

Towards Bridging the Gap from the Benchtop to Electronic Devices:

Manipulating the Self-Assembly of Conjugated Polymers



Kathy Beckner Woody

Organic Semiconductors

Organic Light Emitting Diodes



Image from <http://www.greentechgazette.com>

Solar Cells

Georgia Institute of
Technology



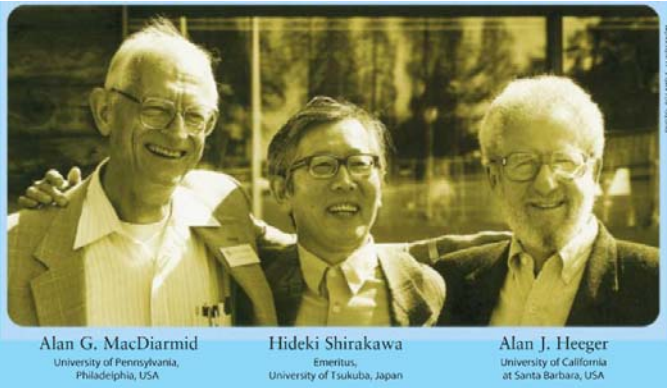
Image from: http://www.livescience.com/technology/041224_solar_panels.html



Image from: http://www.ubergizmo.com/15/archives/2008/01/sony_27inch_oled_tv_prototype.html

Sony 27"
OLED TV

Semiconducting Polymers



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University of Pennsylvania,
Philadelphia, USA

Hideki Shirakawa
Emeritus,
University of Tsukuba, Japan

Alan J. Heeger
University of California
at Santa Barbara, USA

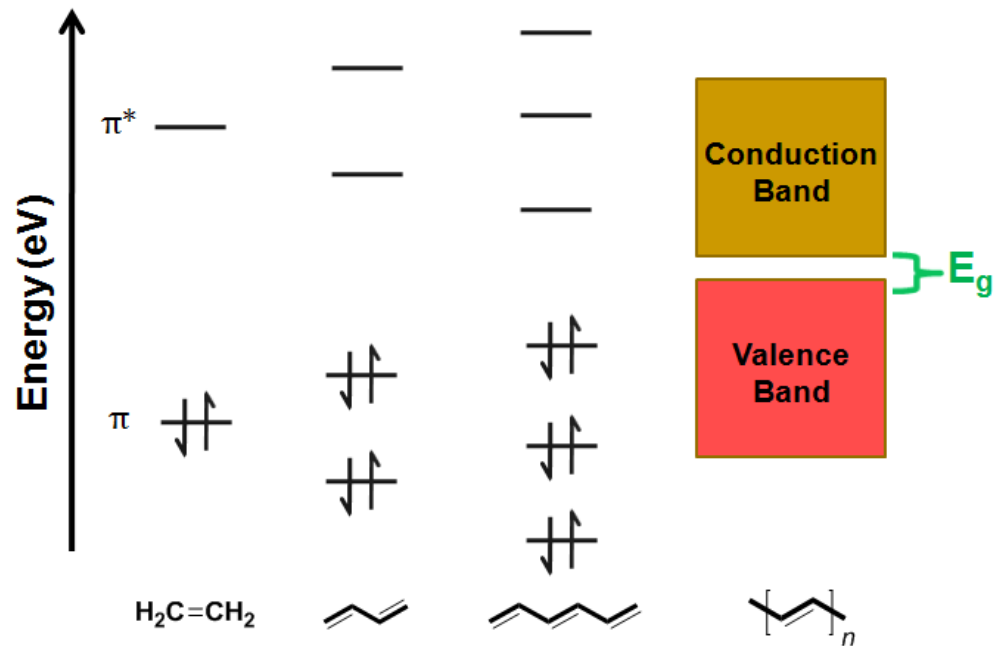
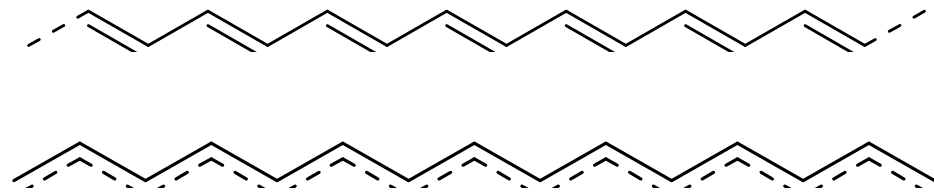
Bandgap (E_g)

Insulator $E_g > 1.5$ eV

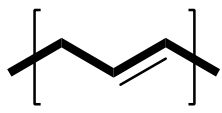
Semiconductor $0 < E_g < 1.5$ eV

Conductor $E_g = 0$

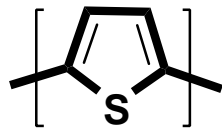
Polyacetylene



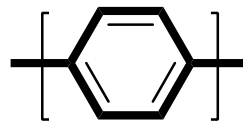
Conjugated Polymer Applications



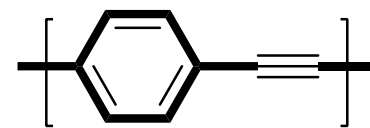
polyacetylene



polythiophene



polyphenylene



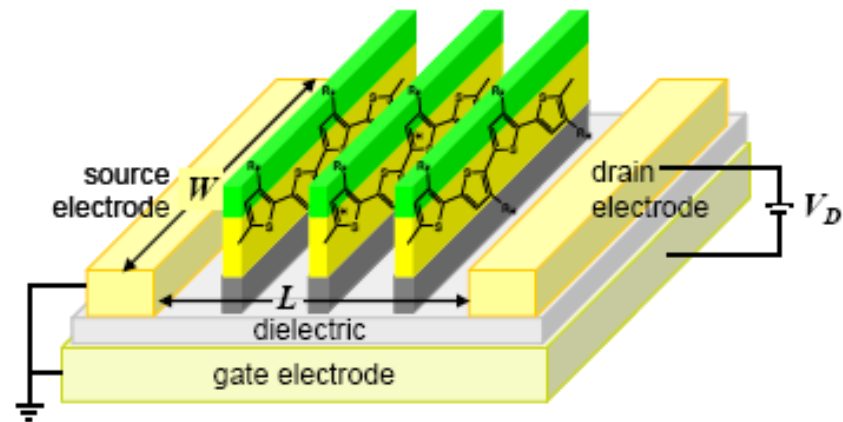
poly(phenylene ethynylene)

**Inorganic vs. Organic Materials:
field effect mobilities**

Si-based FETs: $1 \text{ cm}^2/\text{Vs}$

Polyalkylthiophenes: $10^{-1} \text{ cm}^2/\text{Vs}$

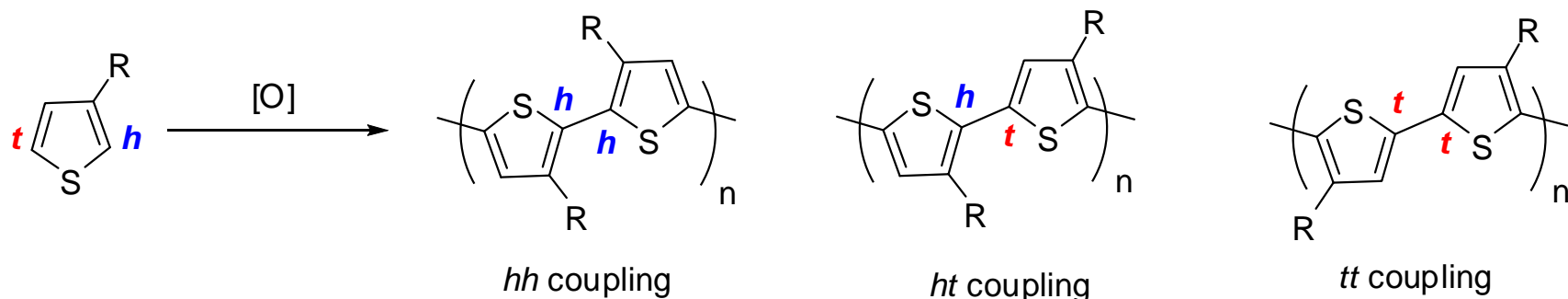
**Optimization: Controlling molecular
packing and alignment**



