Aromatic Diimides – Potential Dyes for Use in Smart Films and Fibers

New aromatic diimide fluorescent dyes have been prepared with potential for use as chemical sensors and in chromogenic polymers. These dyes have been designed to utilize excited state electron transfer reactions as the means for sensing chemical species. For example, an aniline end-capped anthryl diimides functions effectively as an “on-off’ sensor for pH and the detection of phosphoryl halide based chemical warfare agents, such as Sarin. In the absence of analytes, fluorescence from this dye is completely quenched by excited state electron transfer from the terminal amines. Reaction of these amines inhibits electron transfer and activates the fluorescence of the dye. Another substituted anthryl diimide is presented with the capability to detect pH and nitroaromatic compounds, such as TNT. Films prepared by doping small amounts (less than 0.1 weight percent) of several of these dyes in polymers such as linear low density polyethylene exhibit thermochromism. At room temperature, these films fluoresce reddish-orange. Upon heating, the fluorescence turns green. This process is reversible – cooling the films to room temperature restores the orange emission.

Aromatic Diimides – Potential Dyes for Use in Smart Films and Fibers

Advances in Colorants, Chemicals, Finishes and Fibrous Materials Symposium
Greenville, SC
June 3-4, 2008

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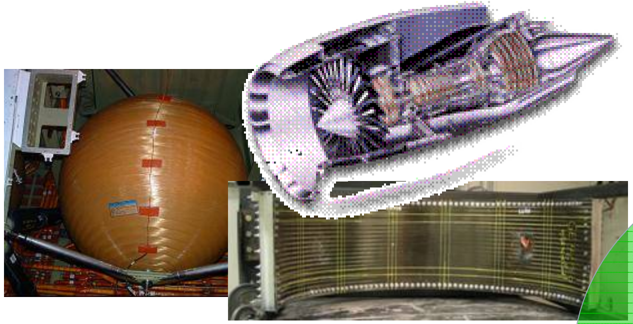
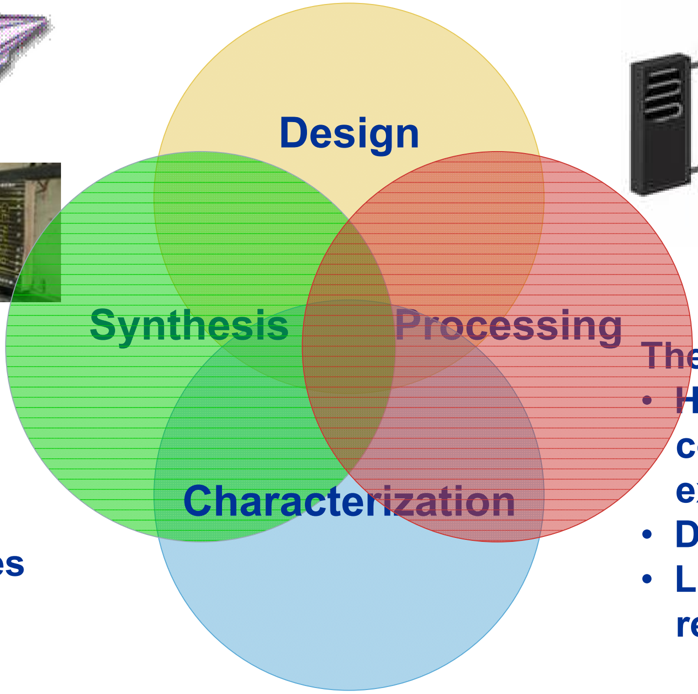
Polymers Branch Overview



Propulsion Materials
- High use temperature polymers and composites
- Material concepts for fan containment
- New polymers and composites for COPVs

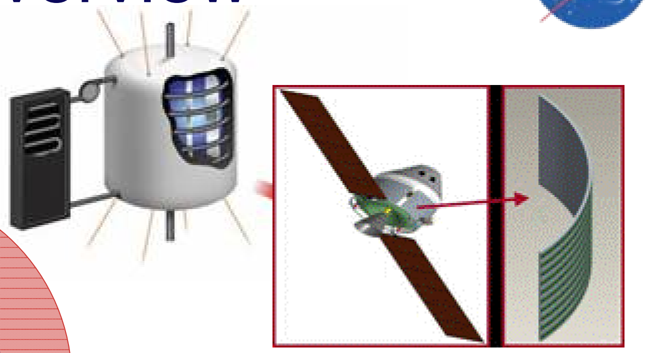


Design

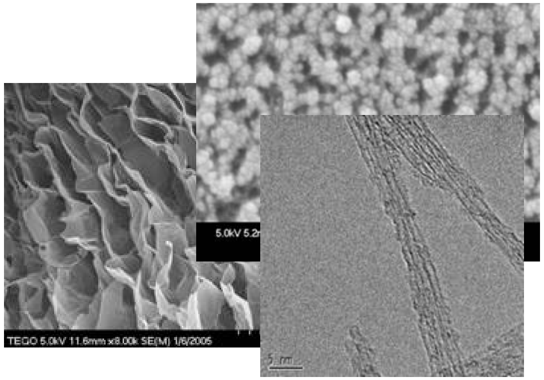
Synthesis

Processing

Characterization

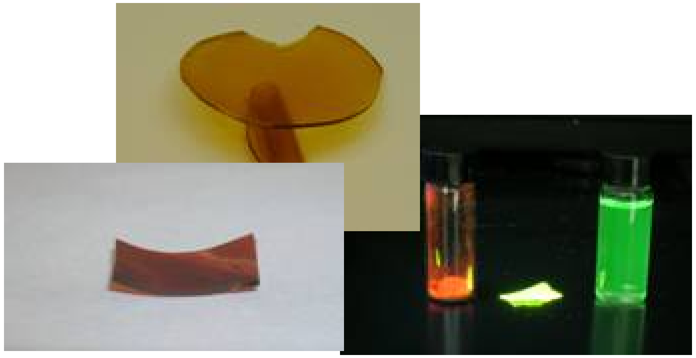


Thermal Control Materials
- High conductivity polymers and composites for radiators and heat exchangers
- Durable, lightweight insulation
- Low permeability, microcrack resistant polymers and composites



Nanostructured Materials
- Nanocomposites (clay, graphene)
- Nanotube based composites
- Durable, polymer cross-linked aerogels

Enable:
- Reduced Mass
- Enhanced Performance
- Improved Durability
- Reduced Cost

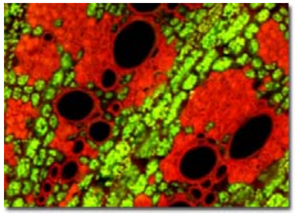


Functional Polymers
- Adaptive polymers
- Fluorescent sensors
- Conductive membranes

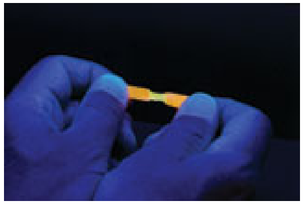
Organic Materials for Molecular Sensors

Technology Background

Fluorescence based methods are highly sensitive for the detection of chemical and biological species and can be used for the determination of strain and/or degradation in materials.



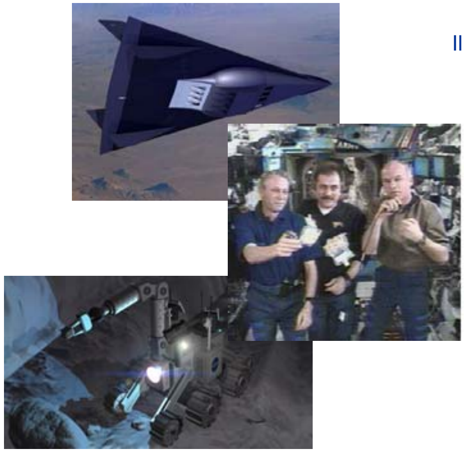
Fluorescent dye enhanced photomicrograph of Alfalfa Root



Fluorescence based strain sensors – *courtesy CWRU*

NASA Applications

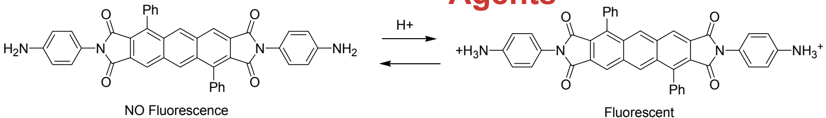
- **Astronaut Health Management**
- **Air & Water Quality Monitoring**
- **Integrated Vehicle Health Management**

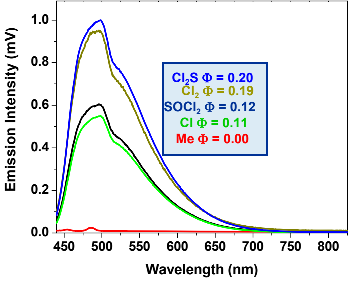


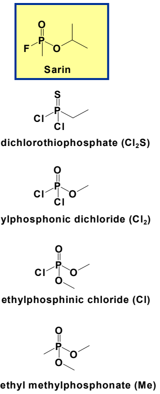
Research and Results

Developed route to novel diimide materials with potential use in molecular sensors, electronics and electroluminescent devices

"On-Off" Fluorescent Sensor for pH and Chemical Warfare Agents







Ethyl dichlorothiophosphate (Cl_2S)

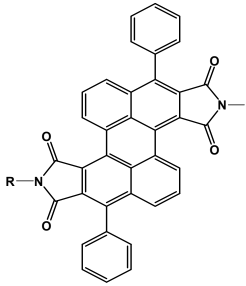
Methylphosphonic dichloride (Cl_2)

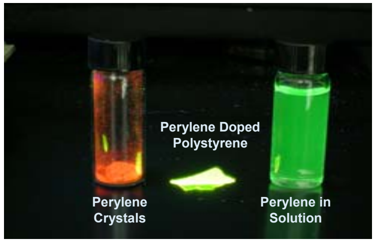
Dimethylphosphinic chloride (Cl)

Dimethyl methylphosphonate (Me)

