Synthesis of Molecular Oligomeric Compounds for Organic Electronics

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Winter Course

Organic Electronics and Optoelectronics

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Chemistry and Chemical Biology

Design Criteria for Small Molecules

Type of conjugated system / charge carriers

HOMO/LUMO Levels & Bandgap

Steric Bulk

Electron donating / withdrawing substituents

Solid State Packing / Self Assembly

Solubility

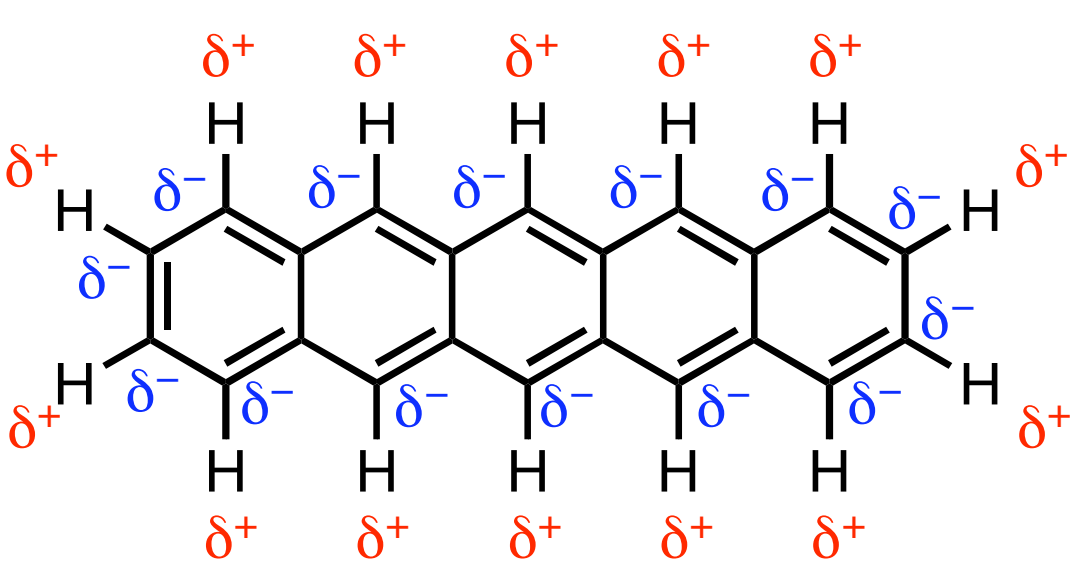
Volatility (UHV)

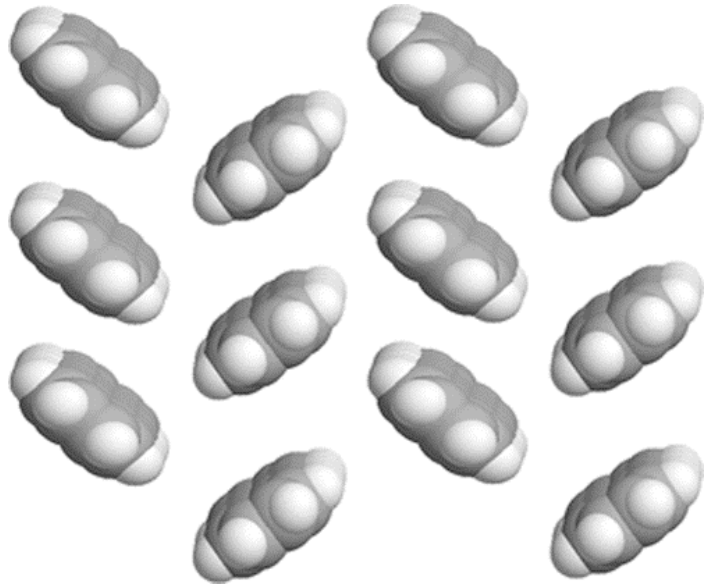
Ease of Synthesis

Outline

1. Design Criteria for Conjugated Molecules
2. Synthetic Strategies For p-Type Compounds
3. Synthetic Strategies For n-Type Compounds
4. Phosphorescent OLED Dopants

Pentacene





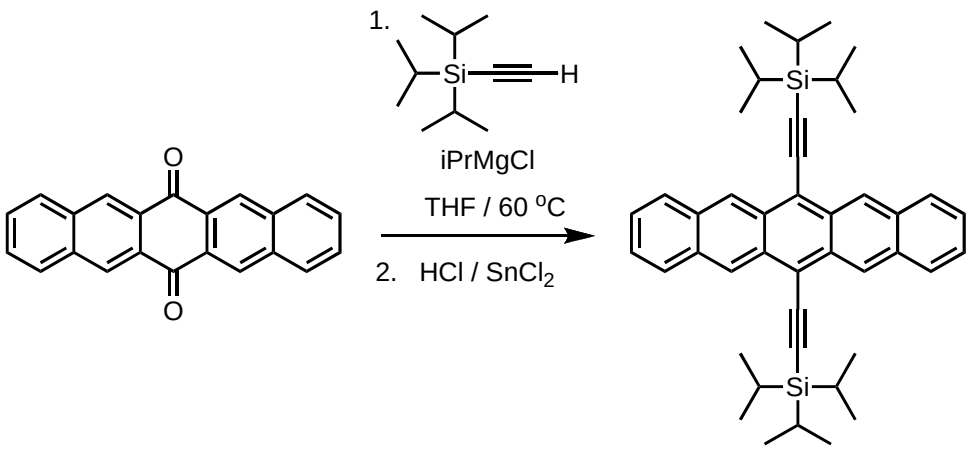
Excellent TFT performance

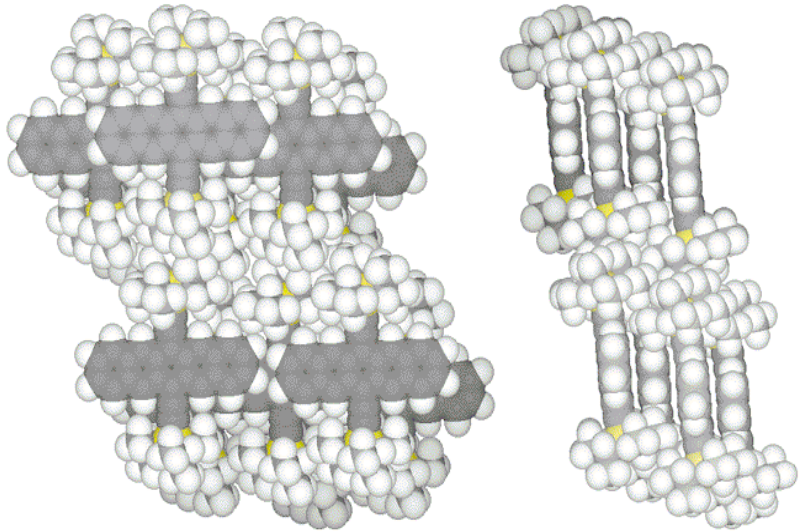
Best TFTs give $\mu > 5\ cm^2/(V\ s)$, $I_{ON}/I_{OFF} = 10^6$