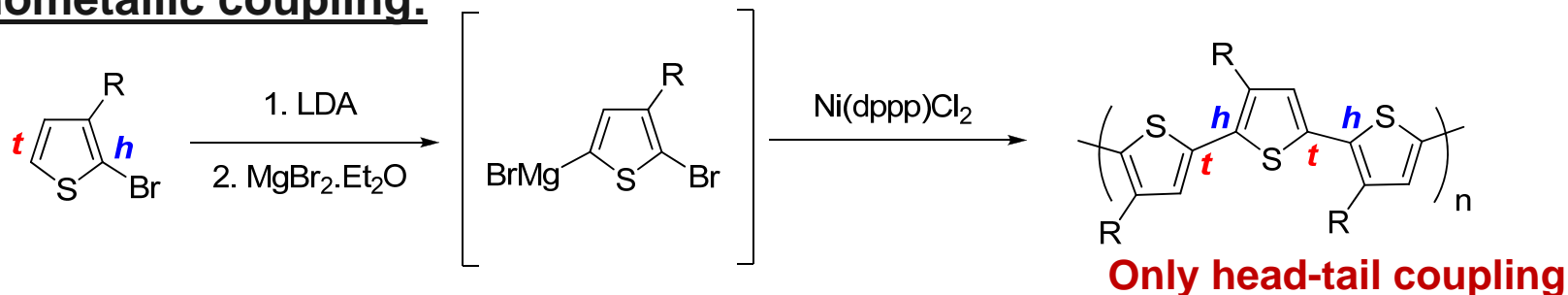
Field Effect Transistor

Regioregular Poly(3-alkylthiophenes) (PATs)

Oxidative polymerization:



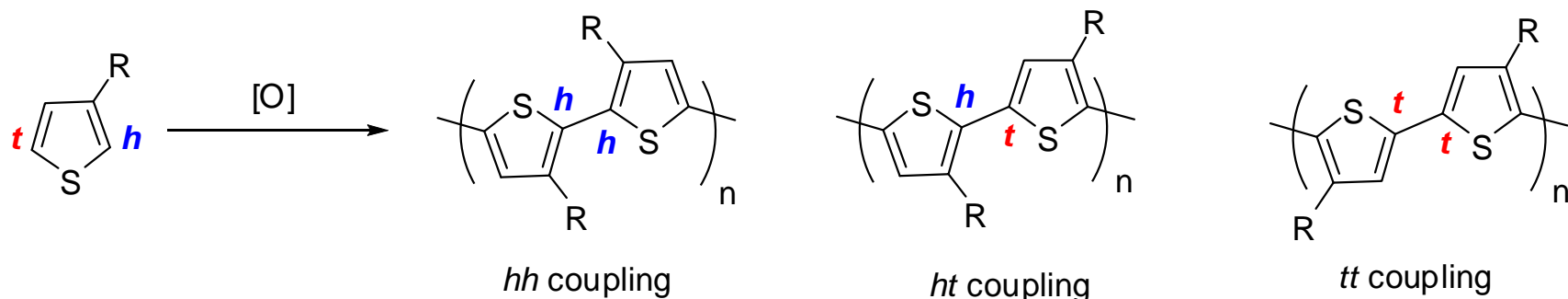
Organometallic coupling:



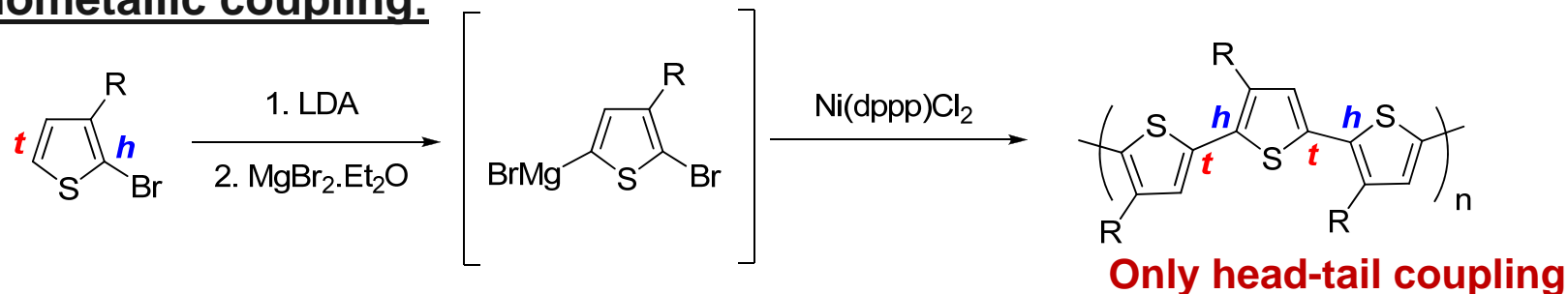
Regioregular PATs have higher crystallinity, red-shifted optical absorption, greater conductivity and smaller band gaps

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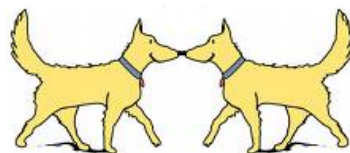
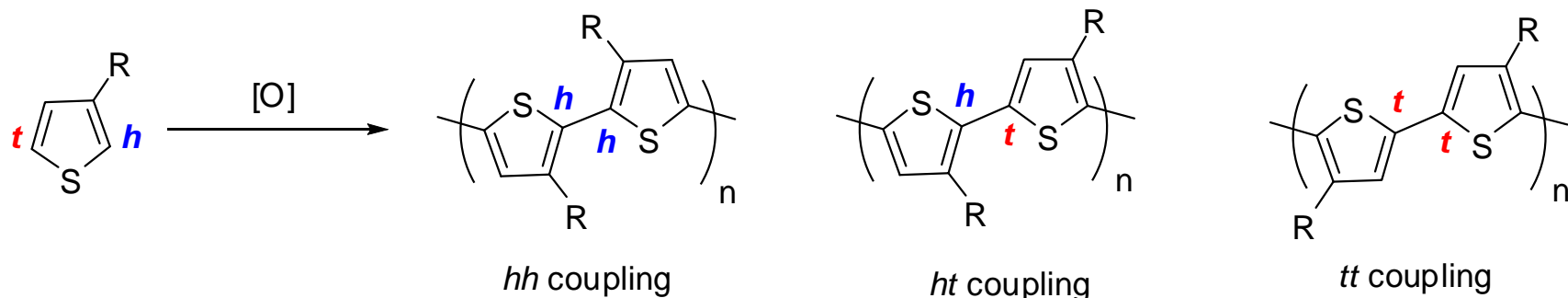
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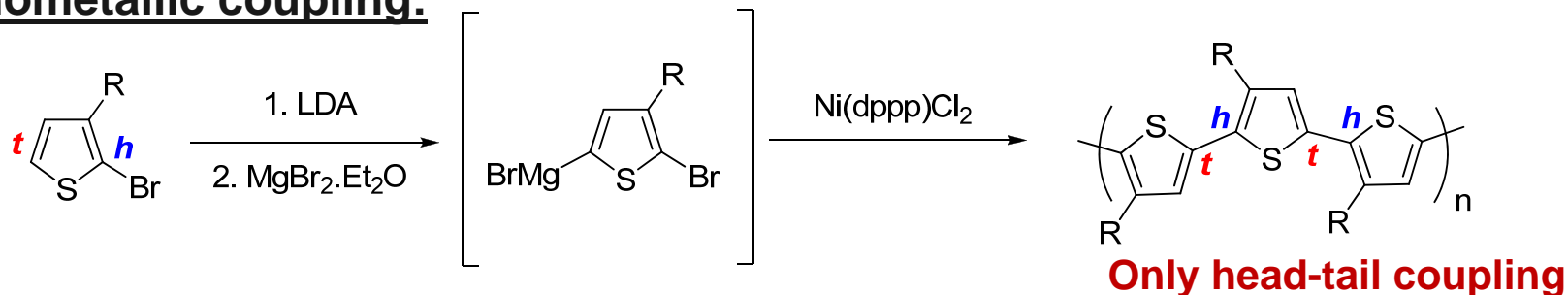
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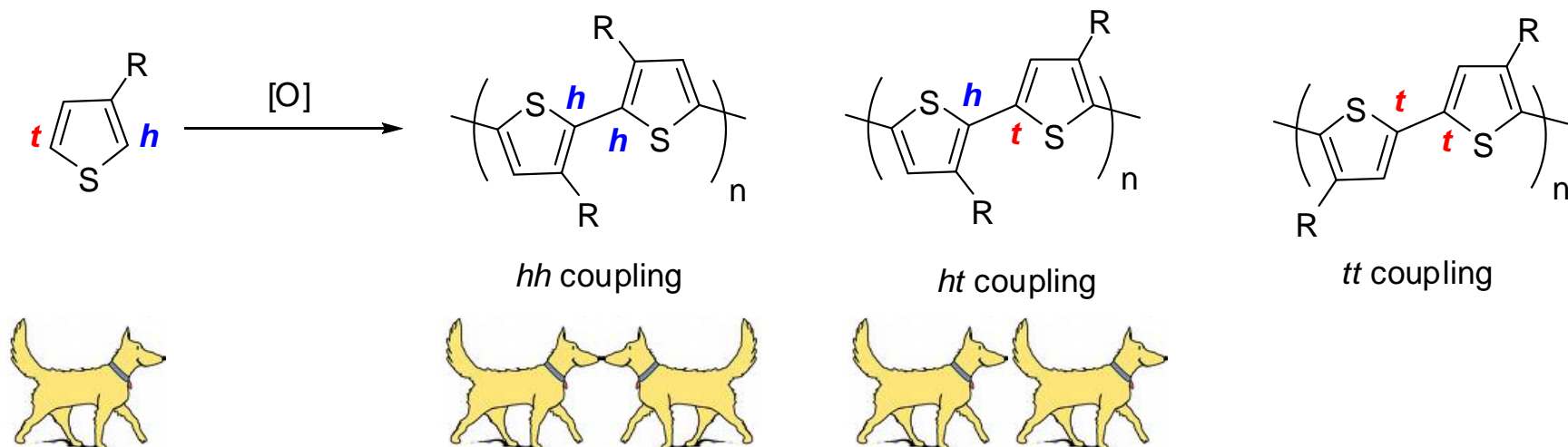
Organometallic coupling:



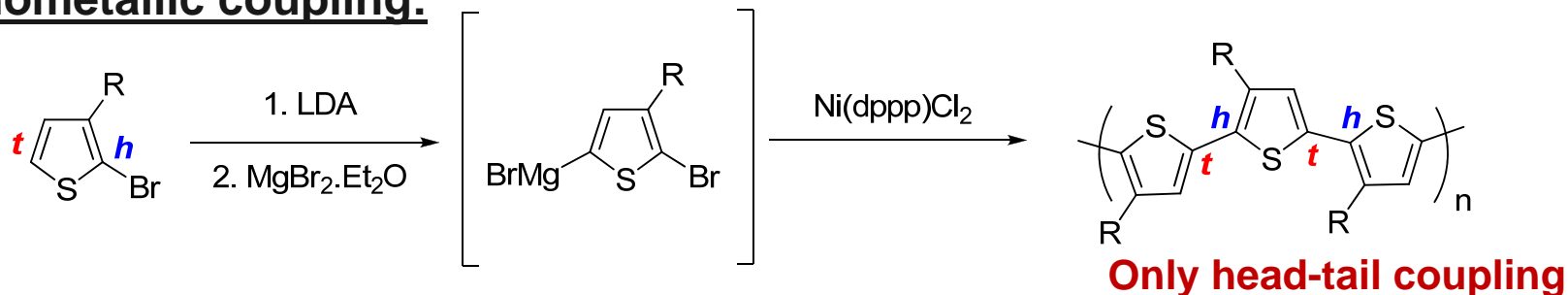
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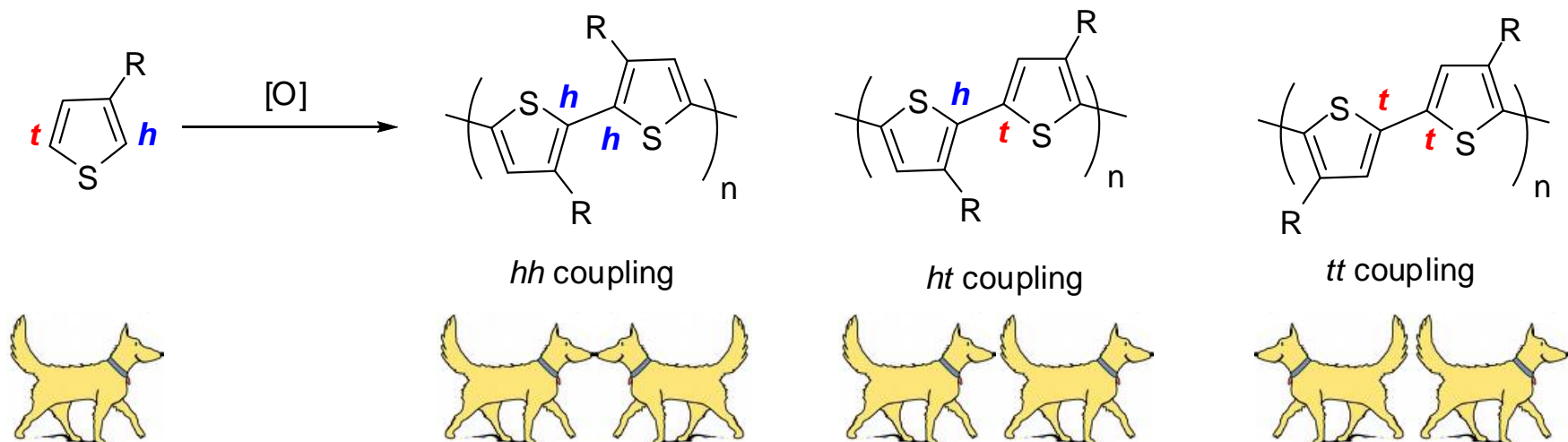
Organometallic coupling:



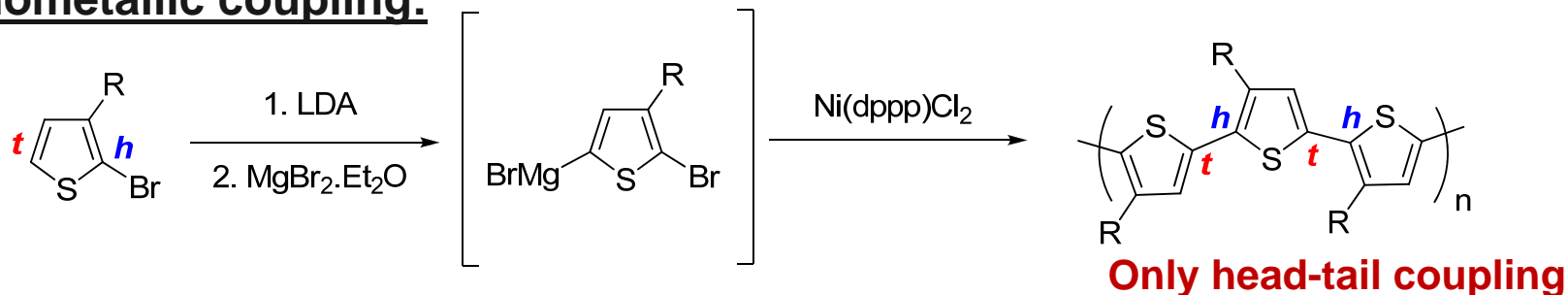
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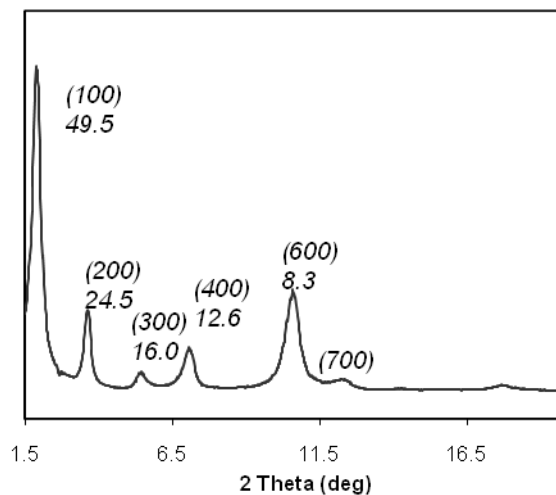
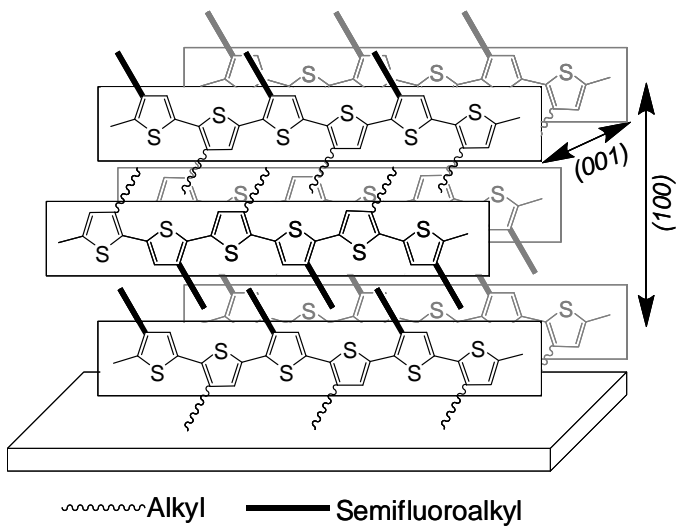
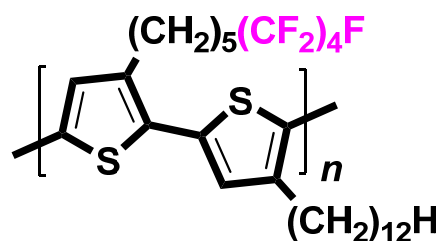