Ilhan, Tyson and Meador *Chemisty of Materials* **2004**, *16*, 2978-80

Novel Perylene Diimide Has Potential as Strain Sensor

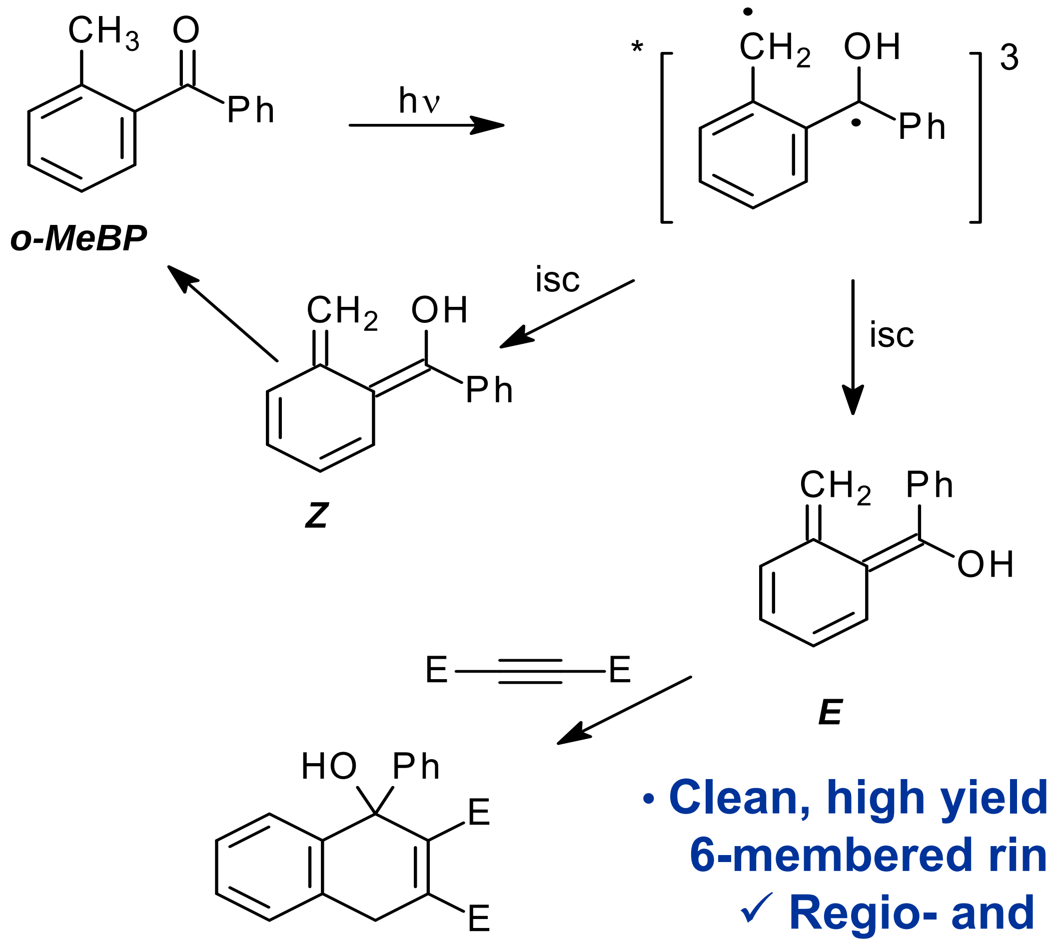




Red Luminesence in Solid State Due to Exciplex

Tyson, Ilhan and Meador *Journal of the American Chemical Society* **2006**, *128*, 702-703

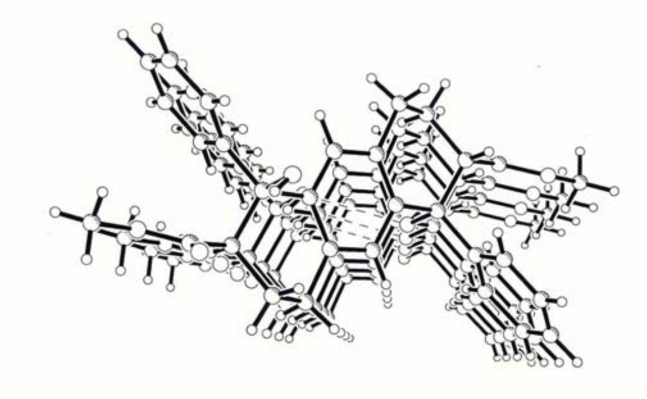
Photoenolization of *o*-Methylphenyl Ketones

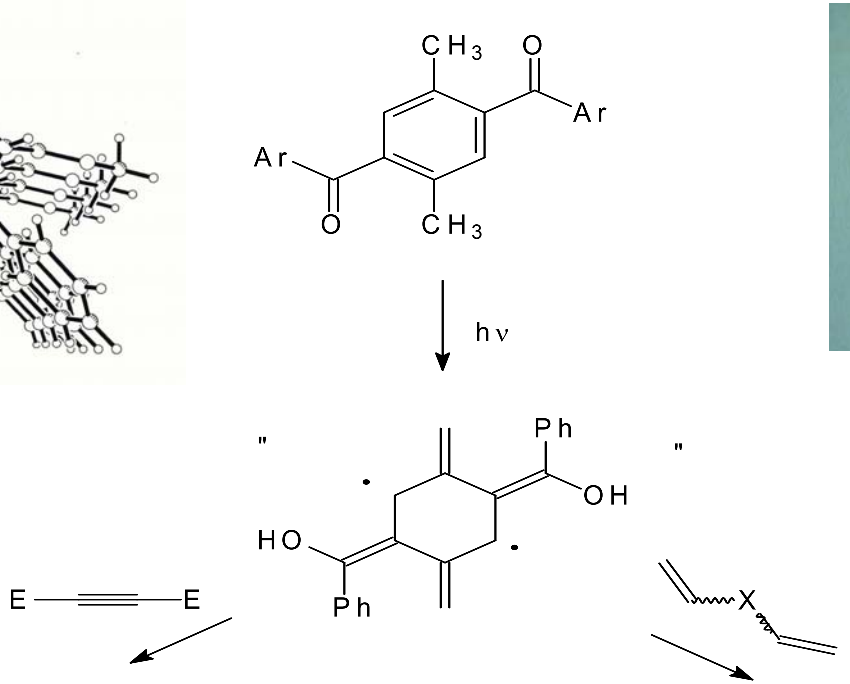


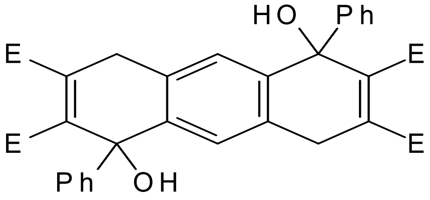
- **Clean, high yield route to fused 6-membered rings**
  - ✓ **Regio- and stereospecific**
- **Not applied to polymer synthesis**

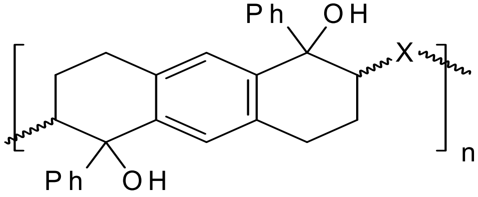
Porter, G.; Tchir, M. *J. Chem. Soc. A* **1971**, 3772
Yang, N.C; Rivas, C.J. *J. Am. Chem. Soc*. **1961**, *83*, 2213