Insoluble: Devices fabricated by vacuum sublimation

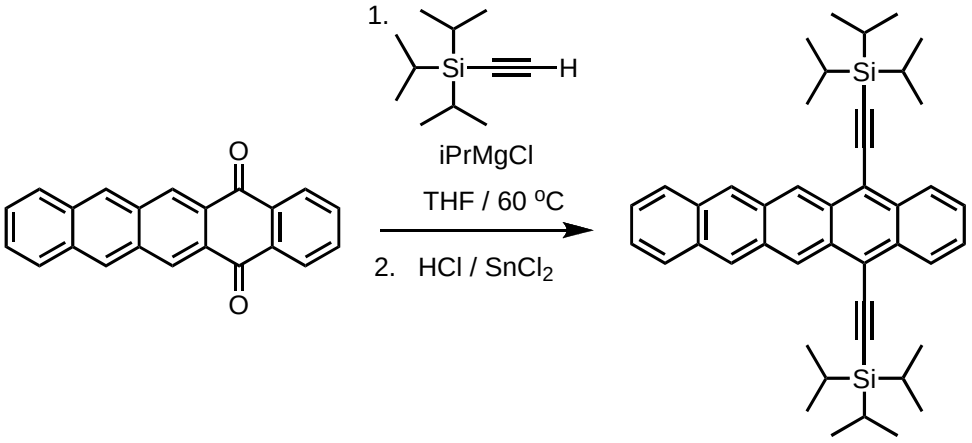
Pentacene is oxygen and light sensitive

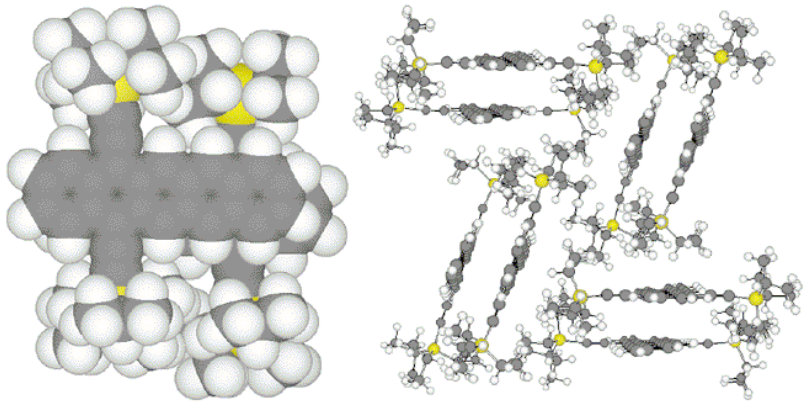
Silyl-Modified Pentacenes





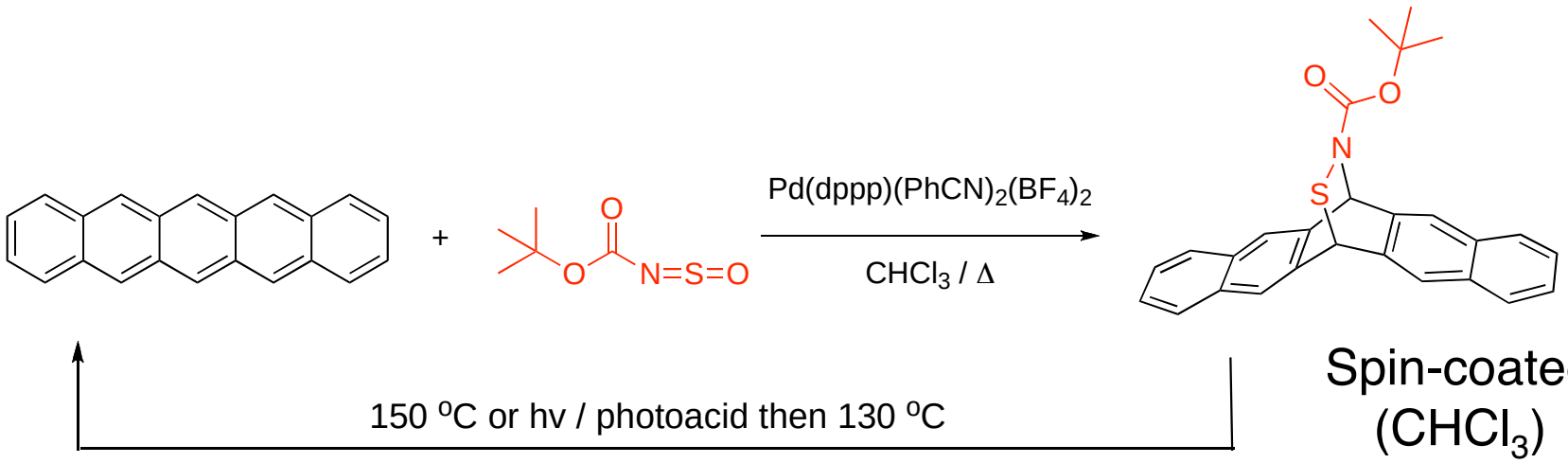
Solution processed TFTs: $\mu > 5\ cm^2/(V\ s)$

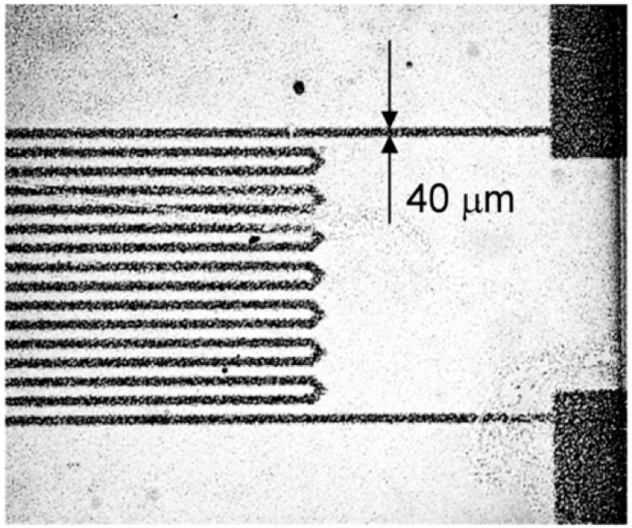




J. E. Anthony; J. S. Brooks; D. L. Eaton; S. R. Parkin; *J. Am. Chem. Soc.* **2001,** *123*, 9482-9483.
S. J. Park; C. C. Kuo; J. E. Anthony; T. N. Jackson; *Tech. Dig. – Int. Electron Devices Meet.* **2006**, 113.