Organometallic coupling:



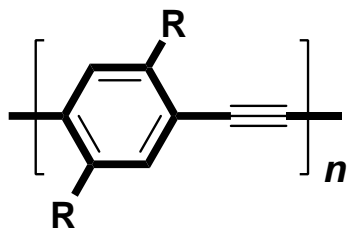
Regioregular PATs have higher crystallinity, red-shifted optical absorption, greater conductivity and smaller band gaps

Semifluoroalkyl PATs



Regioregular alkyl/semifluoroalkyl PATs self-assemble into highly ordered bilayer lamellar structures

Poly(1,4-phenylene ethynylene)s



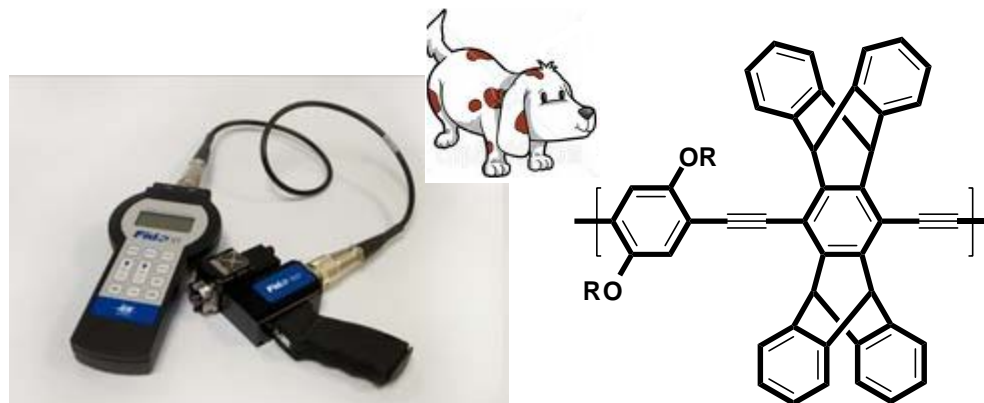
Features:

Linear structure

Strong fluorescence

Solid-state packing

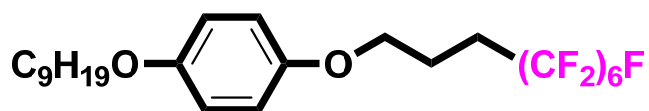
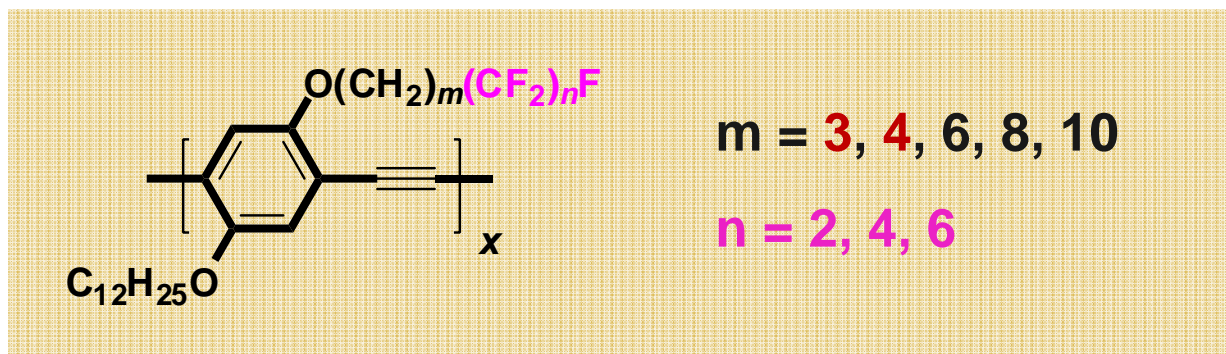
Explosives Detectors, Icx Nomadics, Inc.



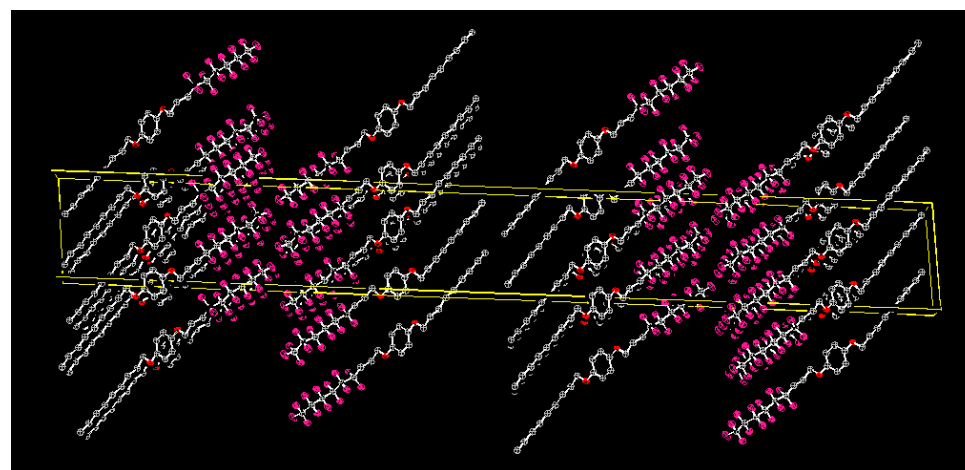
Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339.

Variation of the structure of the side chains provides opportunities to tailor the optical and electronic properties of this versatile class of polymers.

Polymer Design



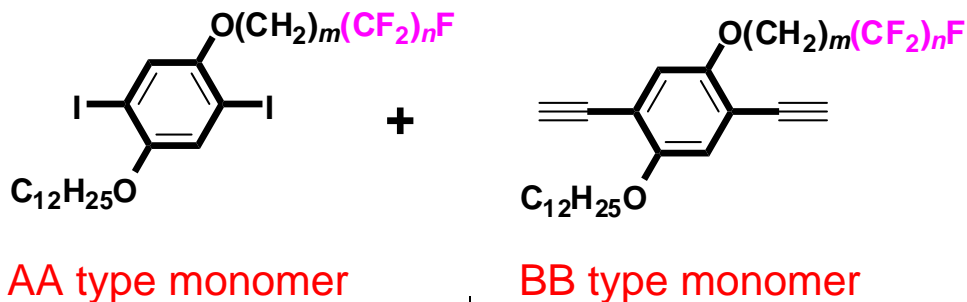
Fluorinated and non-fluorinated side chains segregate, leading to the formation of a bilayer lamellar structure.