Diels-Alder Trapping of Bis(*o*-xylylenol)s is Versatile

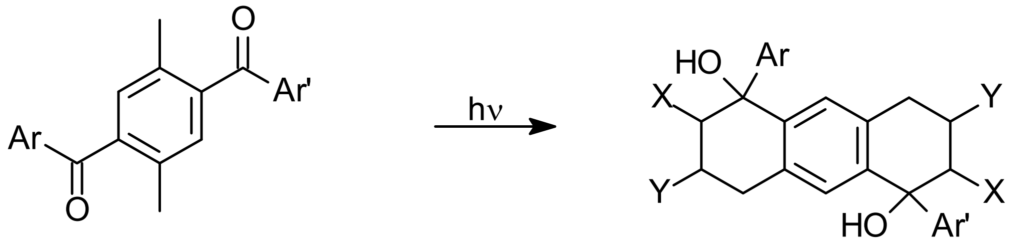








Chemical Yields for Bisadduct Formation are High

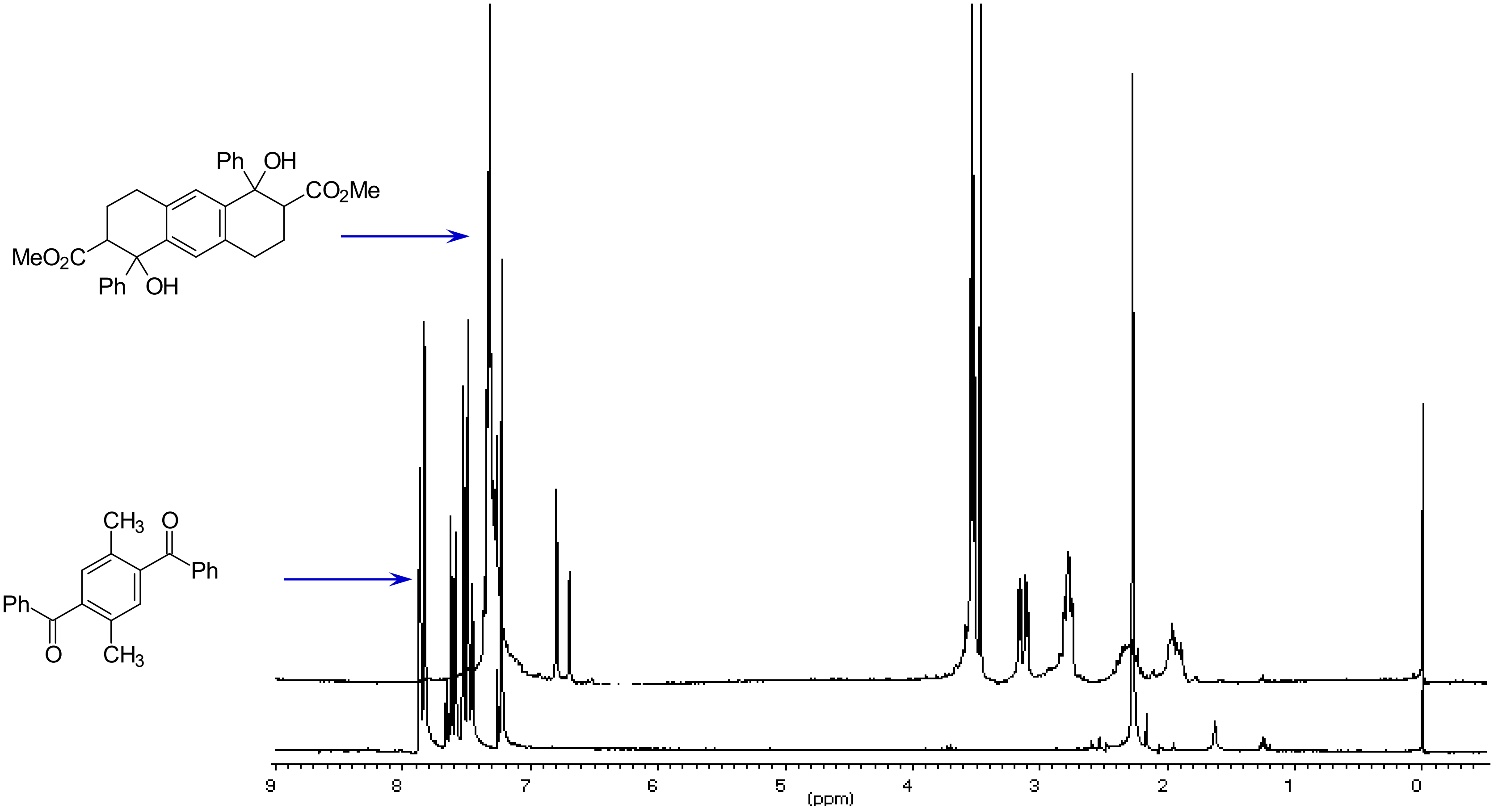


1

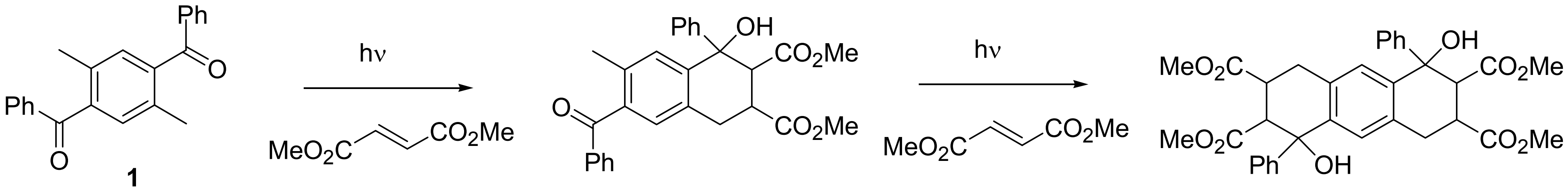
2 (X=CO_2Me, Y=H)
3 (X=Y=CO_2Me)

Ar	*Ar'*		*X*	*Y*	*2*	*3*
Ph	Ph	MeAcry	E	H	25+56	
Ph	Ph	Me_2Fum	E	E		86
4-Me	4-Me	MeAcry	E	H	90	
4-Me	4-Me	Me_2Fum	E	E		82
4-OMe	4-OMe	MeAcry	E	H	75	
4-OMe	4-OMe	Me_2Fum	E	E		86
4-$OC_{12}H_{25}$	4-$OC_{12}H_{25}$	MeAcry	E	H	80	
4-$OC_{12}H_{25}$	4-$OC_{12}H_{25}$	Me_2Fum	E	E		80
4-CN	4-CN	MeAcry	E	H	97	

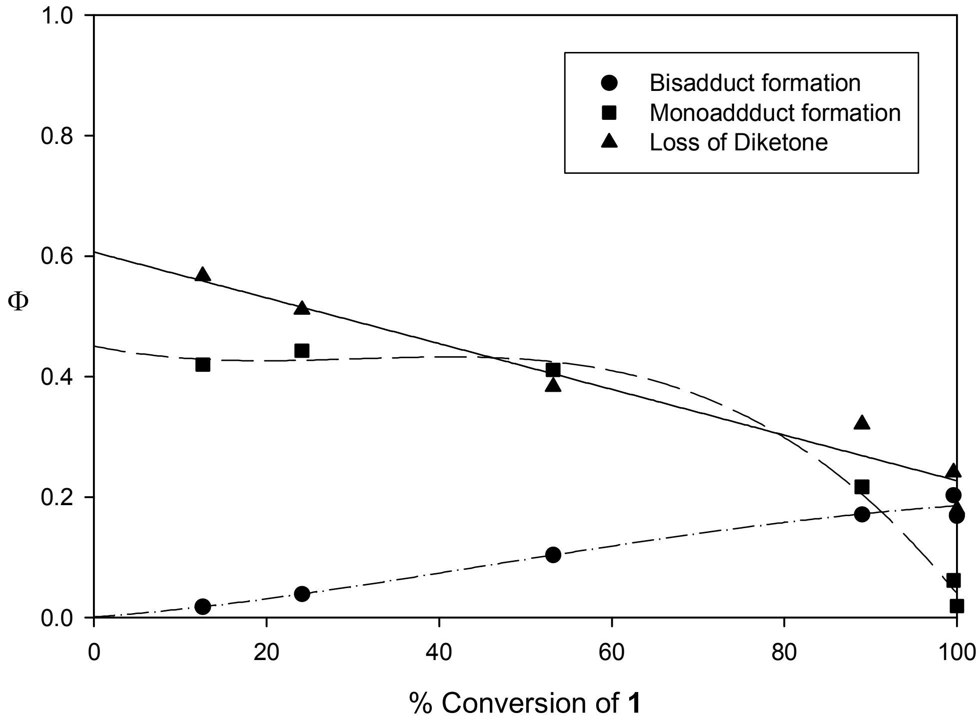
Reaction Progess Can Be Monitored by ^{1}H nmr



Mono- and Bisadduct Quantum Yield Effected by Extent of Diketone Conversion

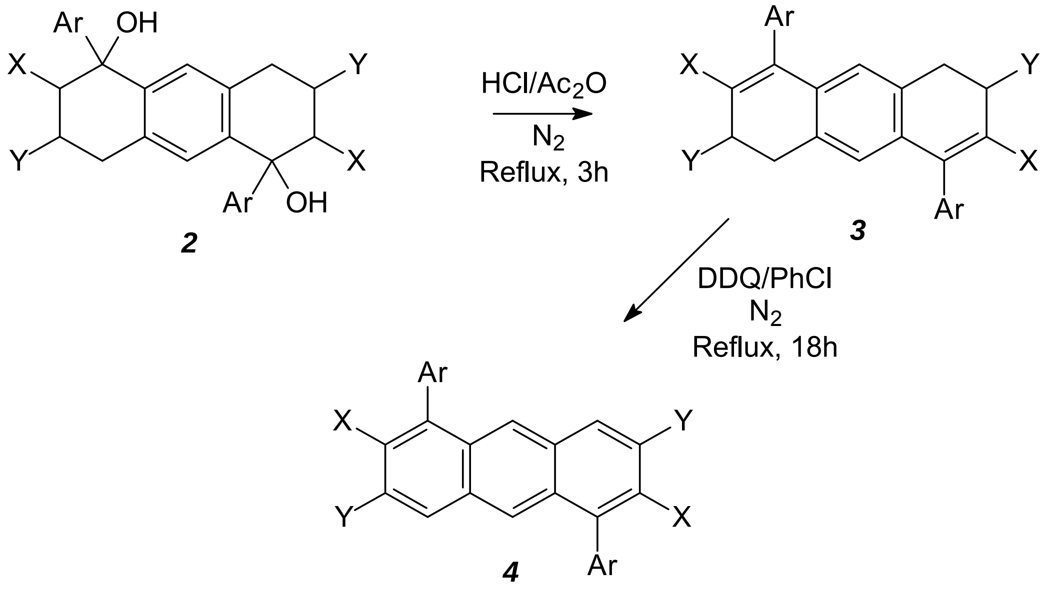


$$\Phi = \frac{\text{moles of photoproduct}}{\text{Einstein of light}}$$



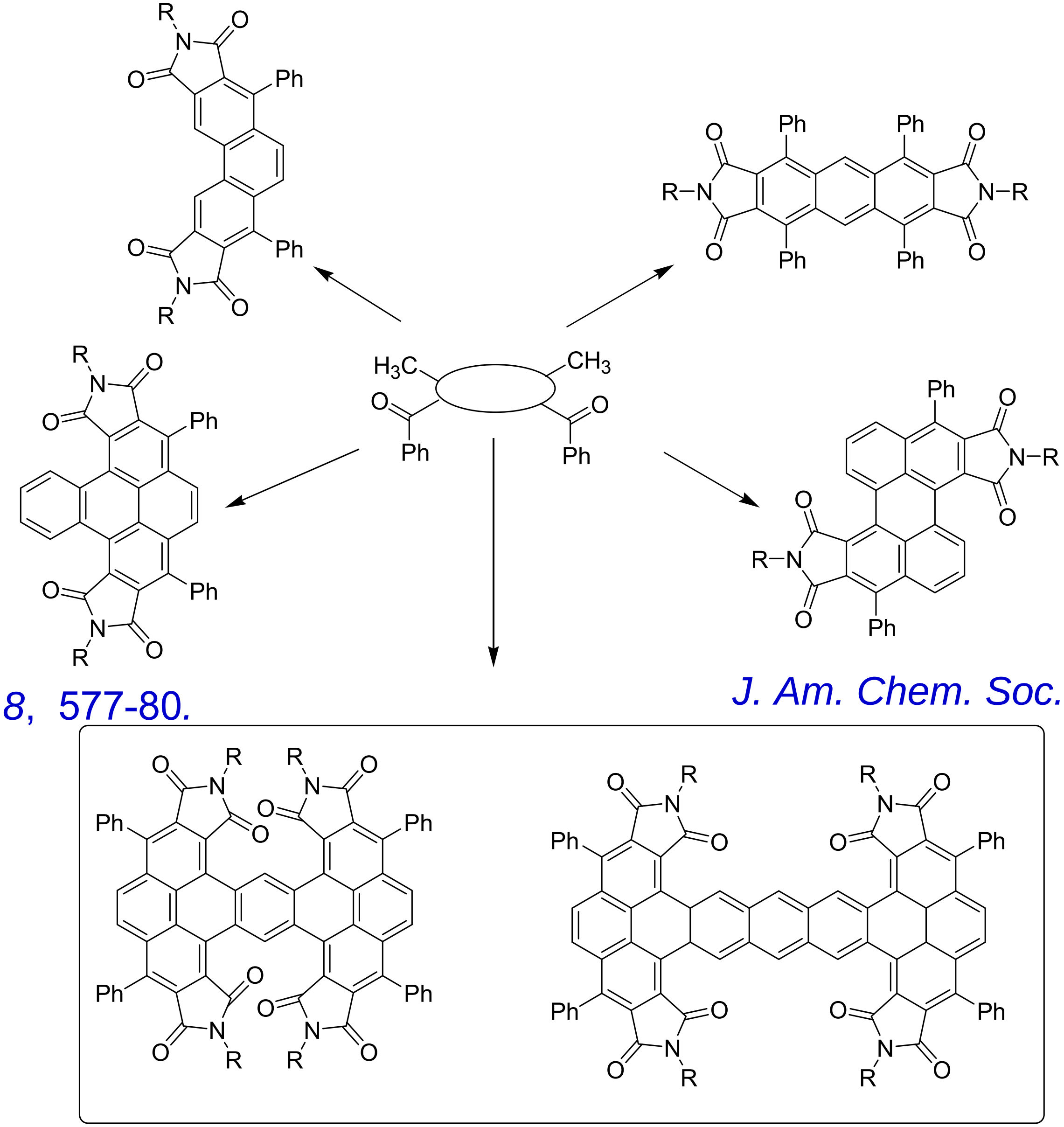
E/Z photoenol formation is 1:1 → Maximum theoretical quantum yield for monoadduct formation is 0.5

