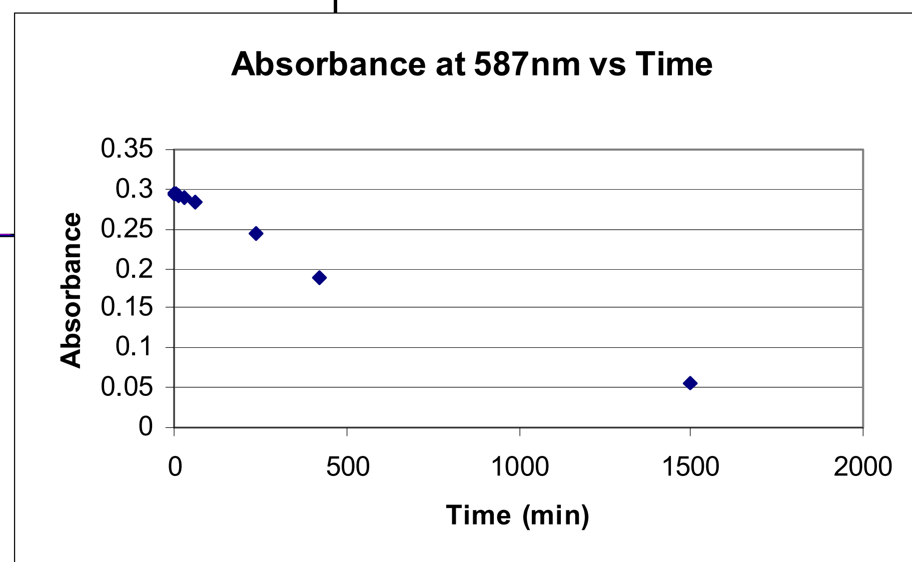
Copolymer (R = octyl) in toluene

Copolymer film (R = octyl)

UV-Vis stability in solution

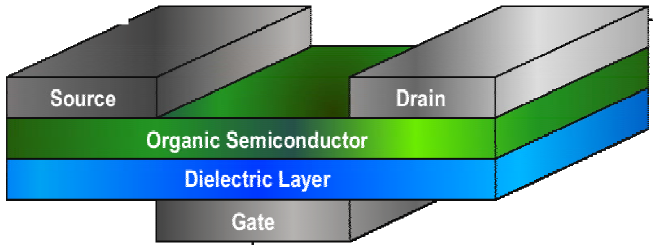


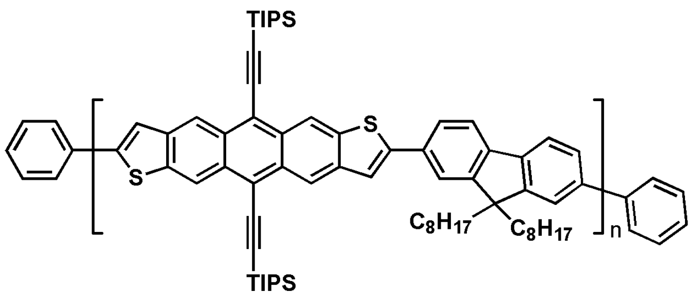
- Absorption measured in ODCB solution
- Decrease in absorption with $t_{1/2}$ ~ **600 min**
- Pentacene $t_{1/2}$ (575 nm) ~ **250 min** in dark[1]