Soluble Precursor Approach

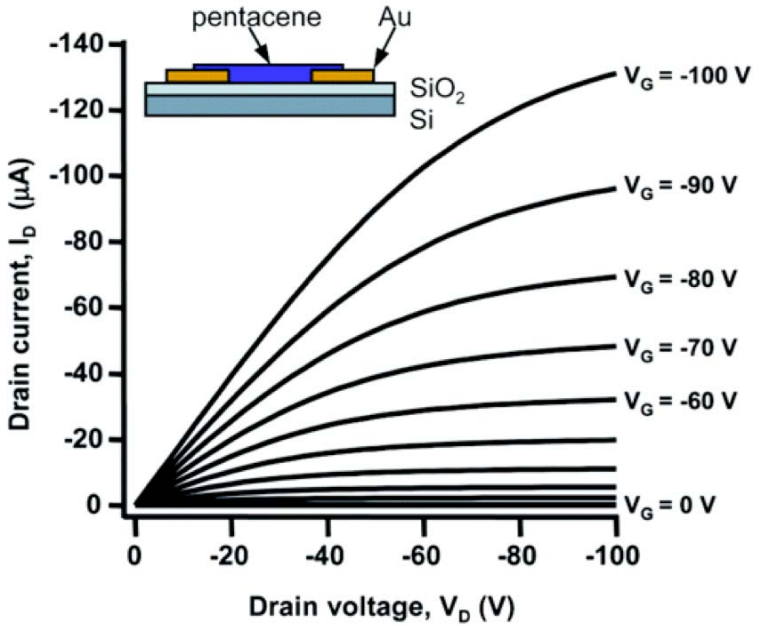




OTFTs

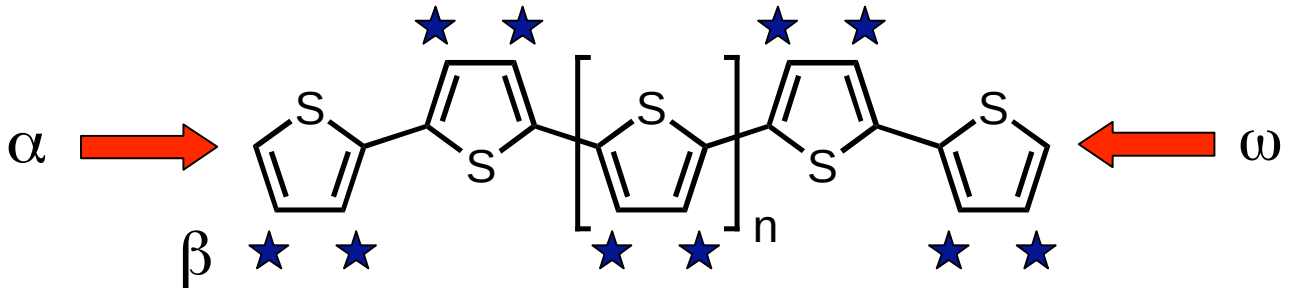
$\mu = 0.1\ cm^2 / V \cdot s$

$I_{ON} / I_{OFF} = 2 \cdot 10^5$



Weidkamp, K. P.; Afzali, A.; Tromp, R. M.; and Hamers, R. J. *J. Am. Chem. Soc.*, **2004**, *126*, 12740.
Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.*, **2002**, *124*, 8812.

Simple Oligothiophene Substitution

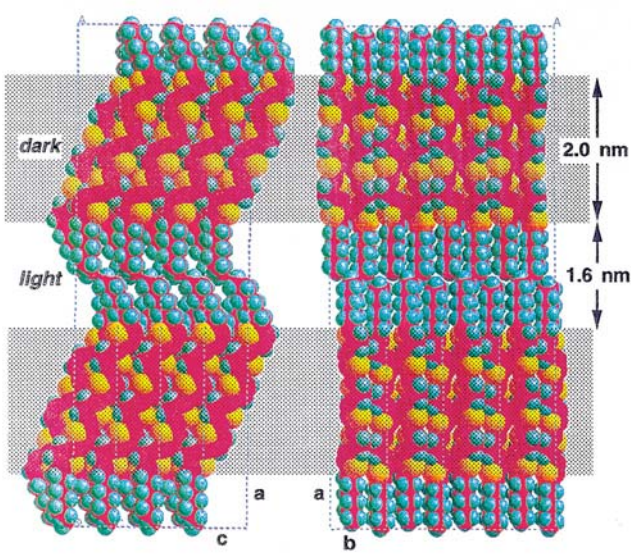


α,ω-disubstituted oligothiophenes

Dihexylsexithiophene

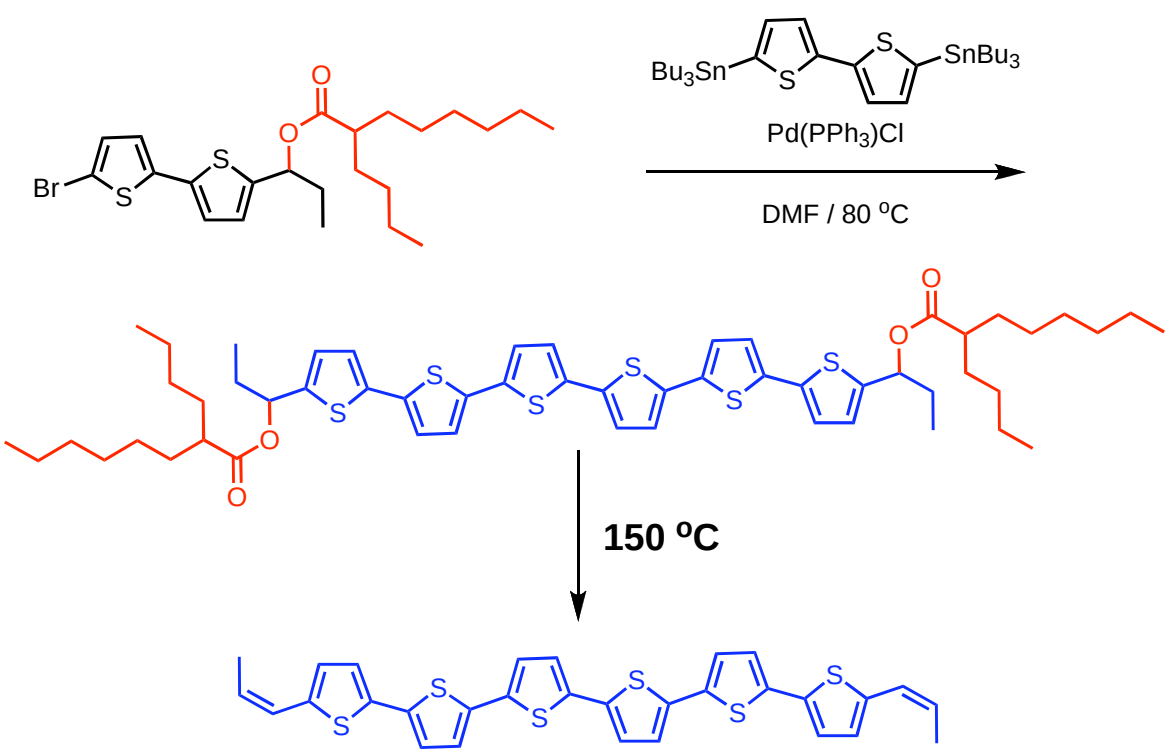
Packing aided by liquid crystalline-like behavior of alkyl chains