Bisadducts are Readily Converted into Anthracenes



Ar	*X*	*Y*	*3*	*4*
Ph	E	H	90	96
Ph	E	E	100	80
4-MeOPh	E	H	87	81
4-MeOPh	E	E	80	80
4-FPh	E	H	89	72
4-FPh	E	E	68	70

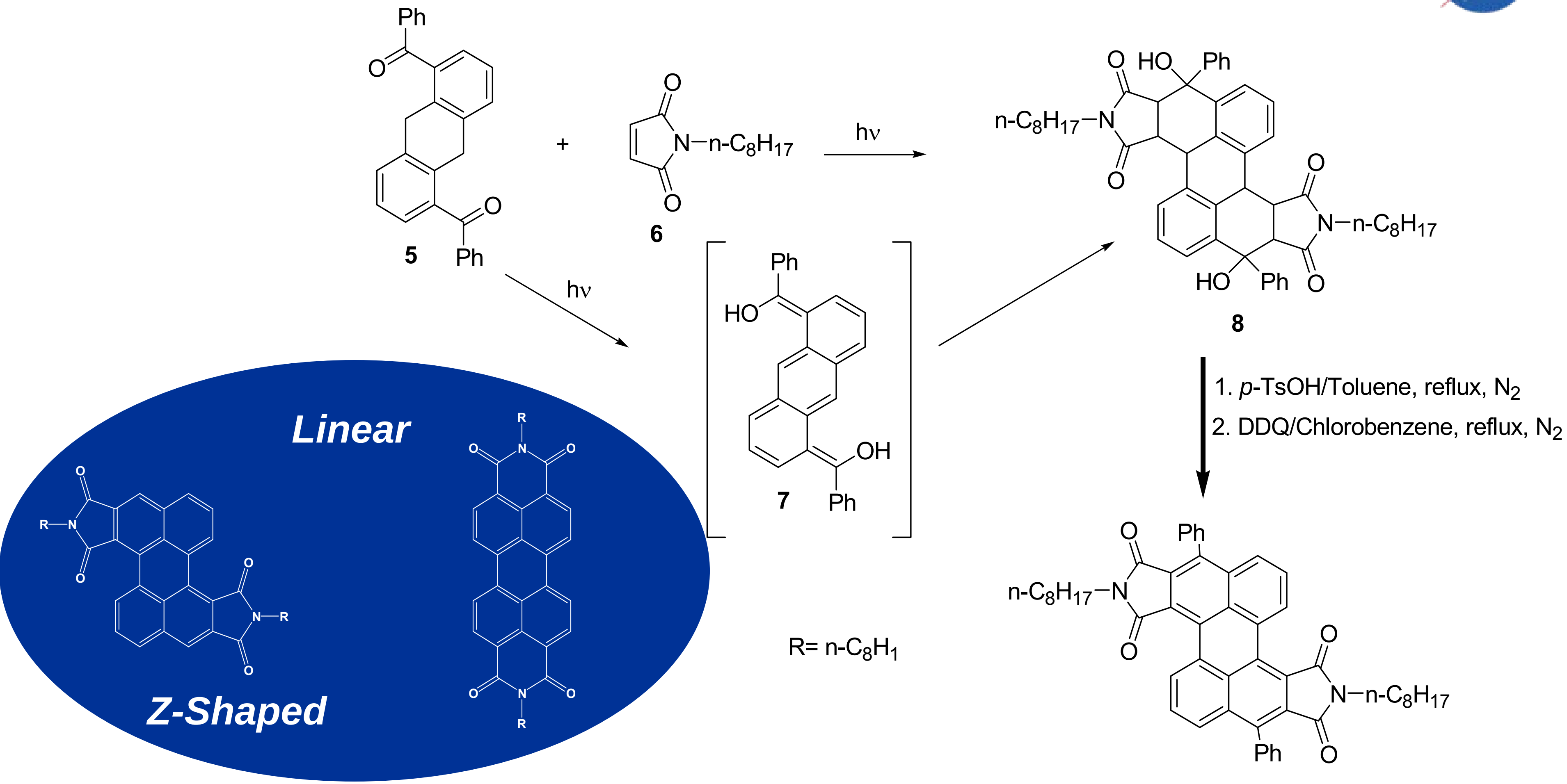
Versatile Route to Arenes



Org. Lett. **2006**, *8*, *577-80.*

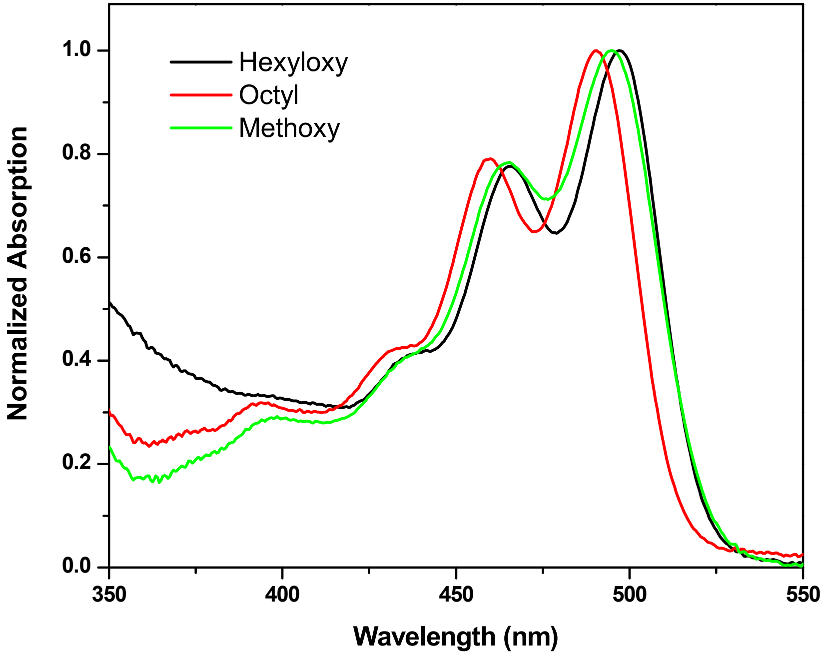
J. Am. Chem. Soc. **2006**, *128*, 702-703

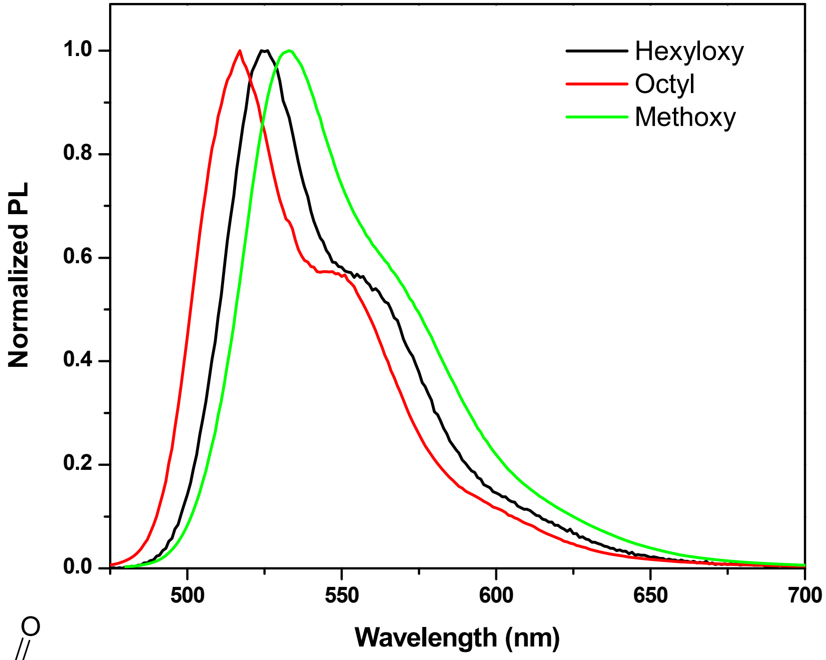
New Approaches to Perylene Diimides



- Perylene diimides are used in a wide array of materials, including electron transfer systems, liquid crystals, photovoltaics, and fluorescent sensors.
- Conventional synthetic routes to perylene dimides focused on *linear* derivatives – commercial availability of dianhydride.
- New approach provides route to *Z-shaped* perylene bisimides

Absorption and Emission Spectra of Various Z-shaped Perylene Diimides

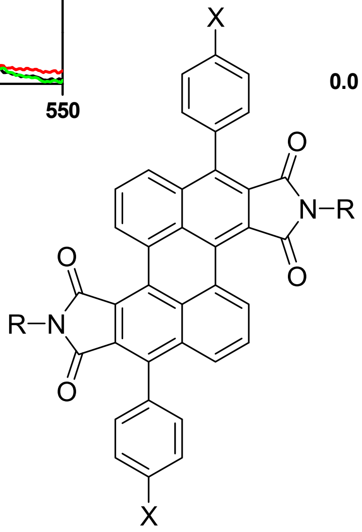




Φ_f (CH_2Cl_2)