54 Å

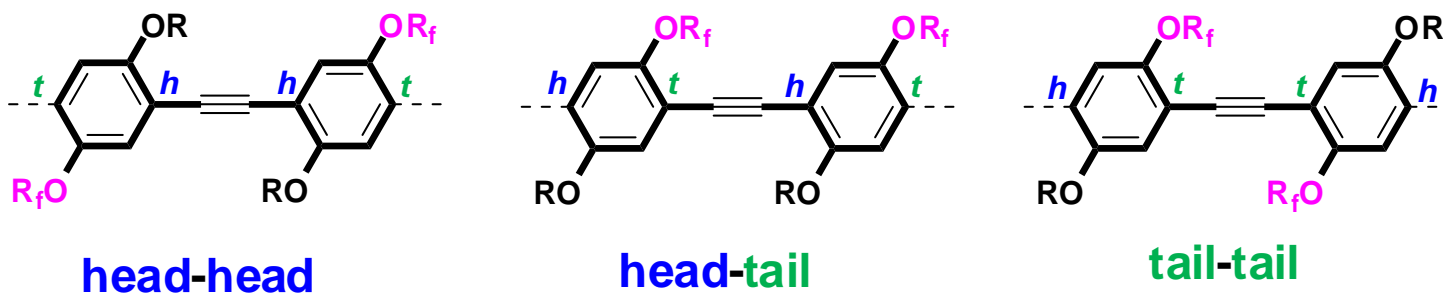
*Hydrogens omitted

Polymer Synthesis



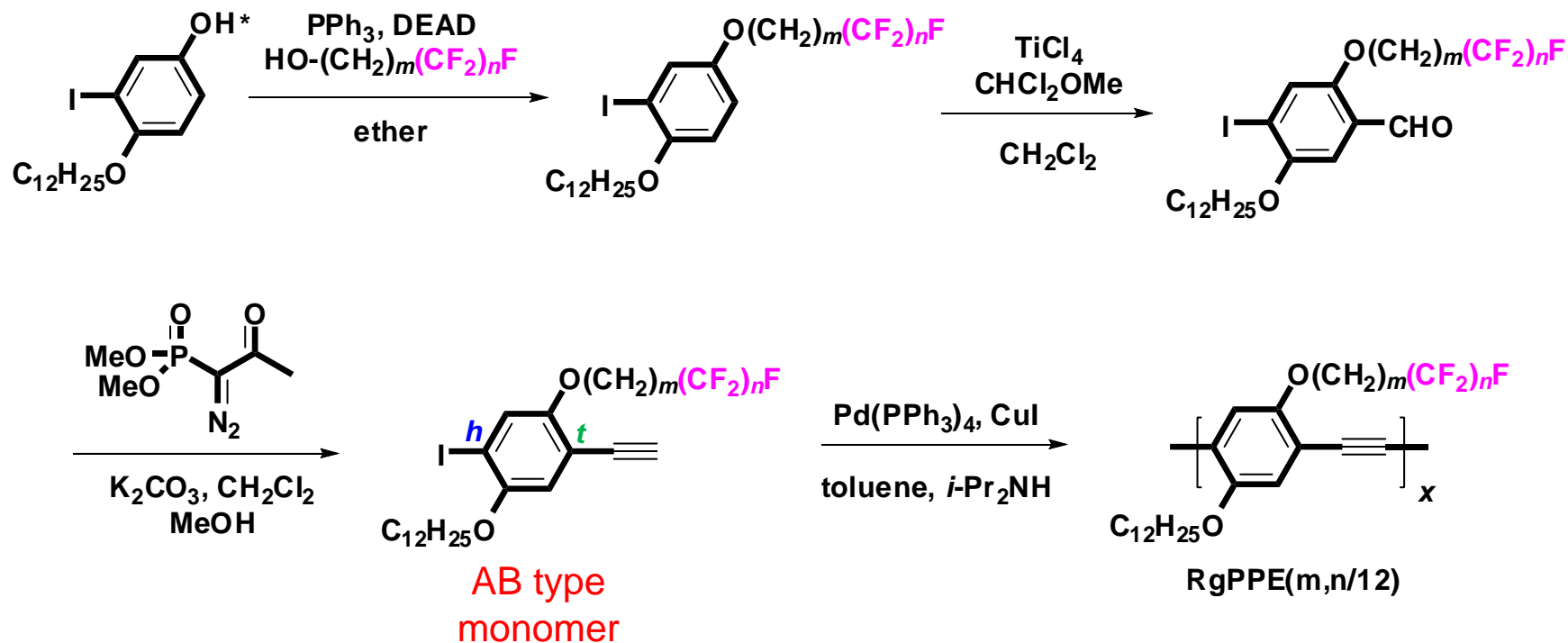
Coupling of AA and BB type monomers leads to regiorandom materials with three types of linkages.

$\text{Pd}(\text{PPh}_3)_4$, CuI
toluene, $i\text{-Pr}_2\text{NH}$



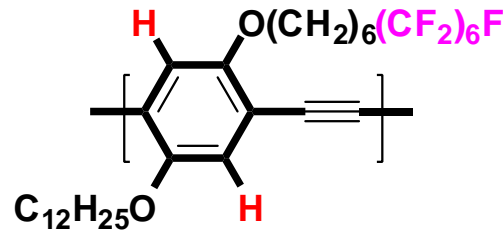
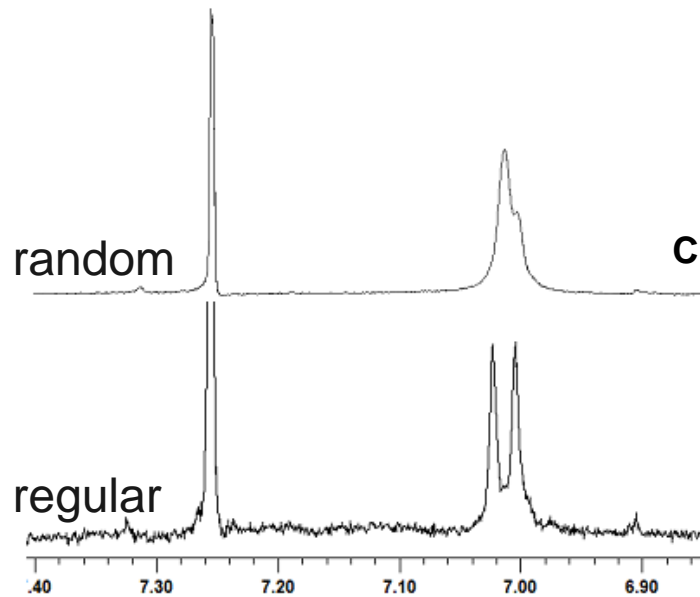
*Symmetrically substituted PPEs are inherently regioregular

Synthesis of Regioregular PPEs



Polymerization of an A-B type monomer gives exclusively head-tail linkage

Polymer Characterization



Melting Transitions

Regioregular 235 °C

Regiorandom 215 °C

Symmetrically substituted
PPE(12/12) 188 °C

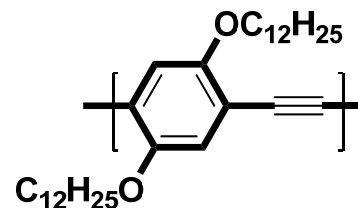
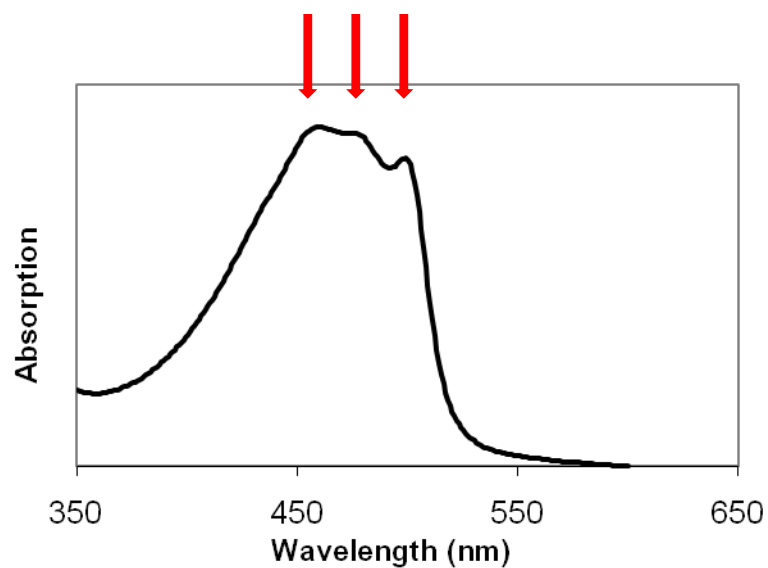
¹H NMR reveals structural differences in regioregular and regiorandom materials

Regiorandom- easily soluble in CHCl_3

Regioregular- low solubility in CHCl_3

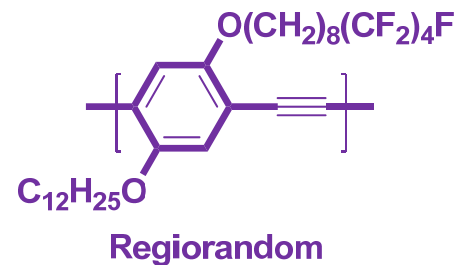
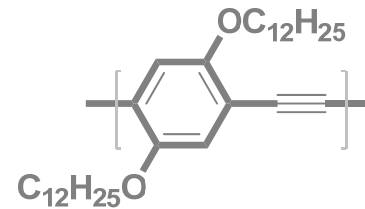
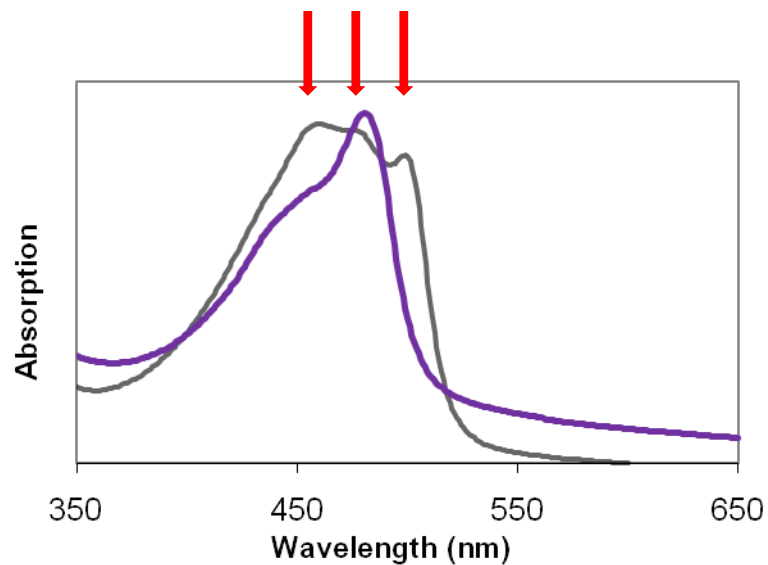
Thermal transition temperatures increase with longer fluorinated segments and also depend on regioregularity