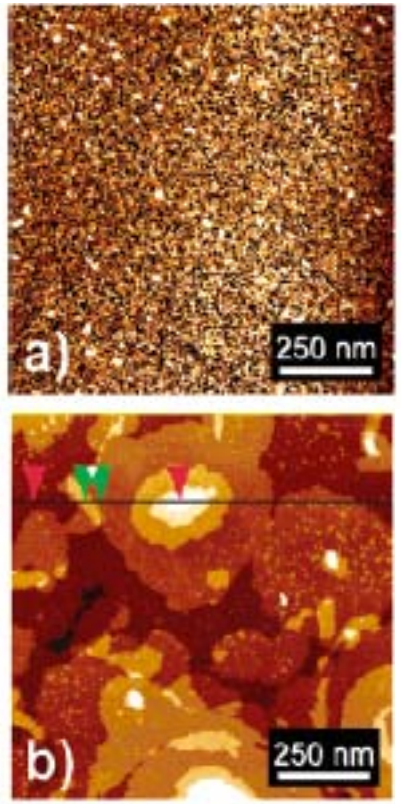
Sparingly soluble in hot organic solvents



A. J. Lovinger; H. E. Katz; A. Dodabalapur *Chem. Mater.*, **1998**, *10*, 3275.

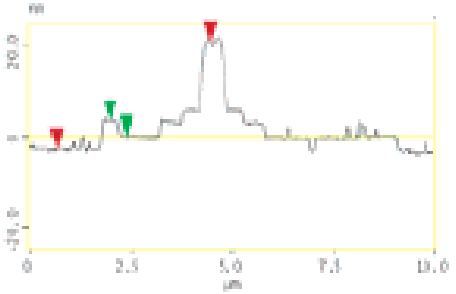
Thermolysis of a Soluble α-T6 Precursor





Precursor is highly soluble in organic solvents

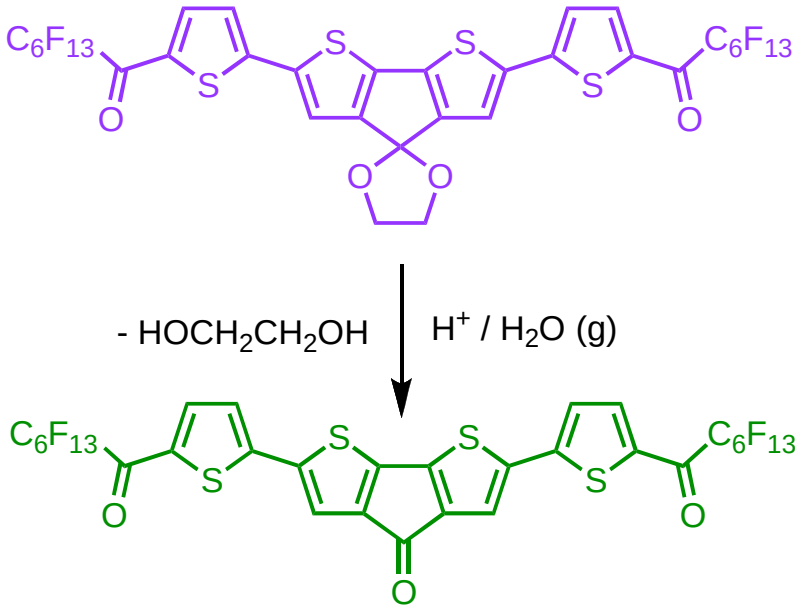
Heating burns off the solubilizing groups, anneals thiophenes into terraced structures

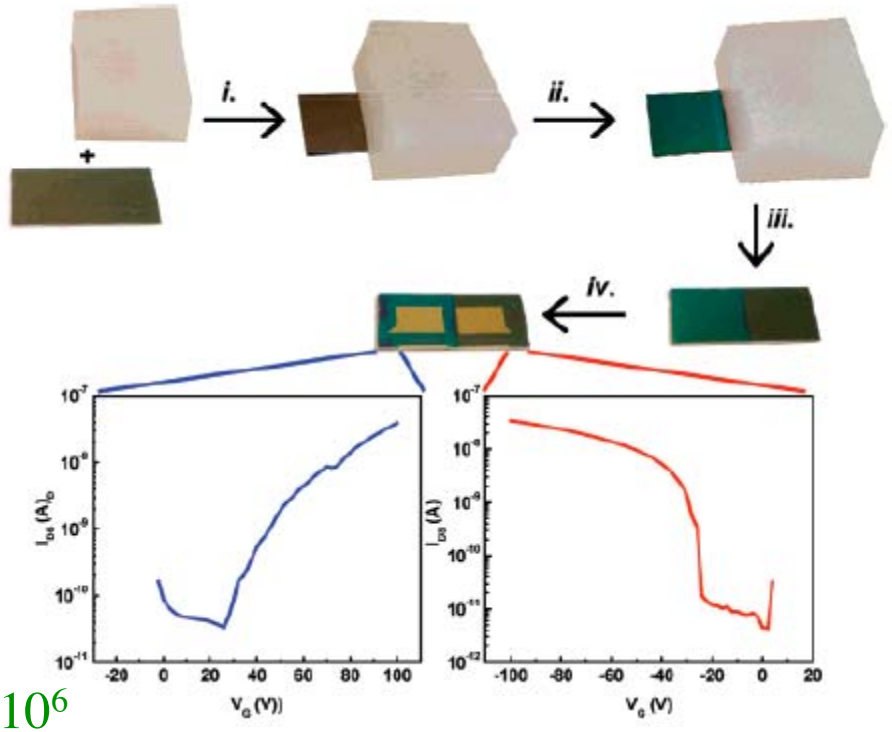


OTFTs: $\mu = 0.05\ cm^2 / V \cdot s$; $I_{ON} / I_{OFF} = 10^5$ after thermal treatment