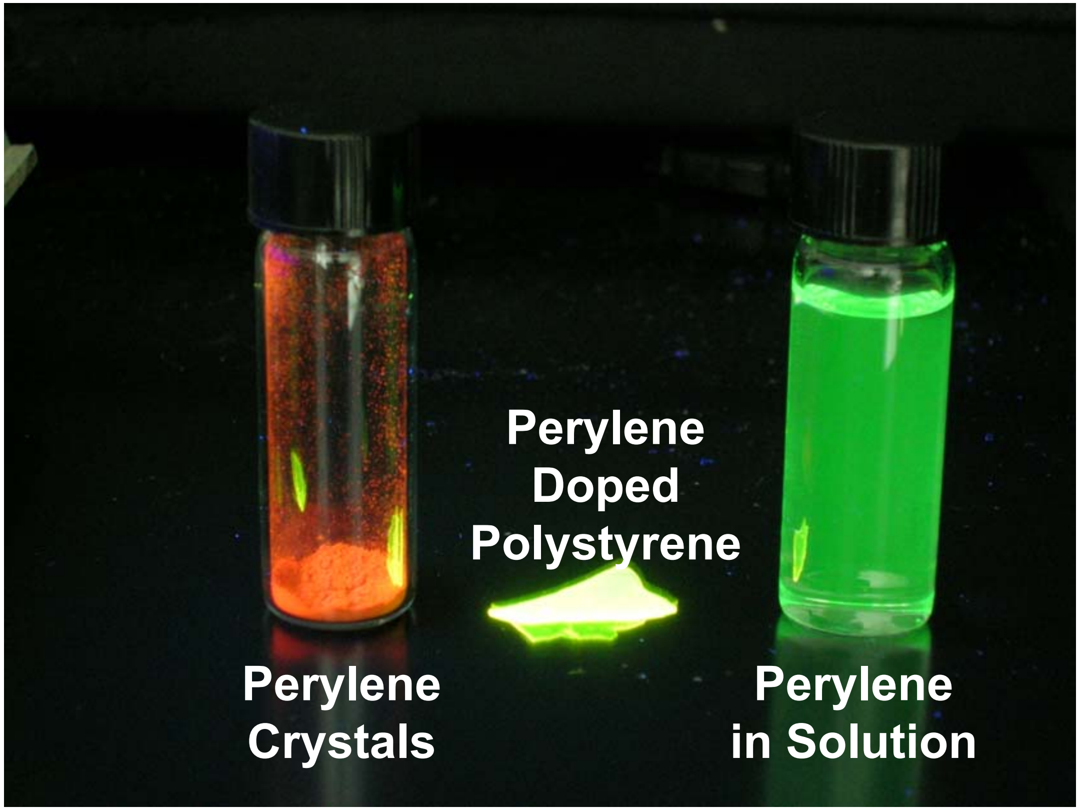
Octyl = 0.67

p- Hexyloxyphenyl = 0.031



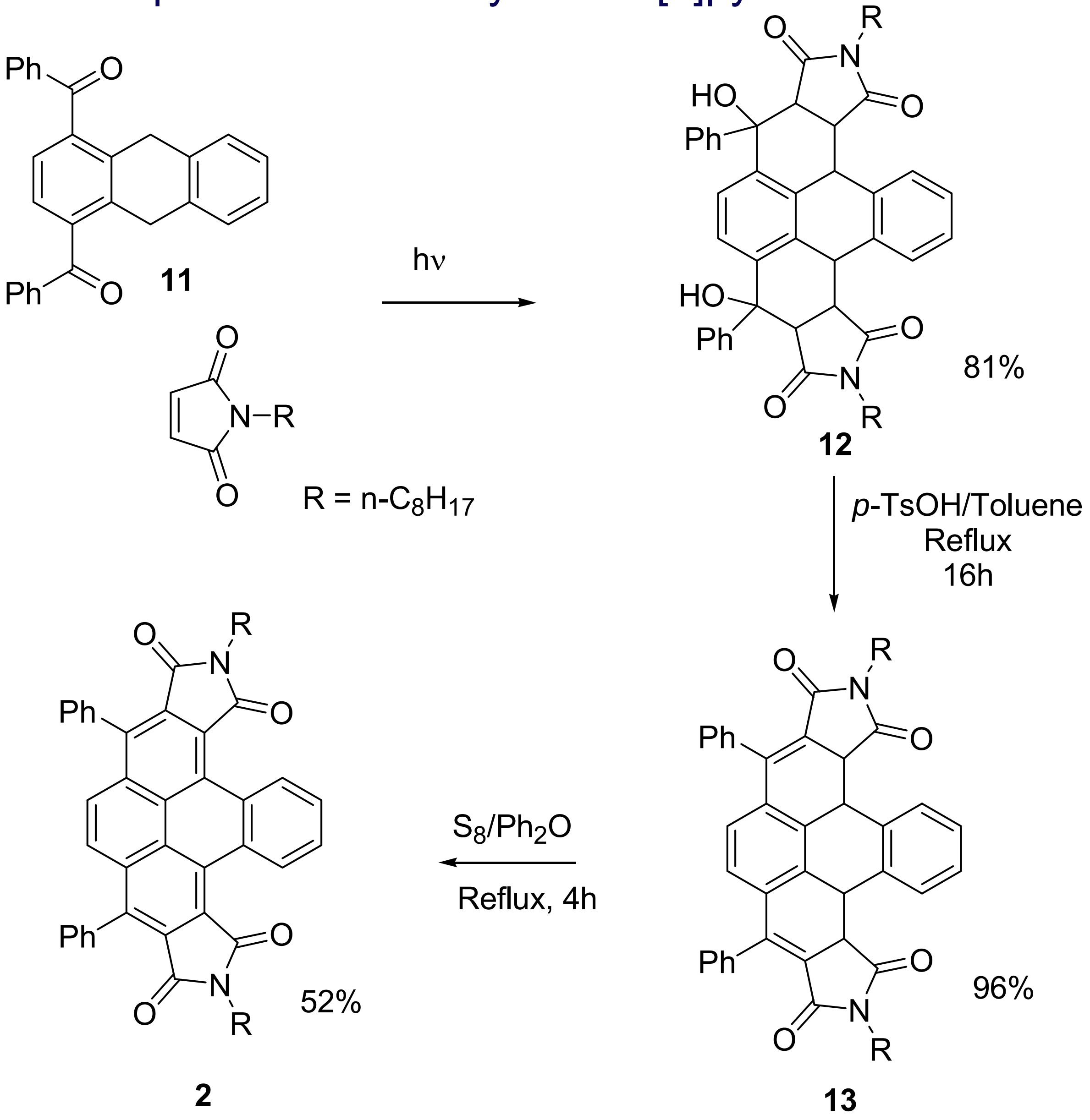
Hexyloxy	R=*p*-C_6H_{13}O-Ph, X = H
Octyl	R = n-C_8H_{17}, X=H
Methoxy	R = n-C_8H_{17}, X=OCH_3

Perylene Diimide Exhibits Excimer Fluorescence in the Solid State



- Difference in emission color due to the formation of excited state complexes (exciplexes) in which perylenes form stacks
- Potential to use this phenomenon in the design of thermo- and mechanochromic polymers

Preparation of N-Octyl Benzo[e]pyrene Diimide



11

R = n-C_8H_{17}

hν

12 81%

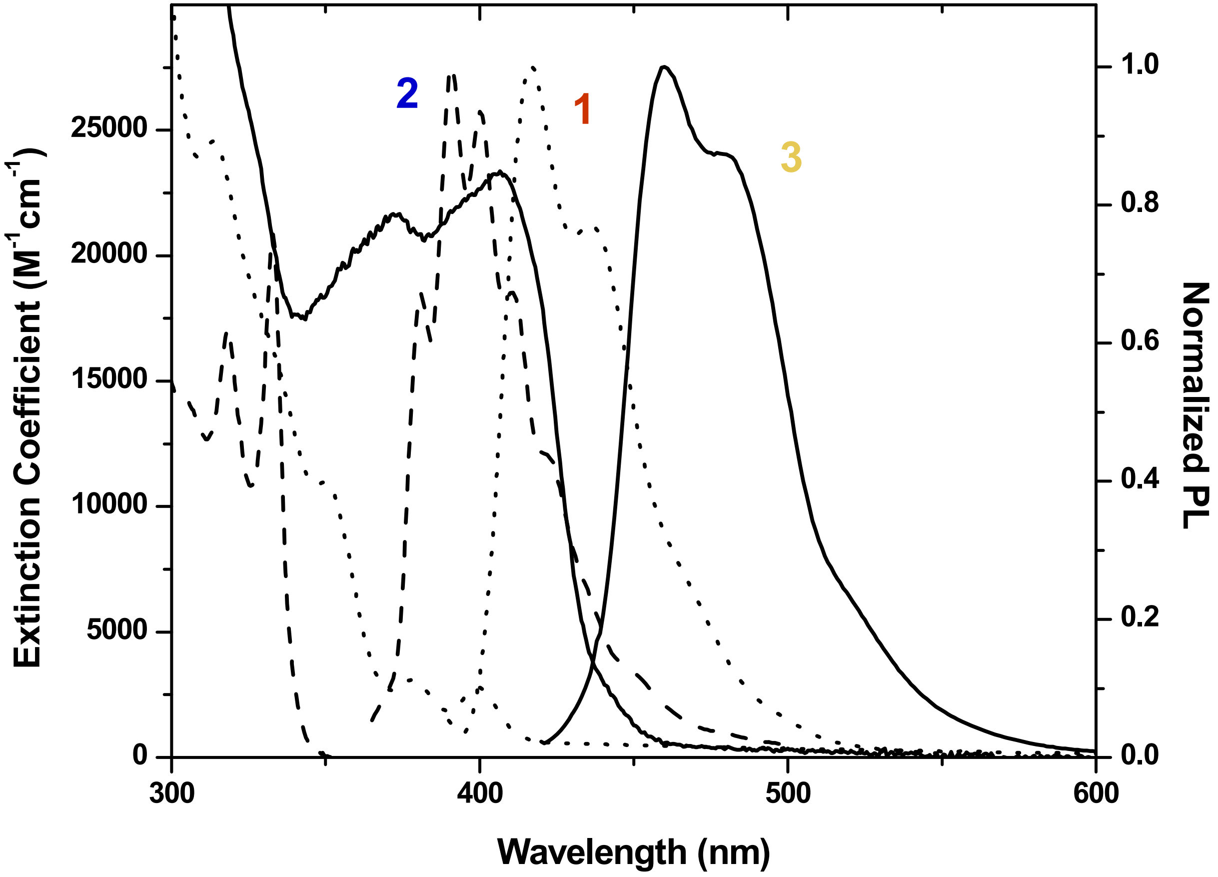
p-TsOH/Toluene
Reflux
16h

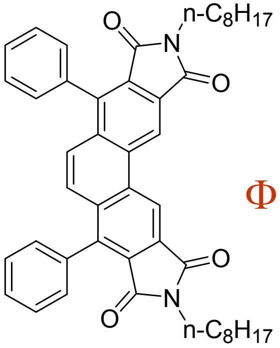
13 96%

S_8/Ph_2O
Reflux, 4h

2 52%

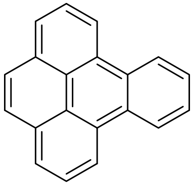
Absorption and Emission of Phenanthrene and Benzo[e]pyrene Bisimides and Benzo[e]pyrene