Solid-State UV-vis Absorption



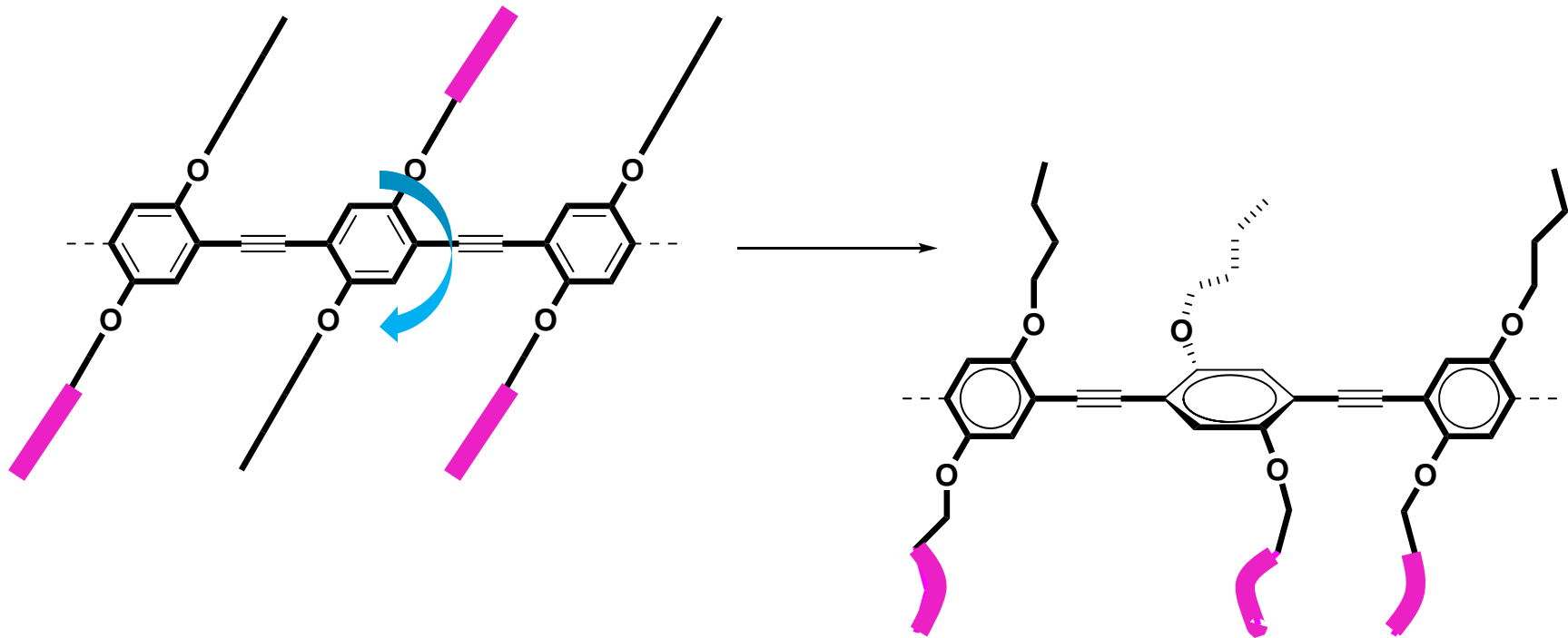
**Symmetrically substituted PPEs
have absorption contributions
at 460, 480 and 500 nm.**

Solid-State UV-vis Absorption



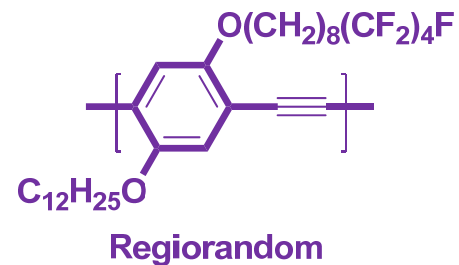
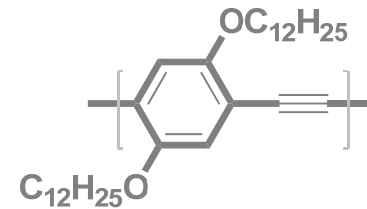
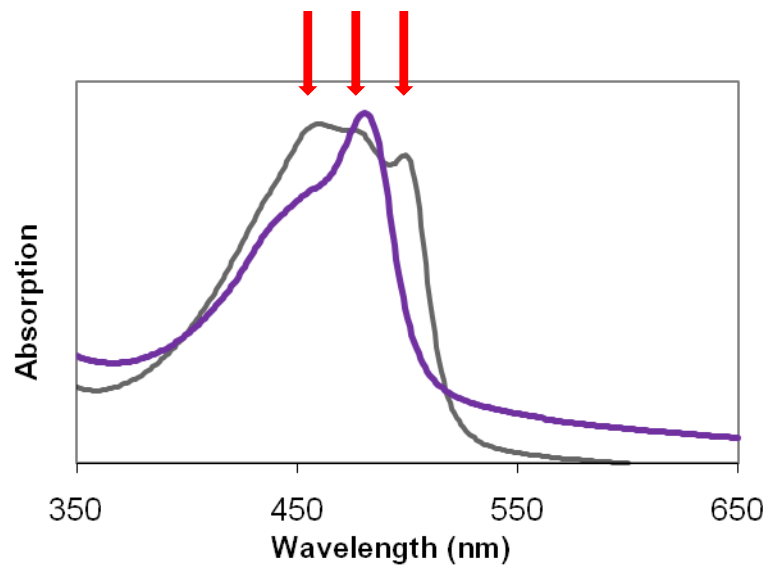
The contribution at 500 nm for regiorandom PPE(8,4/12) is absent.

Regularity of PPEs



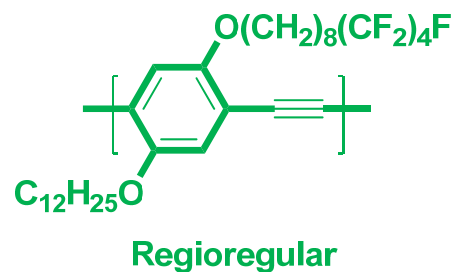
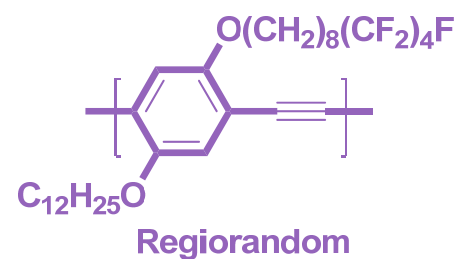
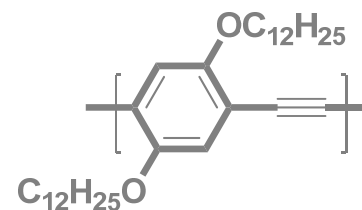
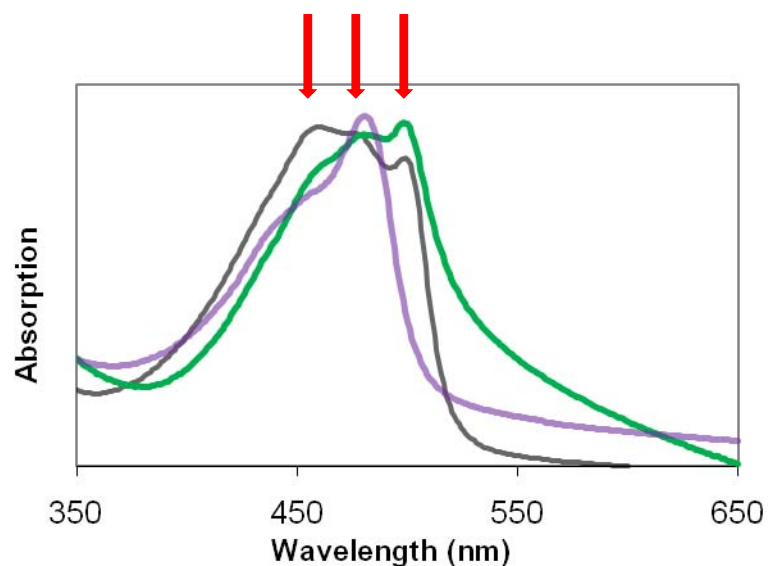
Side chain segregation in amphiphilic PPEs introduce disorder in regiorandom materials