A. R. Murphy; J. M. J. Fréchet; P. Chang; J. Lee; V. Subramanian *J. Am. Chem. Soc.*, **2004**, *126*, 1596.

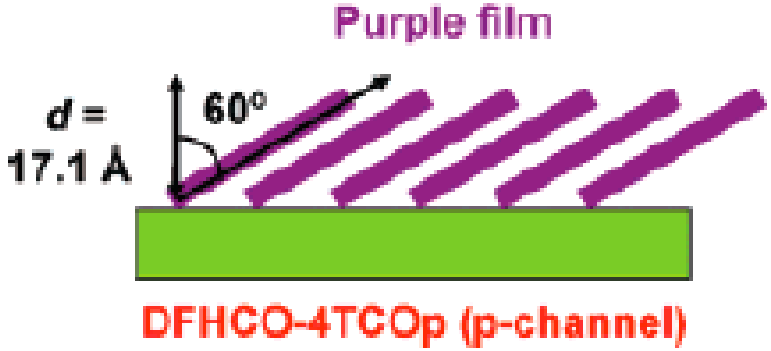
Single Precursor p- and n-type Materials

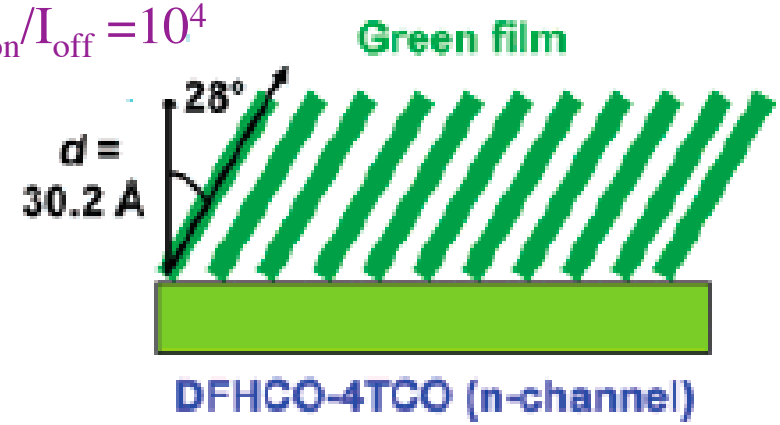




N-type OTFT $\mu = 0.08$ cm^2/Vs and $I_{on}/I_{off} = 10^6$

P-type OTFT $\mu = 2 \times 10^{-4}$ cm^2/Vs and $I_{on}/I_{off} = 10^4$





M.-H. Yoon; S. A. DiBenedetto; M. T. Russell; A. Facchetti; T. J. Marks *Chem. Mater.*, **2007**, *19*, 4864–4881.

Outline

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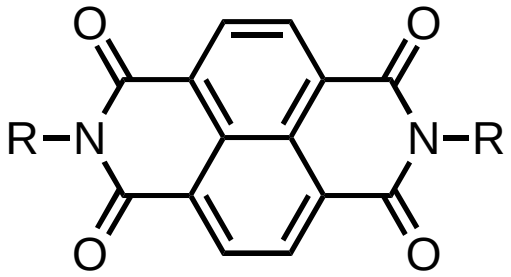
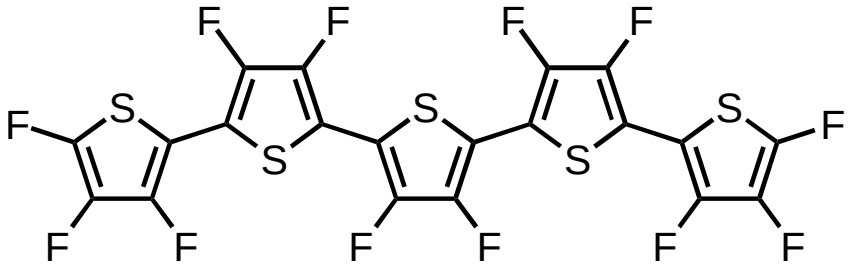
3. Synthetic Strategies For n-Type Compounds
4. Phosphorescent OLED Dopants

N-type Materials - Strategies

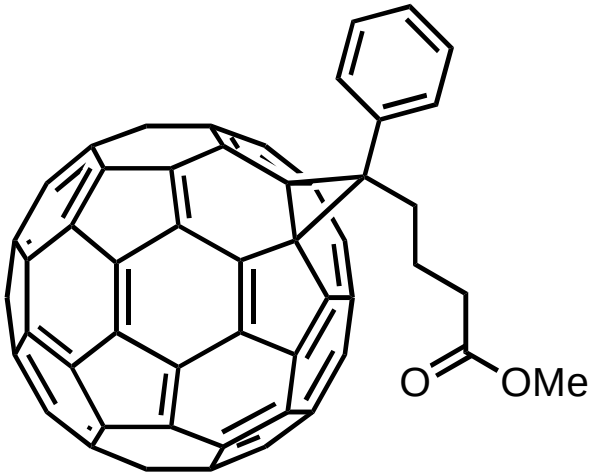
"Natural" n-type materials



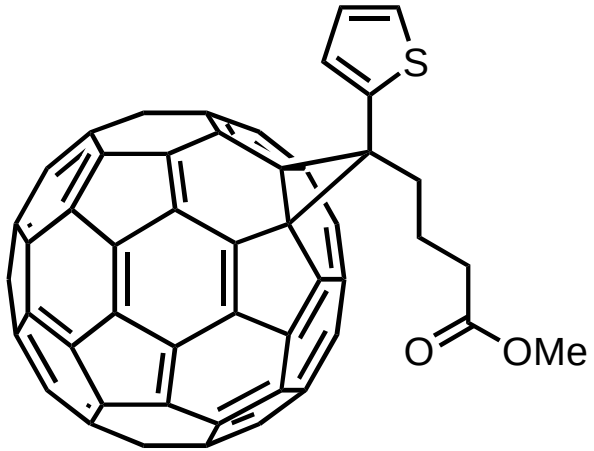
Adding electron-withdrawing substituents



Fullerene Derivatives



Phenyl C60 Butyric Acid Methyl Ester (PCBM)