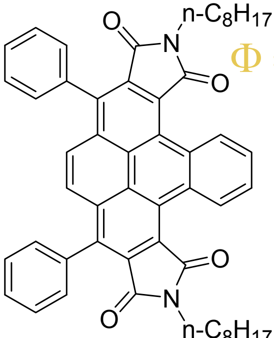
1

$\Phi = 0.24$



2

$\Phi = 0.037$

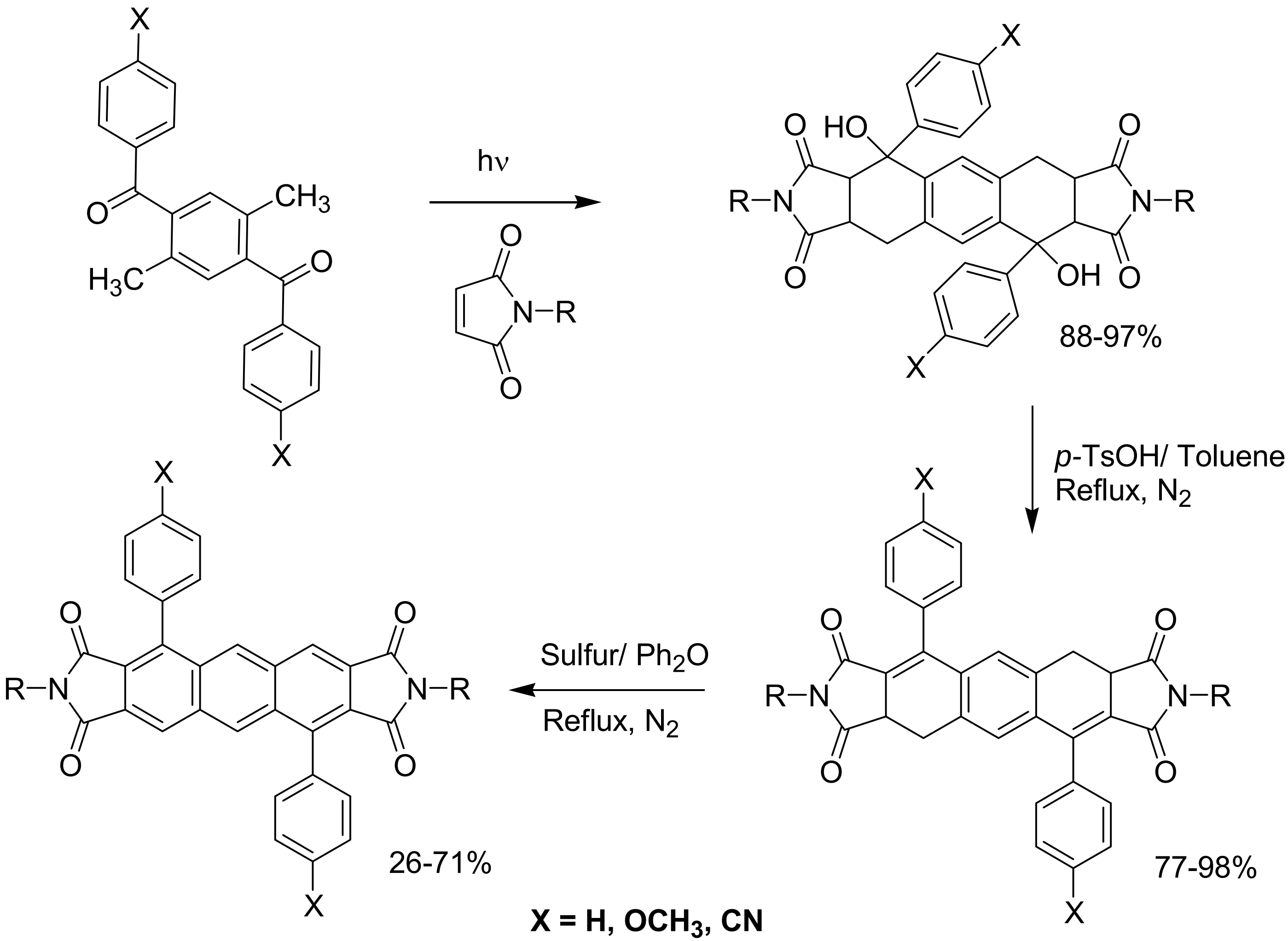


3

$\Phi = 0.054$

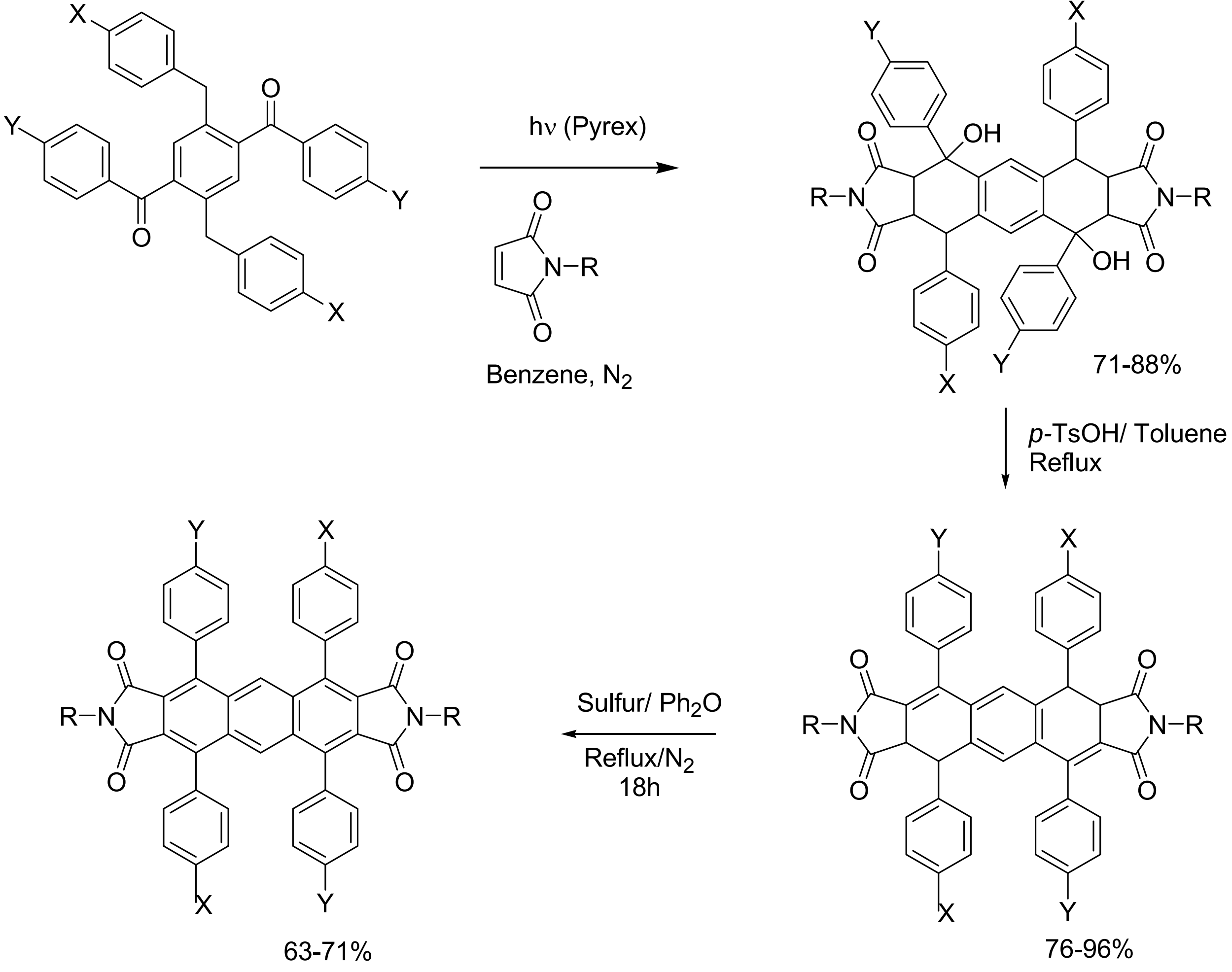
Spectra and quantum yields measured in CH_2Cl_2

Synthesis of Anthracene Diimides



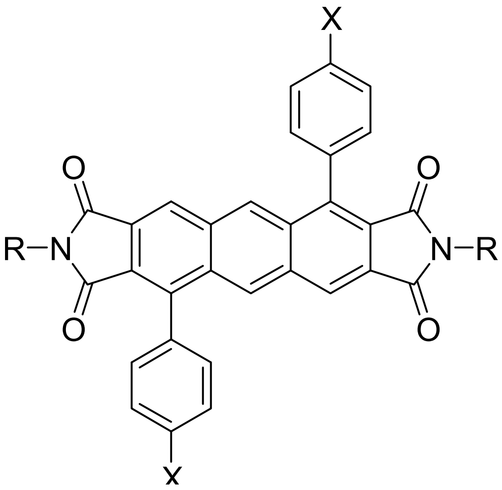
X = H, OCH_3, CN
R = n-C_8H_{17}, Ph, 4-MeOPh, 4- ($C_6H_{13}O$)Ph, 4-NO_2Ph

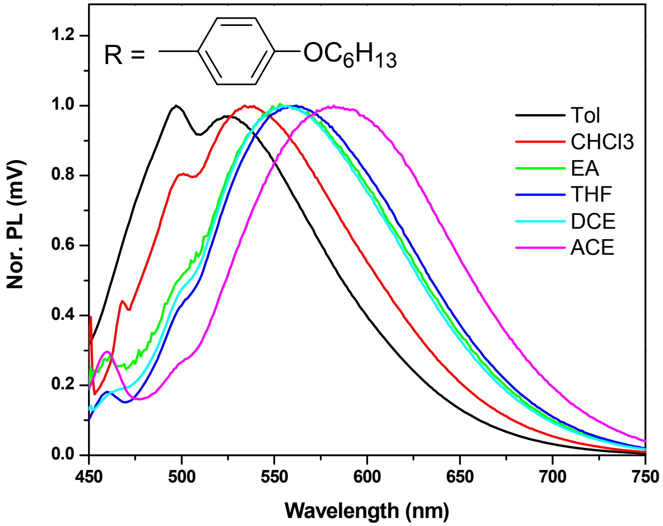
Synthesis of Tetraaryl Diimides – Trapping Unaffected by Steric Hindrance