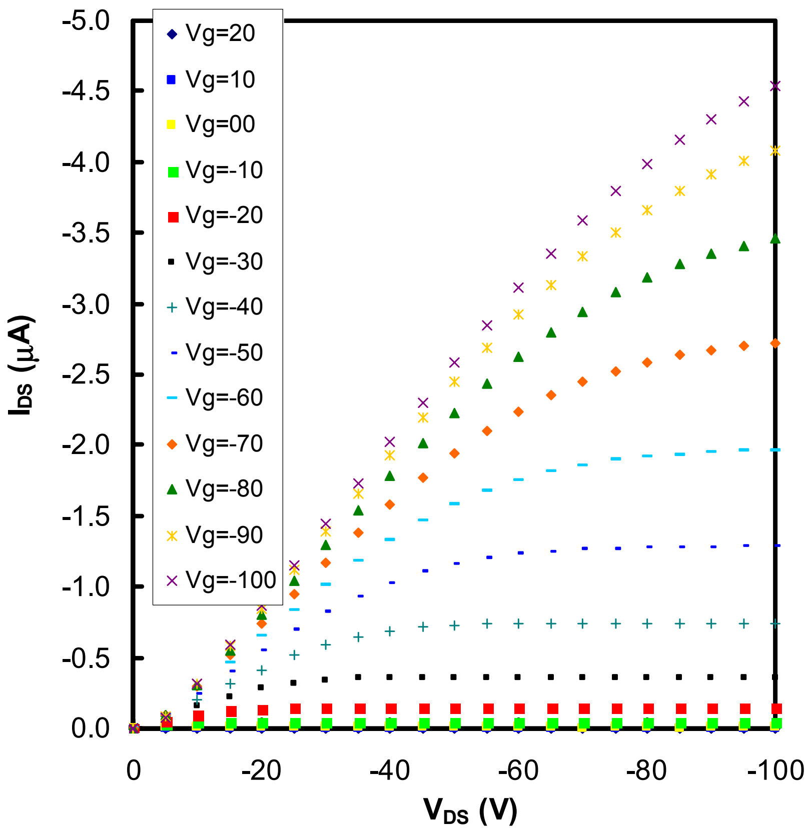


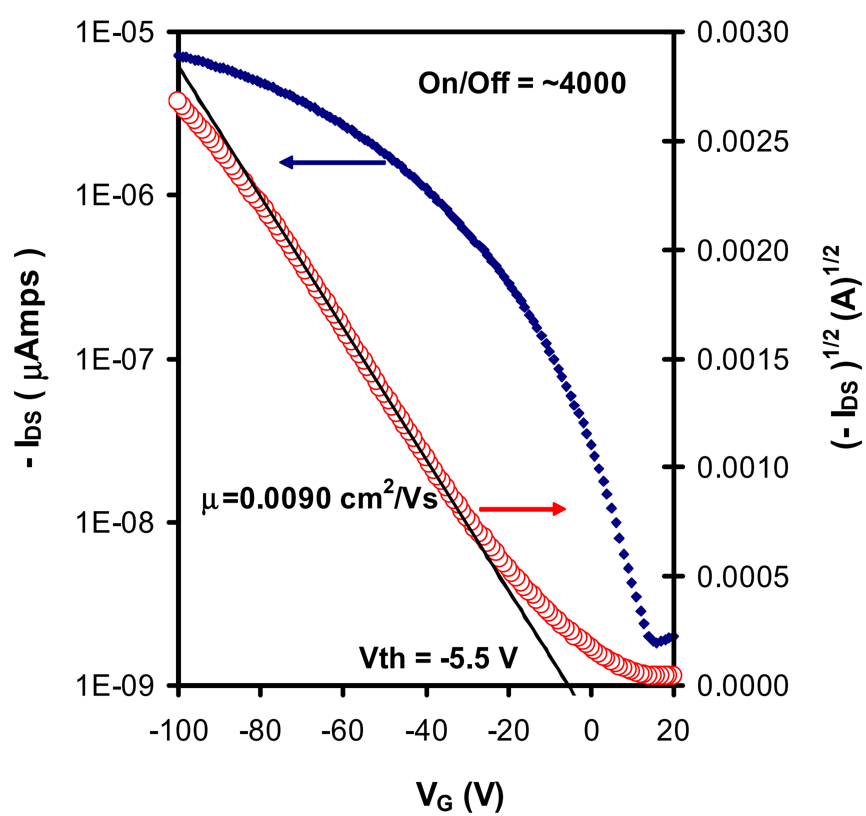
1 Chem Mater, Vol 16, No 24, 4980

Thin film field-effect mobility