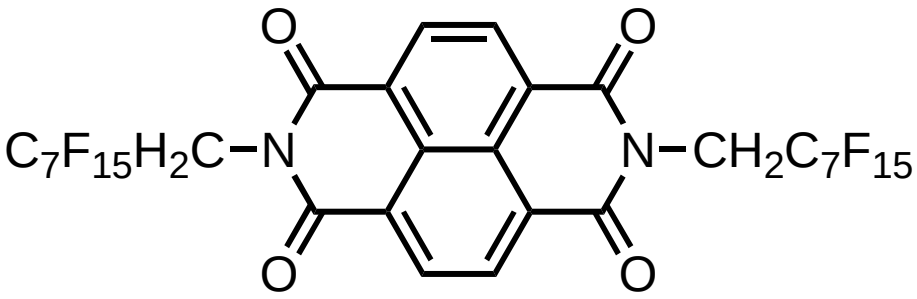
Thienyl CBM (ThCBM)

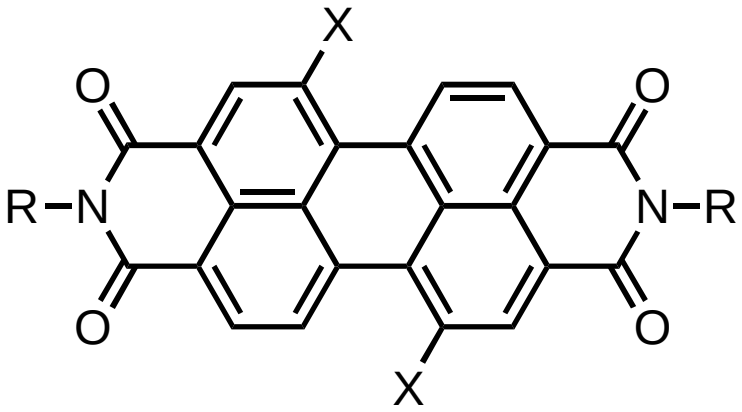
ThCBM has similar electronic properties to PCBM.

Synthetic chemists continue to work on fullerene chemistry

THCBM: Lacramioara M. Popescu, Patrick van 't Hof, Alexander B. Sieval, Harry T. Jonkman, and Jan C. Hummelen Appl. Phys. Lett. 89 213507 (2006)

Aromatic Bis(imide) Acceptors





One of the early organic n-FET successes.

Also used in a inverter circuit with a thiophene p-FET.

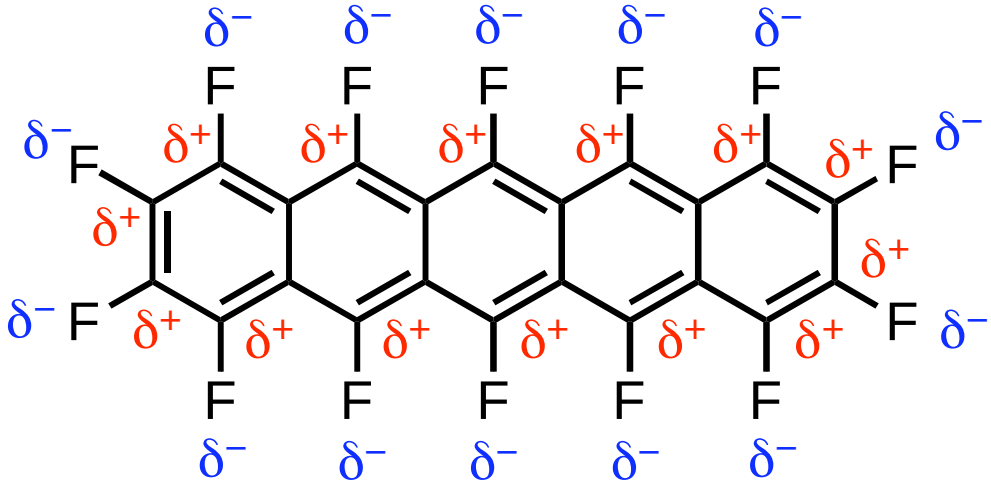
X often CN

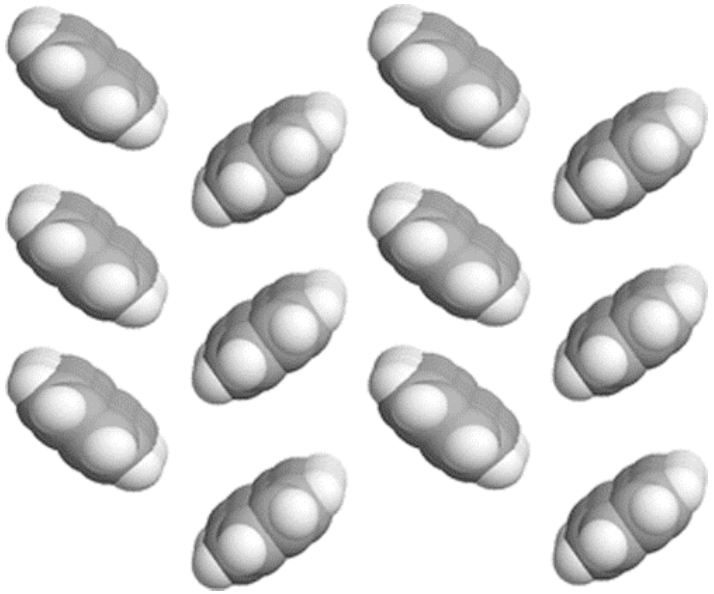
Regioselectivity issue. Be aware!

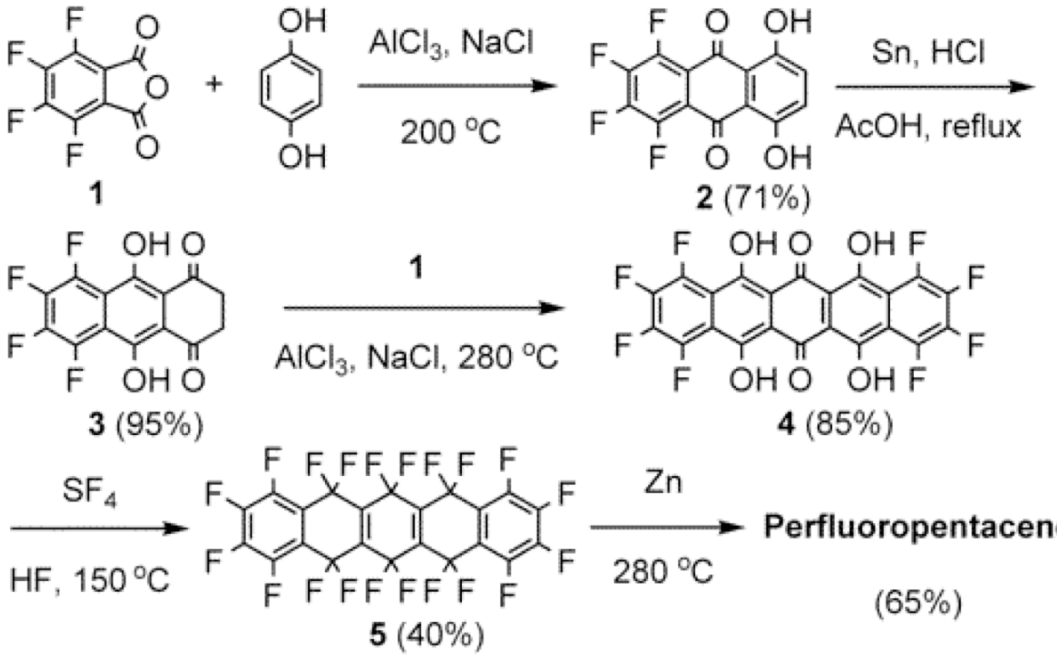
Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Slegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478