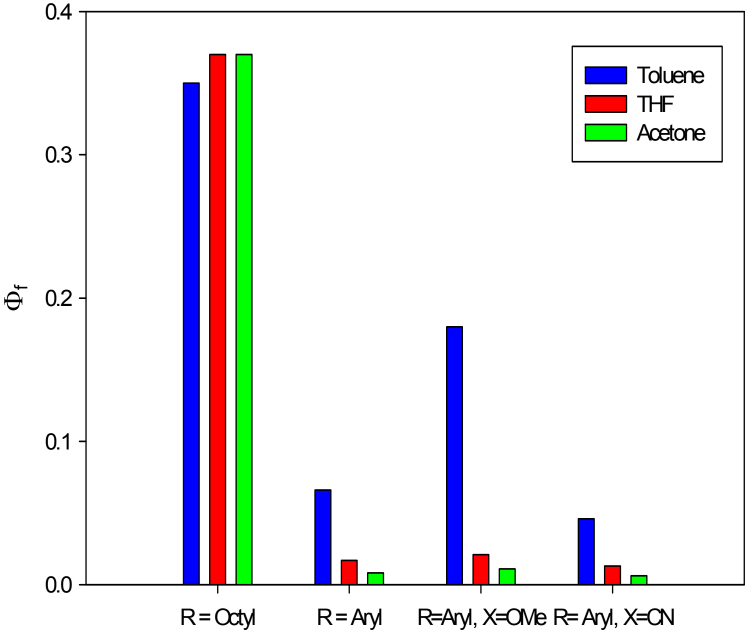


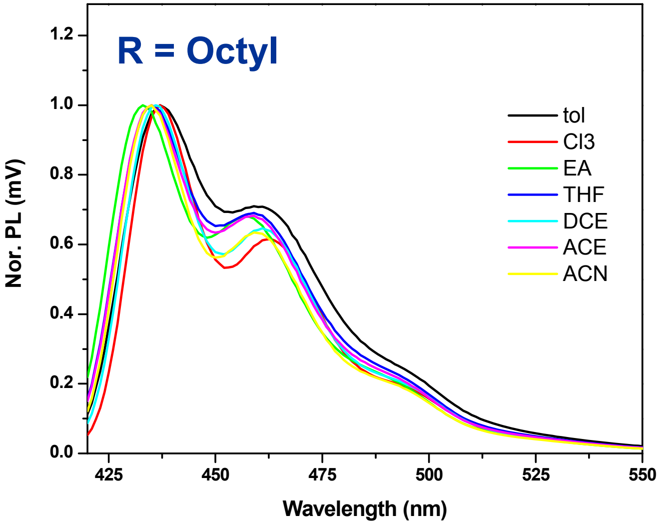
X = H, OCH_3,
Y = H, OCH_3, CN
R = n-C_8H_{17}, *p*-($C_6H_{13}O$)Ph

Substituent and Solvent Effects on Photophysics of Anthryl Diimides

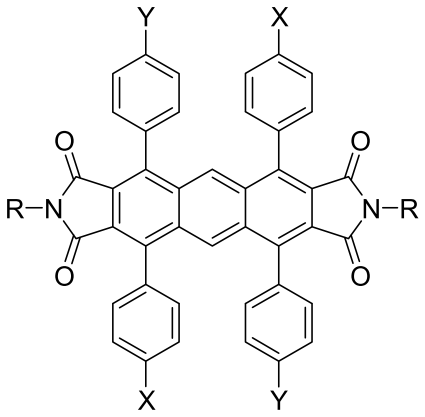


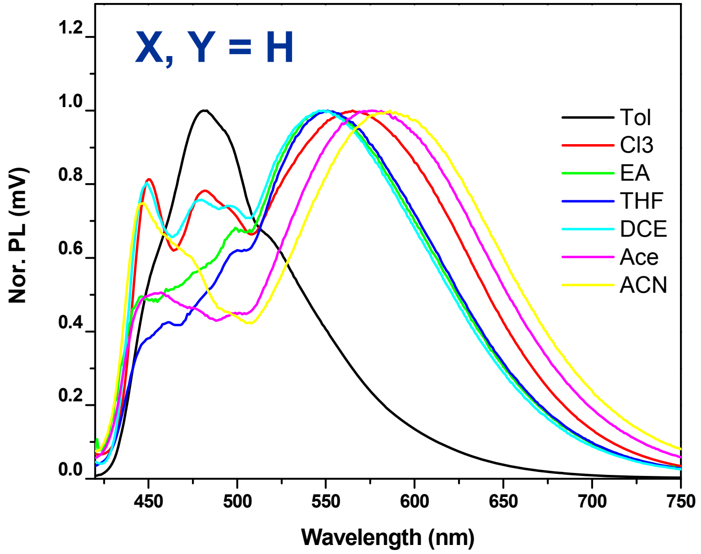



Effect of Solvent on Fluorescence Quantum Yields

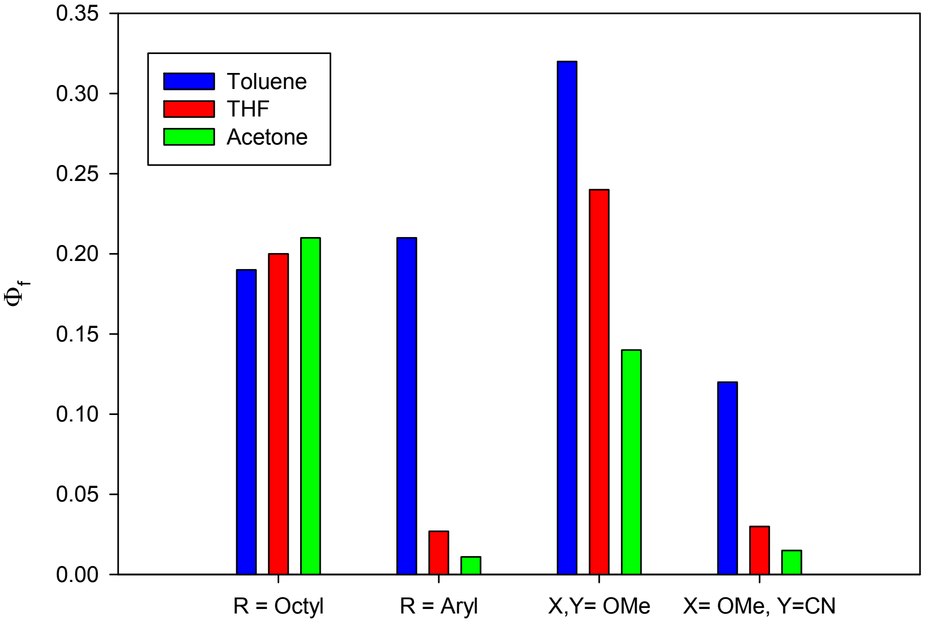


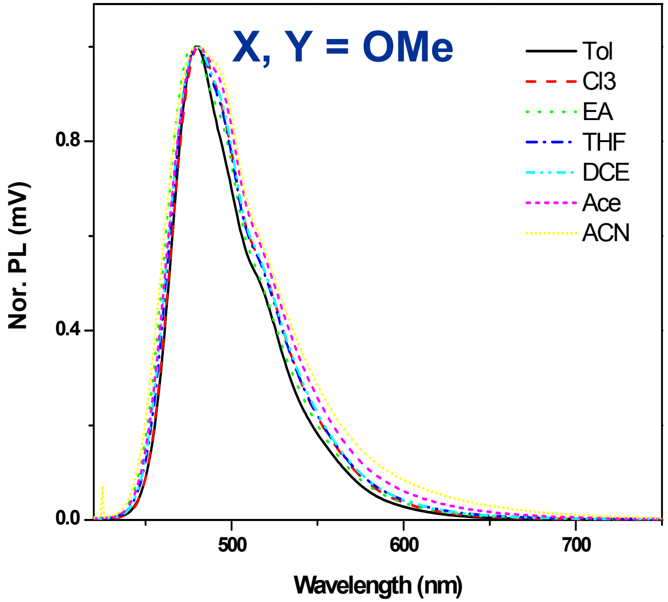
Substituent and Solvent Effects on the Photophysics of Diimides