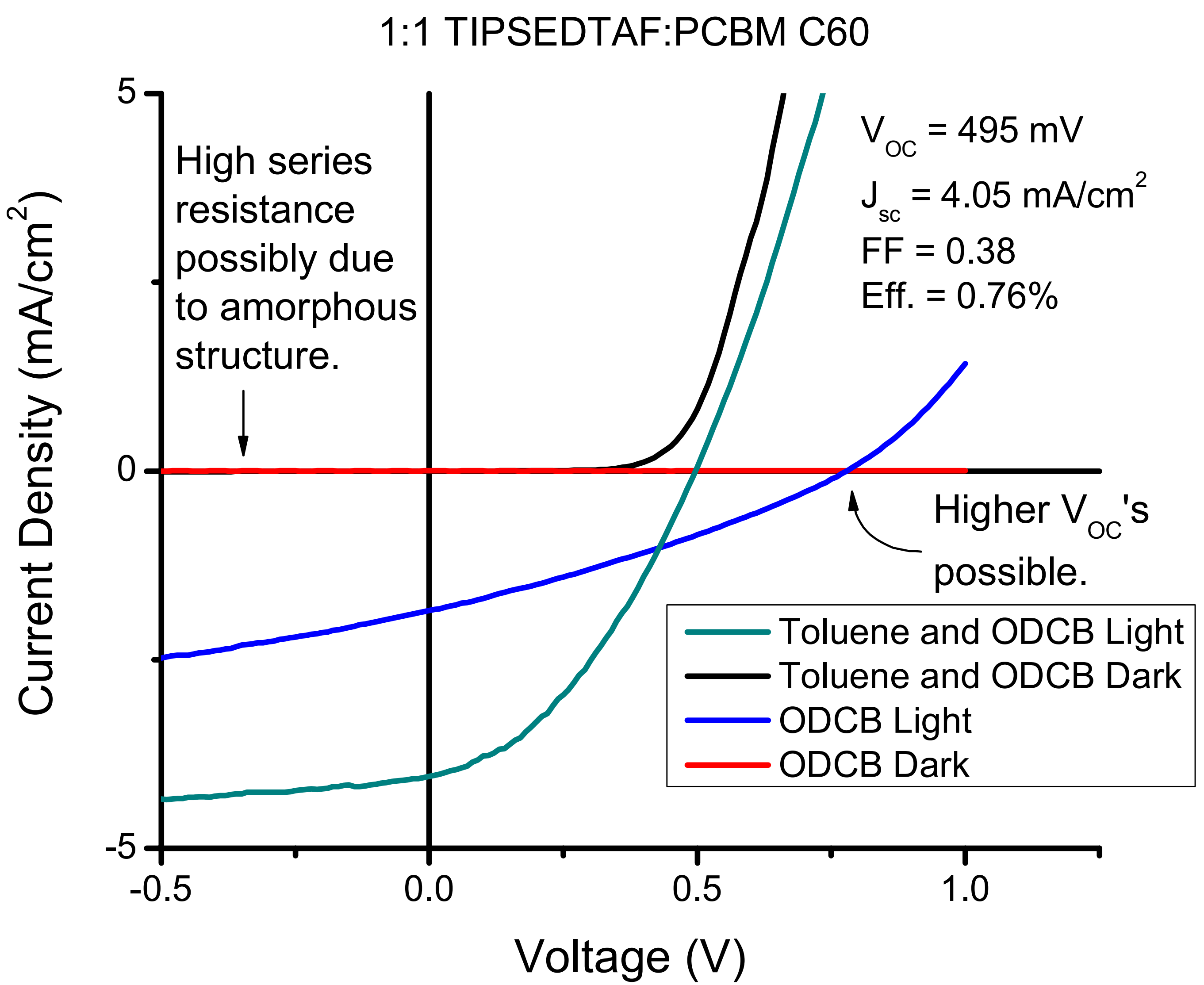




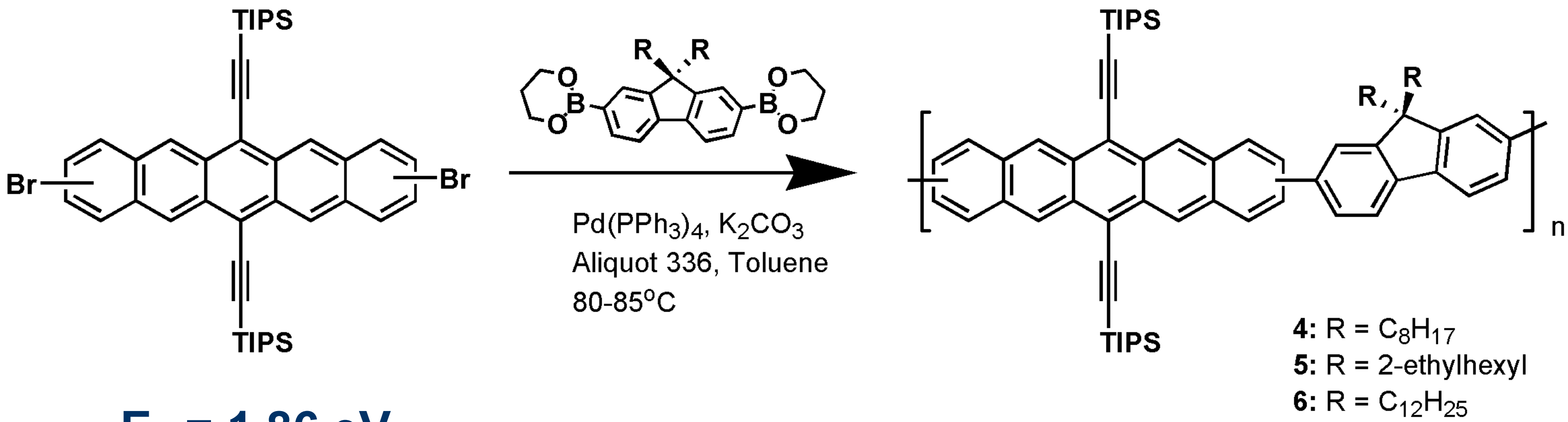




Preliminary solar cell results