F. Würthner; V. Stepanenko; Z. Chen; C. R. Saha-Möller; N. Kocher; D. Stalke *J. Org. Chem.* **2004**, *69*, 7933.

Fluoropentacene







$\mu = 0.22\ cm^2/Vs$
and $I_{on}/I_{off} = 10^5$

Y. Sakamoto; T. Suzukil; M. Kobayashi; Y. Gao; Y. Fukai; Y. Inoue; F. Sato; S. Tokito *J. Am. Chem. Soc.*, **2004**, *126*, 8138–8140.

Outline

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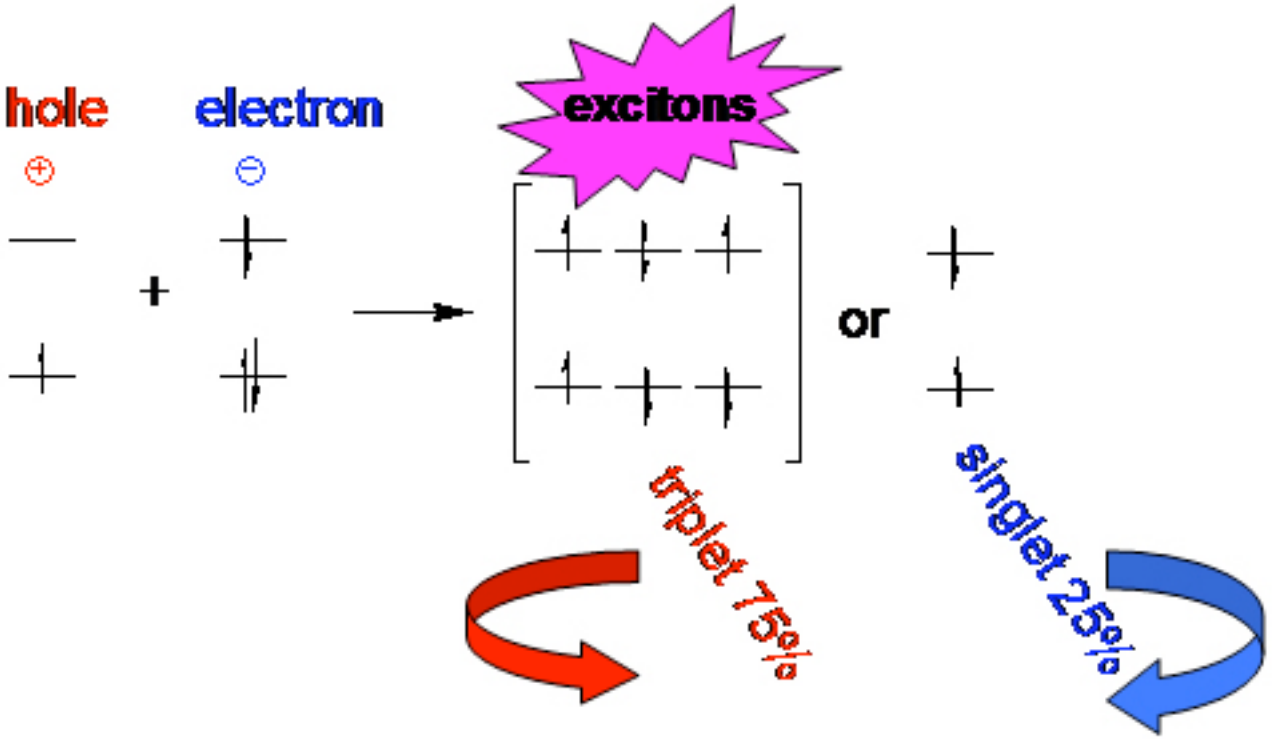
OLEDs & Phosphorescent Emitters



Harvested only by phosphorescent dyes	Harvested by both fluorescent & phosphorescent dyes