Solid-State UV-vis Absorption



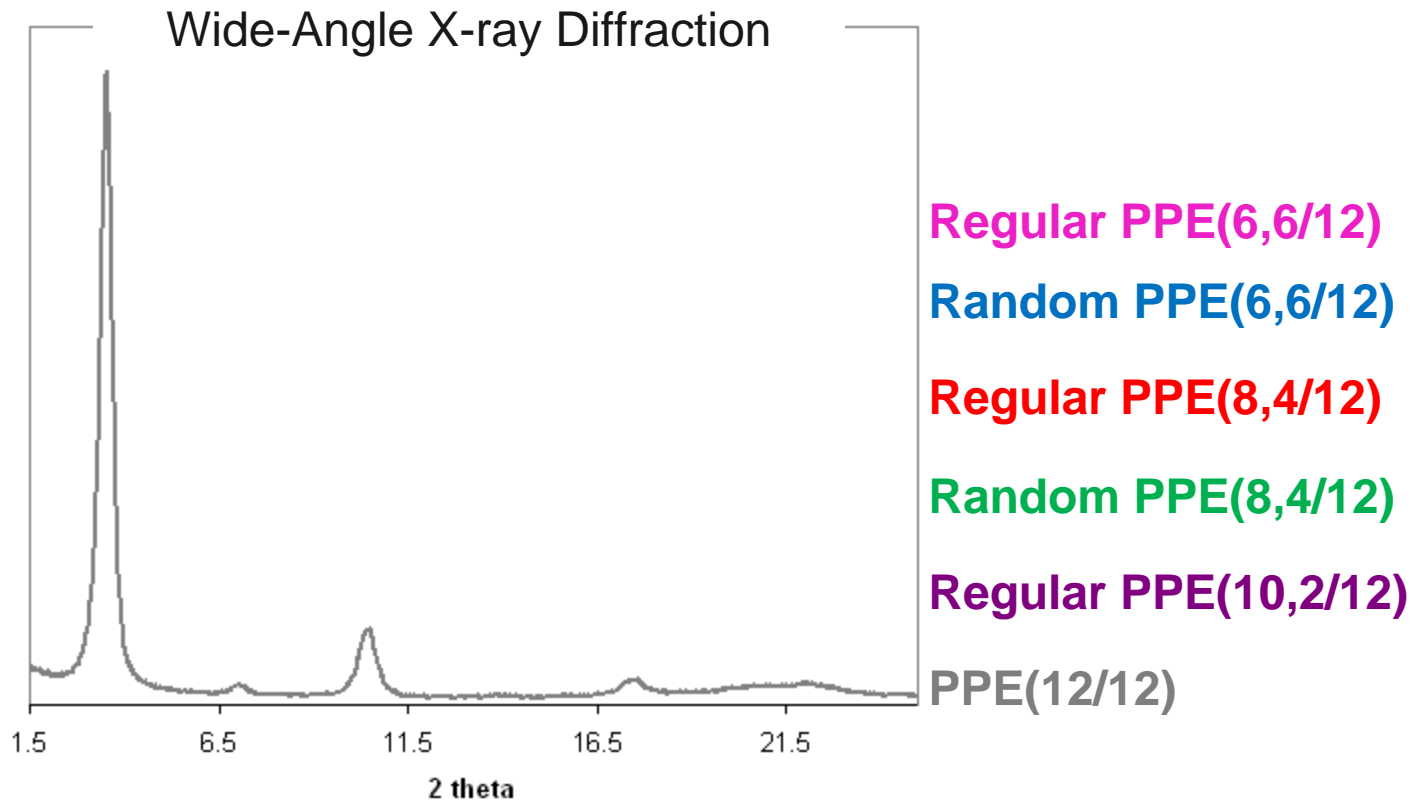
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Solid-State UV-vis Absorption

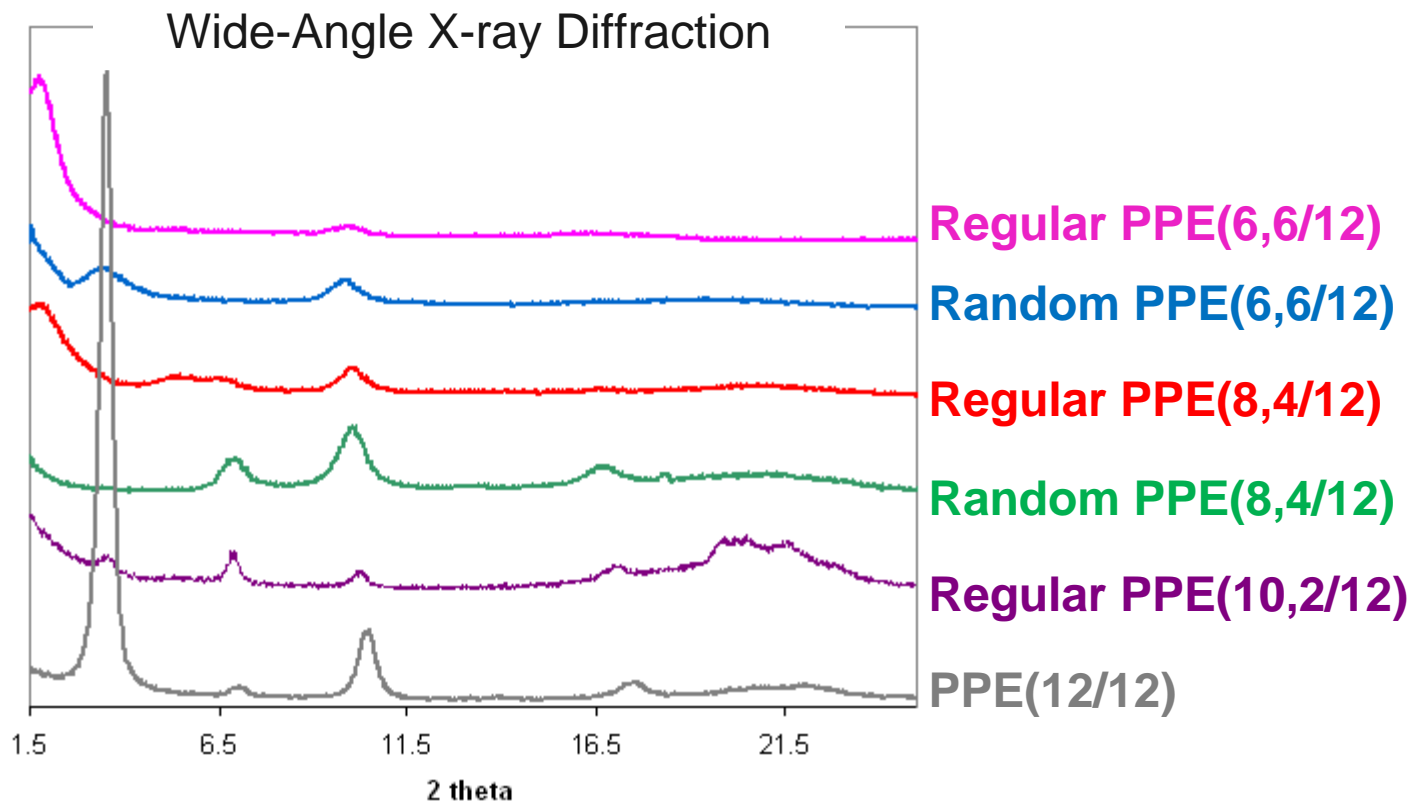


The contribution at 500 nm is strongest in regioregular PPE(8,4/12).