TIPSEP-fluorene copolymer

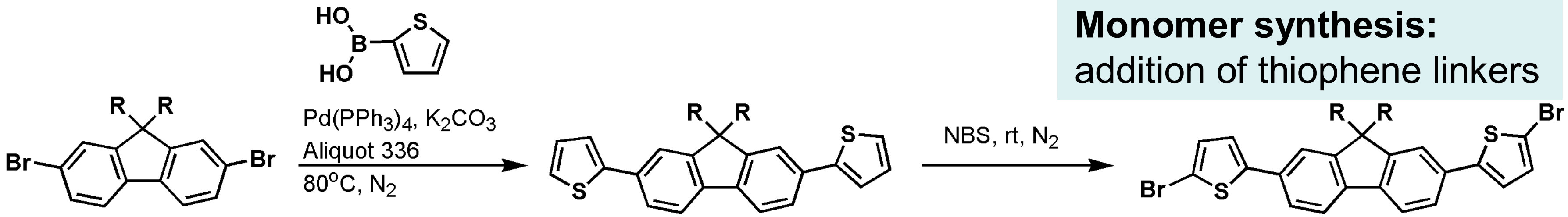


E_g = 1.86 eV

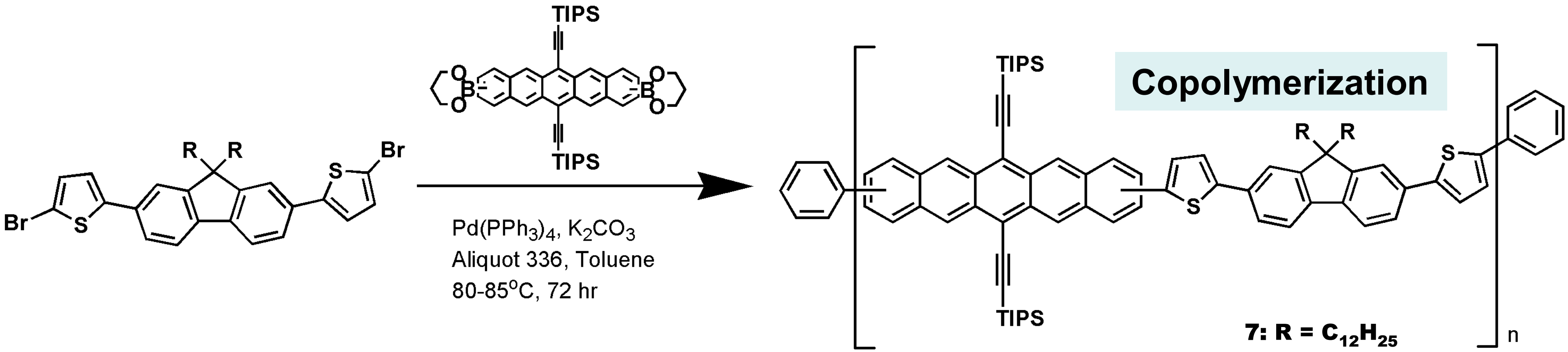
R	M_n	M_w	PDI	HOMO (eV)	Optical Band Gap (eV)
Octyl	36×10^3	117×10^3	3.21	5.20	1.78
Dodecyl	18×10^3	49×10^3	2.77	5.19	1.79
2-Ethylhexyl	8.2×10^3	17×10^3	2.06	5.17	1.80