Max theoretical quantum efficiency	Fluorescent	Phosphorescent
Internal	25%	100%

Covering the Display Spectrum

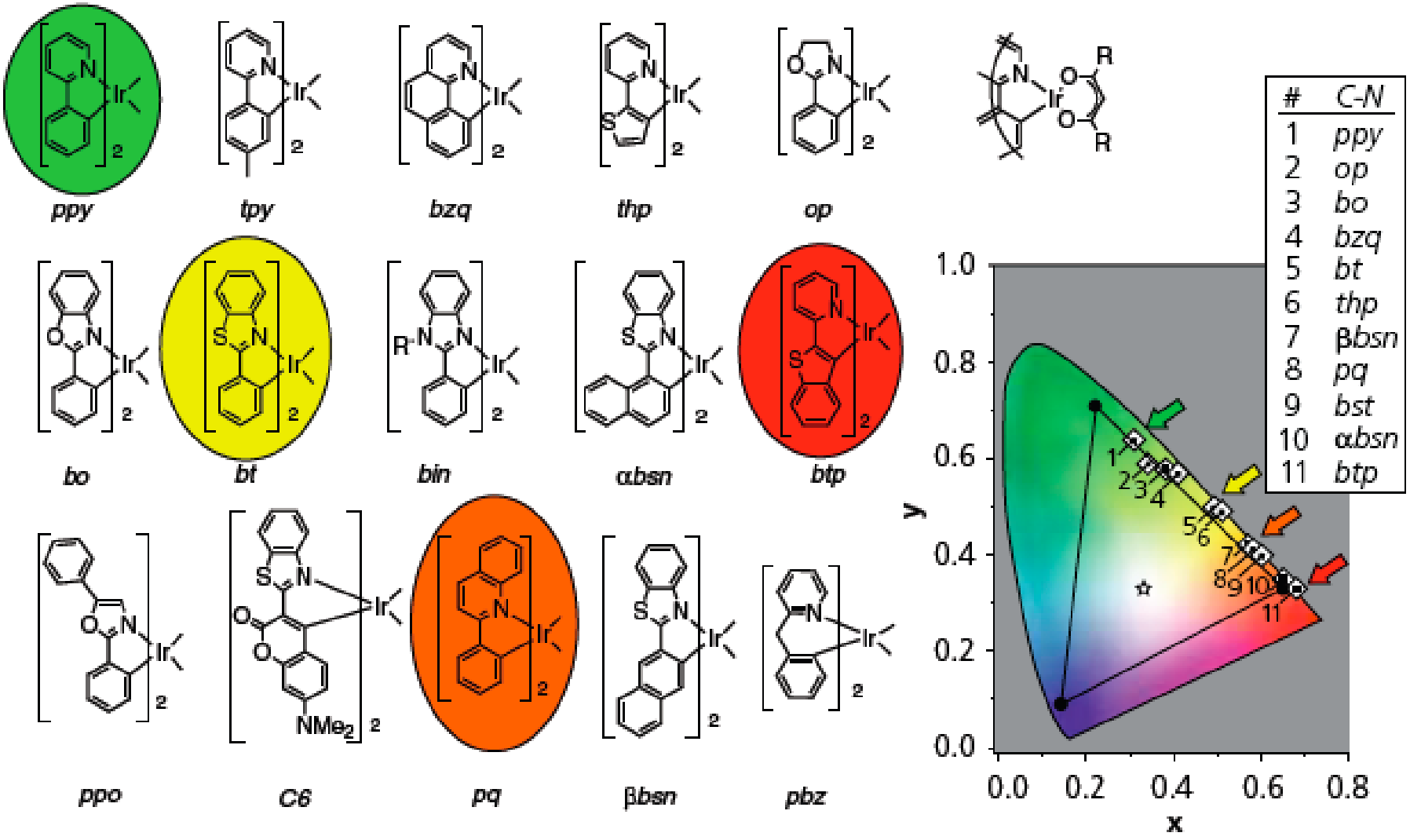
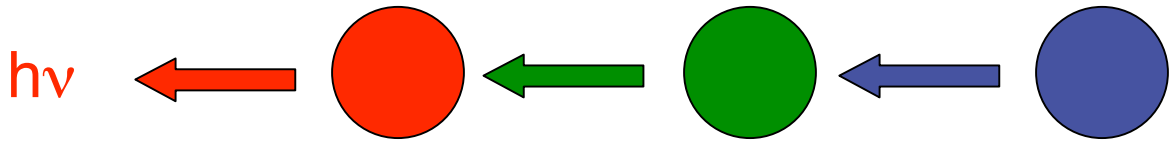


Image courtesy Prof. Mark Thompson, USC

The Color Mixing Problem

In order to use OLEDs for illumination, need white light

No problem! Mix several emitters into one device!

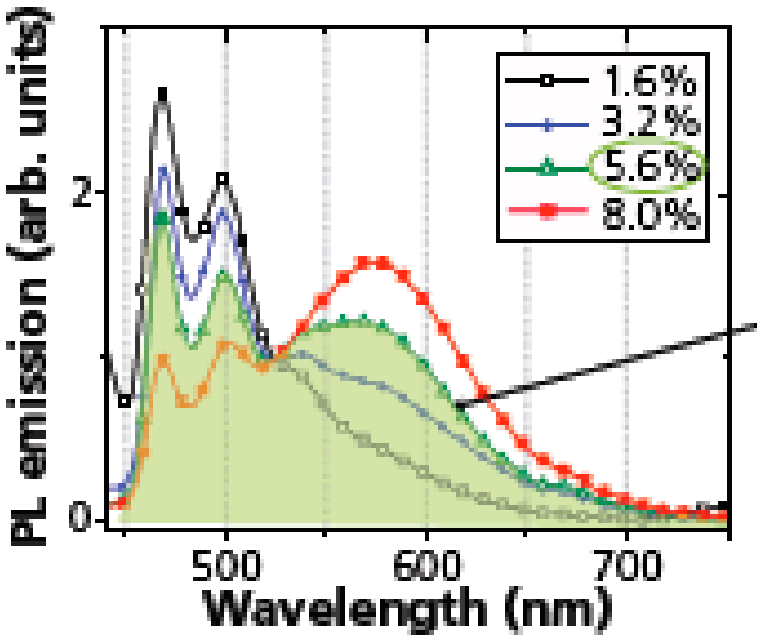


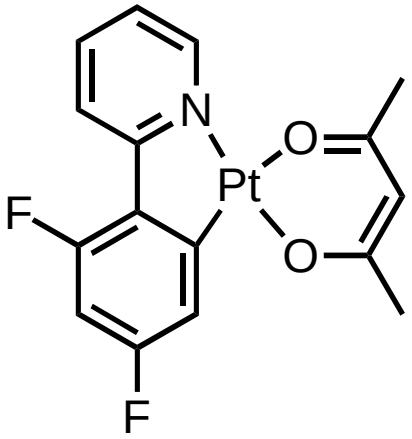
Challenges:

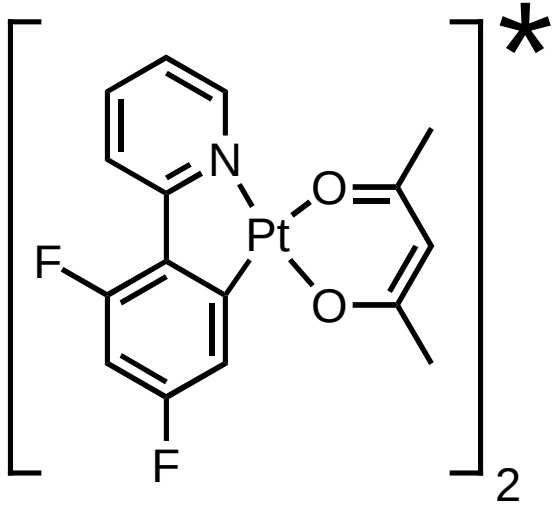
Different degradation rates

Energy transfer

White Light from a Single Dopant







excimer

Control relative emission by doping concentration, steric bulk on ligands

Cocchi, M.; Kalinowski, J.; Virgili, D.; Fattori, V.; Develay, S.; Williams, J. A. G. *Appl. Phys. Lett.* **2007**, *90*, 163508/1.

Conclusions

Synthetic chemistry imparts versatility on the field of organic electronics

Versatility means more than just rearranging substituents - look for opportunities to use fundamental molecular phenomena

Significant development of n-type materials and gaining more precise control over self-assembly at molecular length scales are important chllenges today.