Molecular Assembly

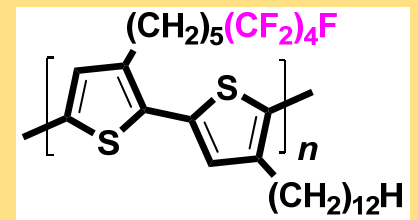
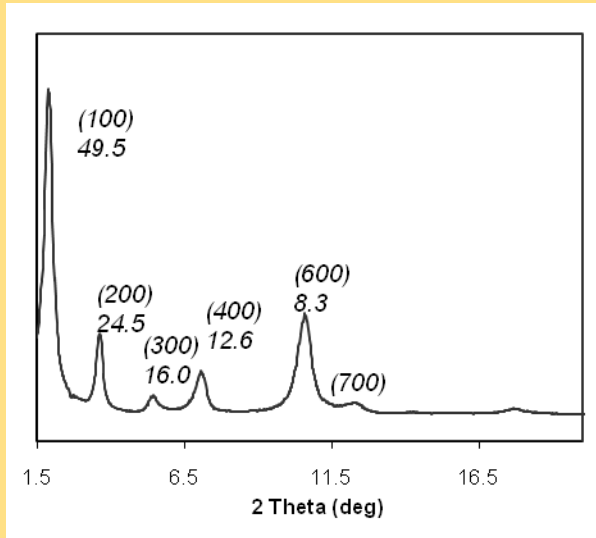
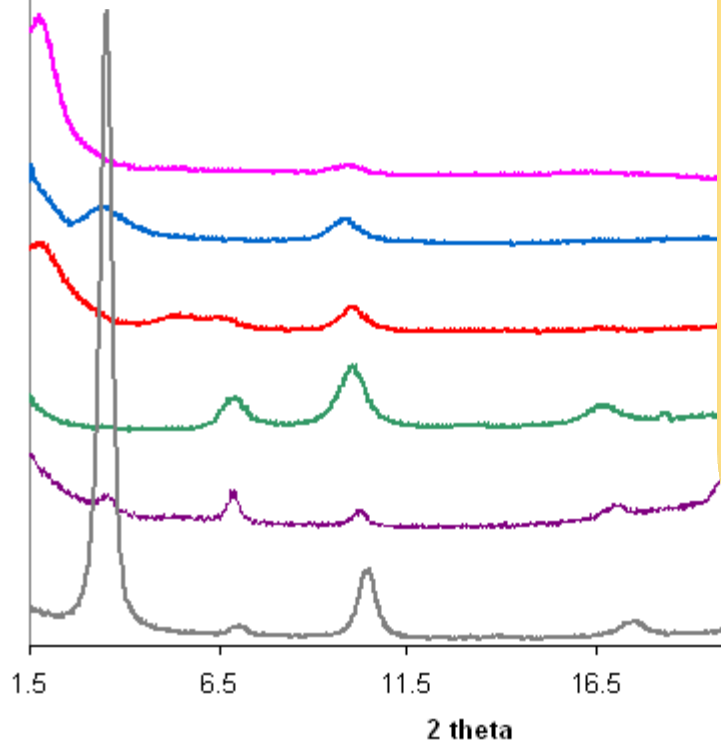


Molecular Assembly

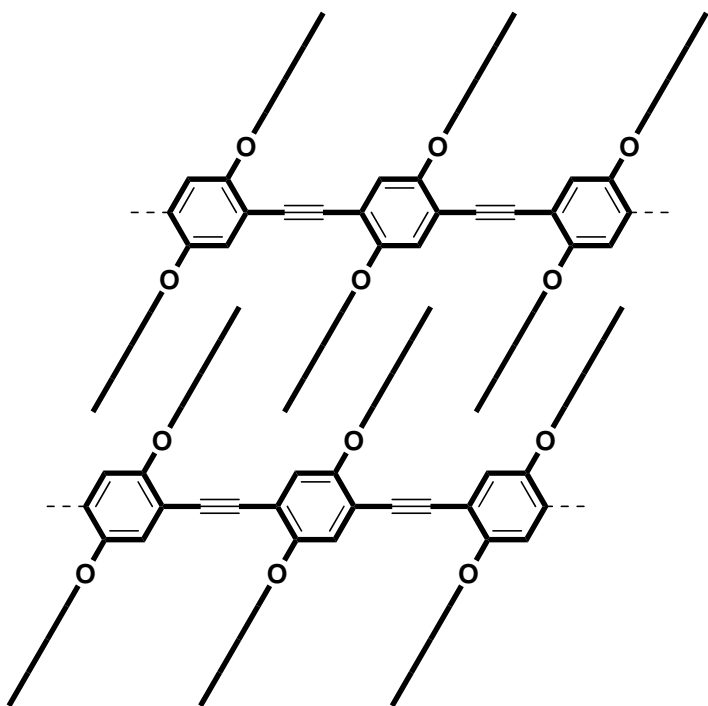


Molecular Assembly

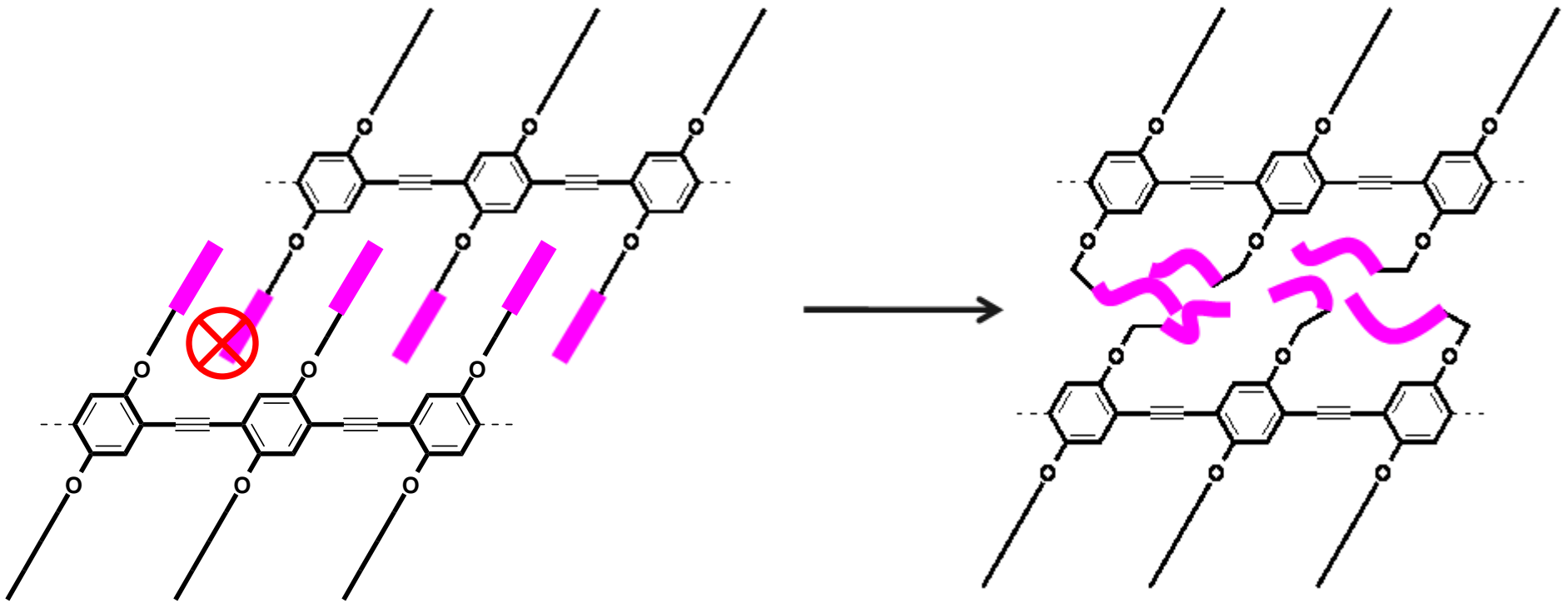
Wide-Angle X-ray Diffraction



Molecular Assembly



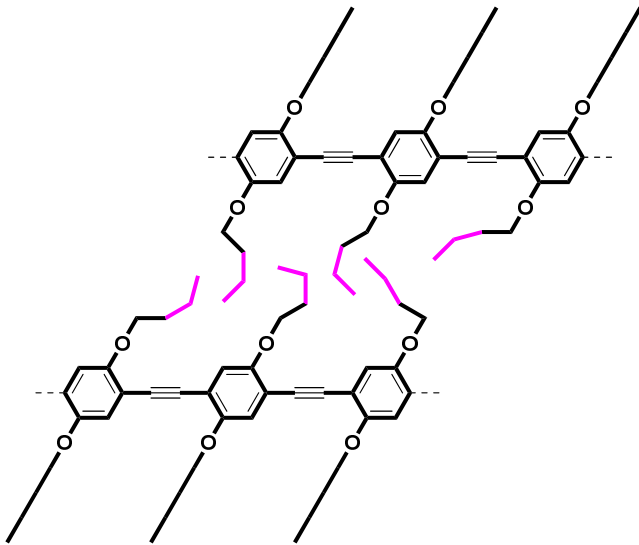
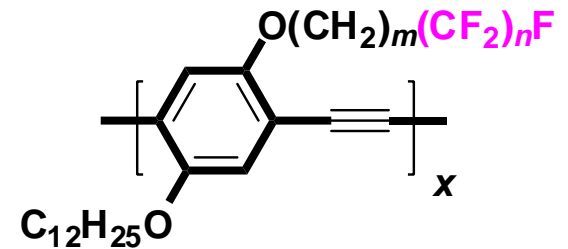
Molecular Assembly



Interdigitation of semifluoroalkyl side chains leads to disorder in packing

Conclusions

- Synthesis of a new class of amphiphilic alkyl/semifluoroalkyl PPEs
- Fluorinated segments enhanced thermal stability of the PPEs



- Absorption bands of amphiphilic, regioregular PPEs have higher contribution at lower energies
- Interdigitation of side chains leads to disorder in packing

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Team Collard

Dr. Art Ragauskus



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