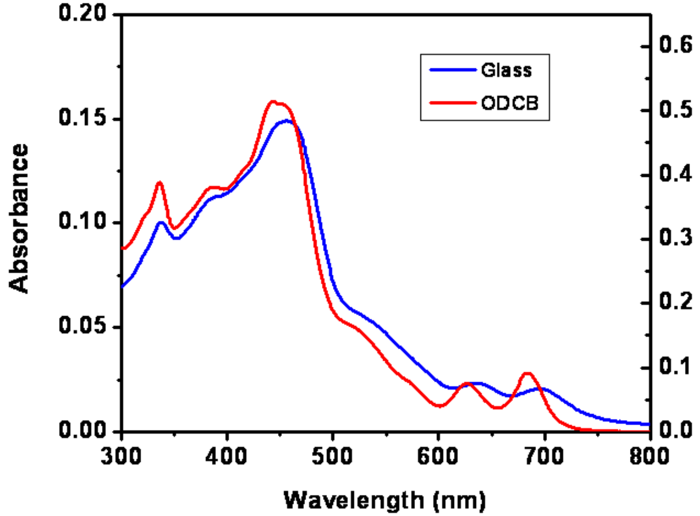
TIPSEP-dTfluorene copolymer

Monomer synthesis:
addition of thiophene linkers



Copolymerization

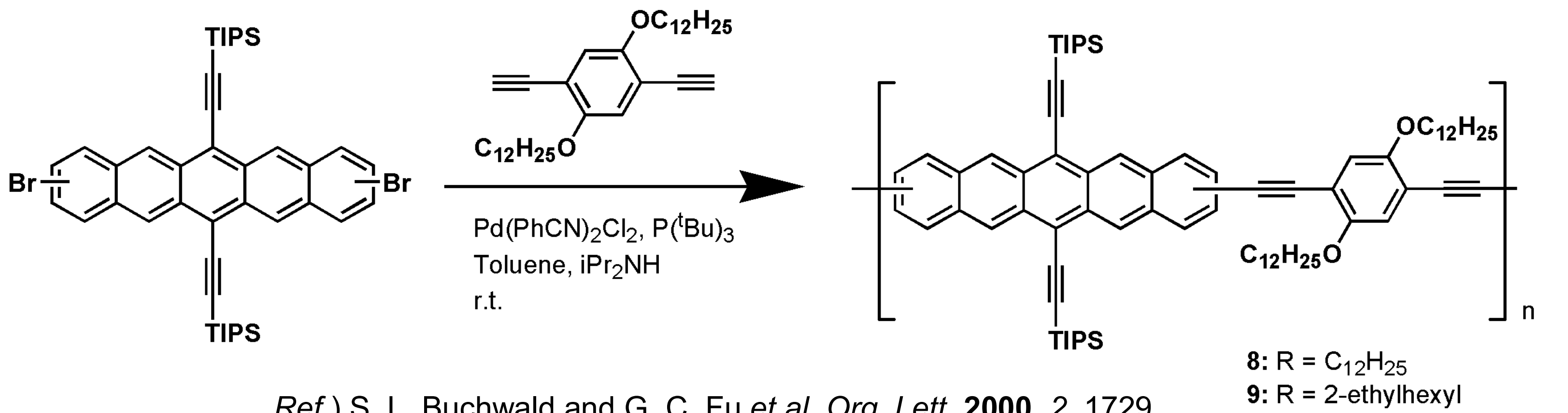




	λ_{onset} (nm)	λ_{max} (nm)	Eg (eV)
In ODCB	715	443	1.74
On Glass	745	457	1.67

UV-Vis absorption spectra of TIPSEP-dTfluorene copolymer

TIPSEP-diethynylbenzene copolymer

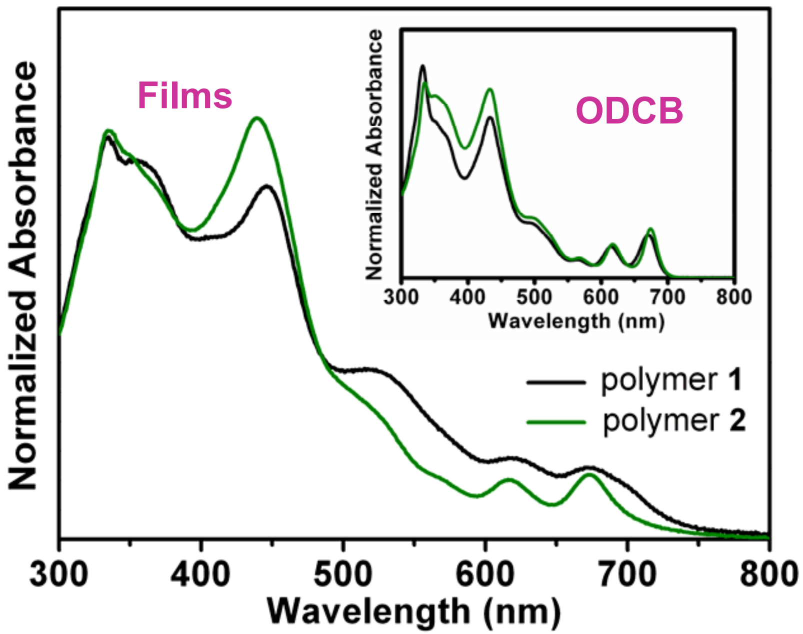


Ref.) S. L. Buchwald and G. C. Fu *et al. Org. Lett.* **2000**, *2*, 1729

R	M_n	M_w	PDI	E_g (eV)
Dodecyl	11×10^3	25×10^3	2.21	1.68
2-Ethylhexyl	24×10^3	58×10^3	2.41	1.76

Dark Green Film
(Polymer **9**)

Modest solubility in common organic solvents (< 5 mg/ml)



Summary and future work

- Molecular design towards stable, low bandgap materials for OPV
- Synthesized copolymers with promising properties

- Continue to build and characterize a library of pentacene-derivative-containing copolymers
- Fabricate devices to assess materials

Acknowledgements

Synthesis

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Solar Cell Device

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