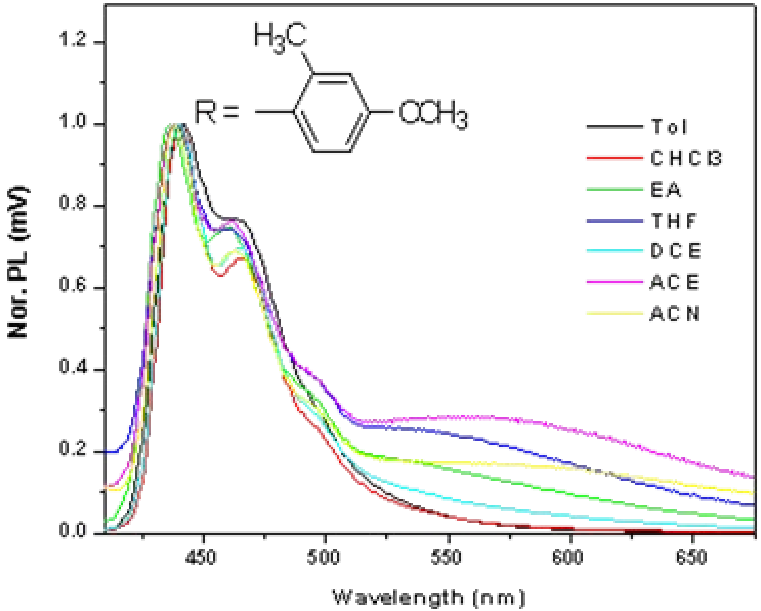


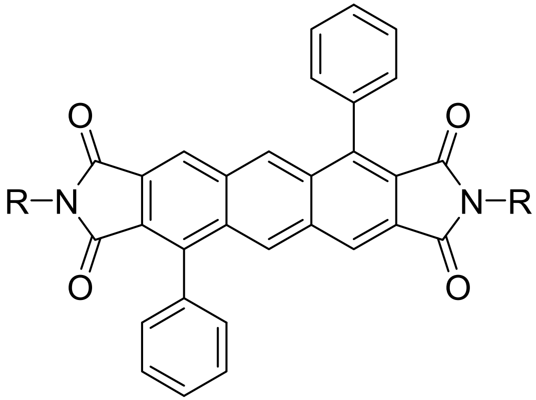
Fluorescence Quantum Yields

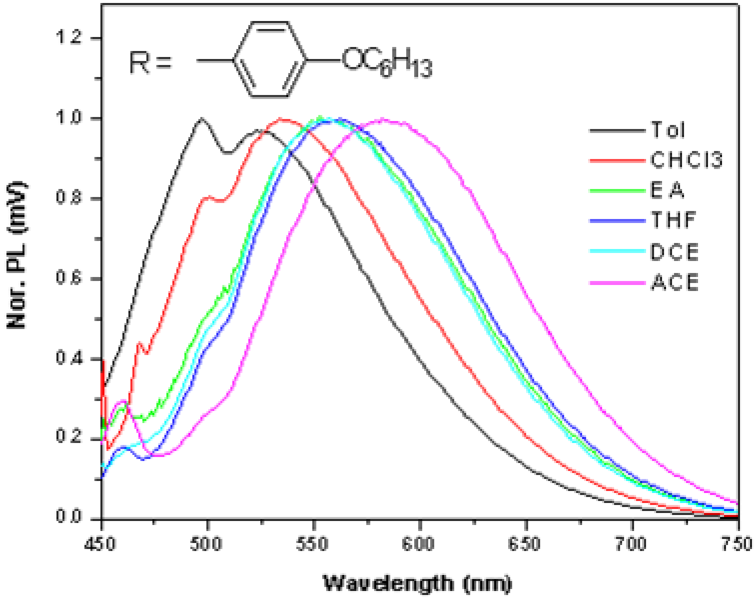


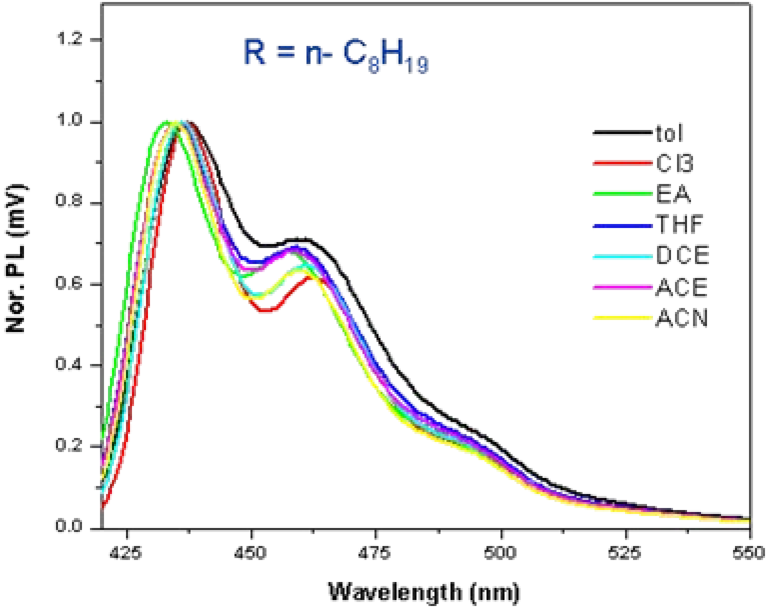


Twisting of N-Aryl Group Inhibits Charge Transfer

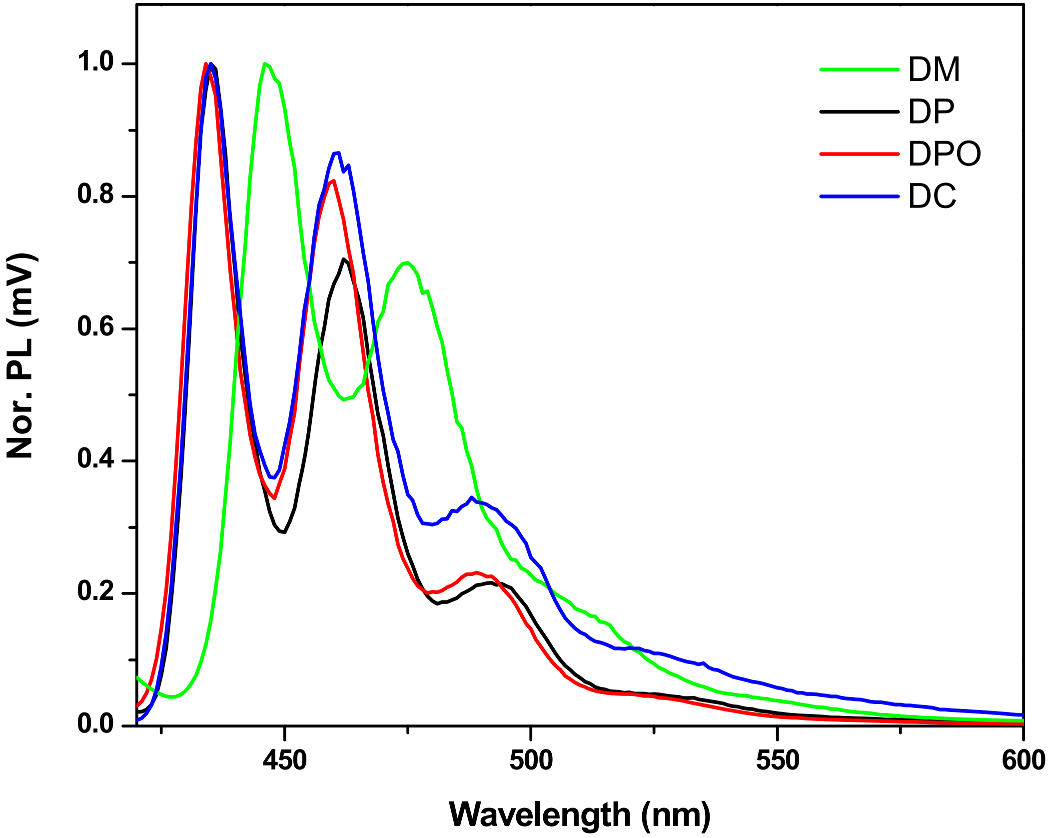








Low Temperature Emission Spectra

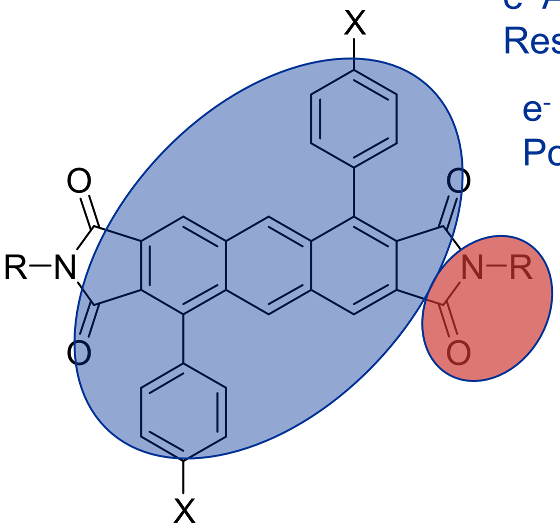


Spectra measured in MeTHF at 77°K

Reducing temperature:

- Reduces rotational motion
- Inhibits charge transfer

Steric and Electronic Effects Regulate Excited State Photophysics

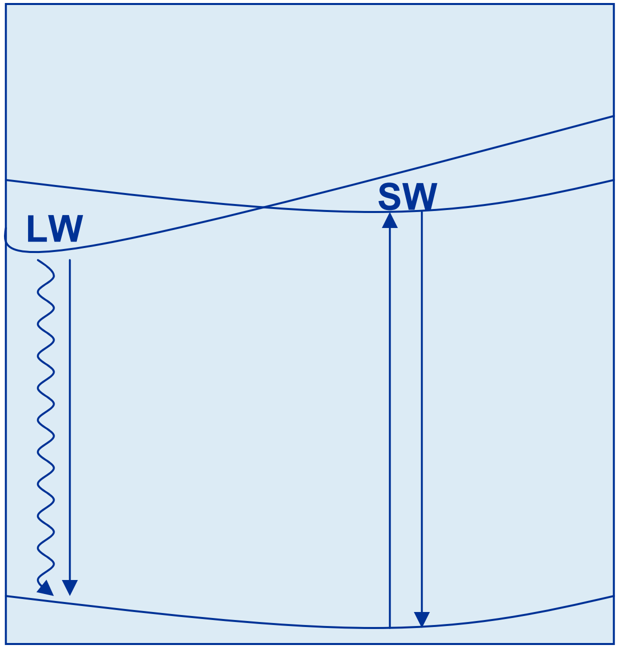


↑

e^- Acceptor R's
Restricted Rotation

e^- Donor R's
Polar Solvents

↓



↑

e^- Acceptor X's

e^- Donor X's

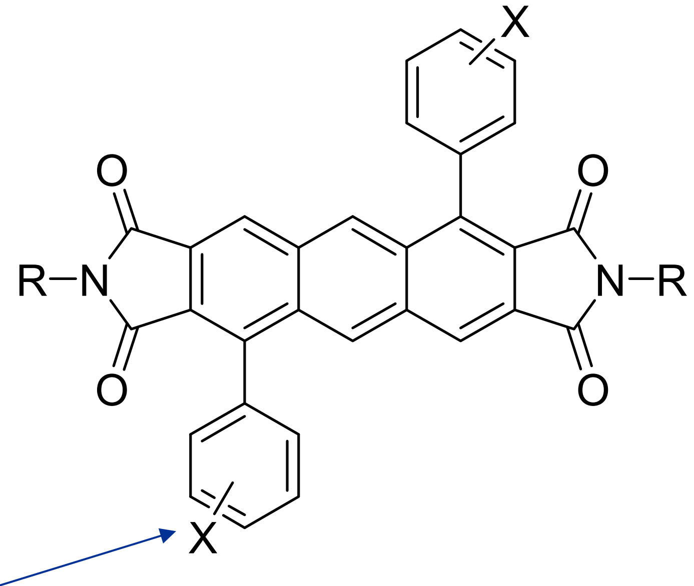
↓

Only LW Observed
Electron donating *N*-aryls
+
Electron withdrawing X
+
Polar solvents

Dual emission
Electron donating *N-aryls*
+
Electron donating X
Or
Electron donating *N*-aryl
+
Non-polar solvents

Only SW observed
- *N*-octyl diimides
- Sterically crowded *N*-aryl R's
- Low temperatures

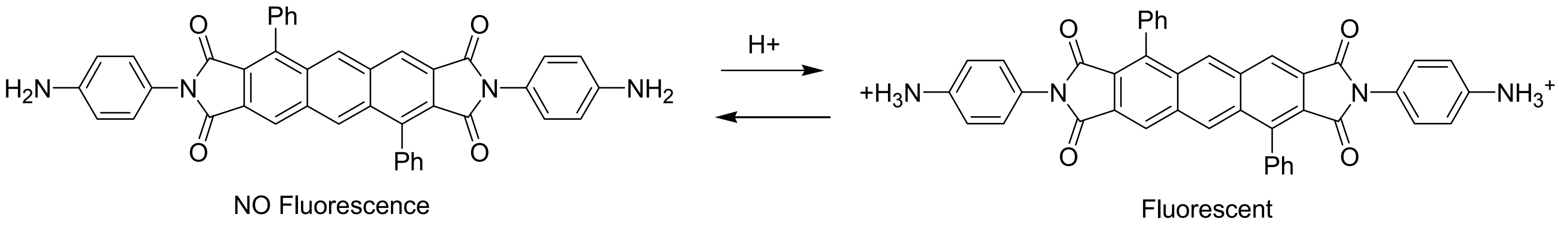
Anthracene Diimide Provides Platform for Charge Transfer Mediated Fluorescent Sensors

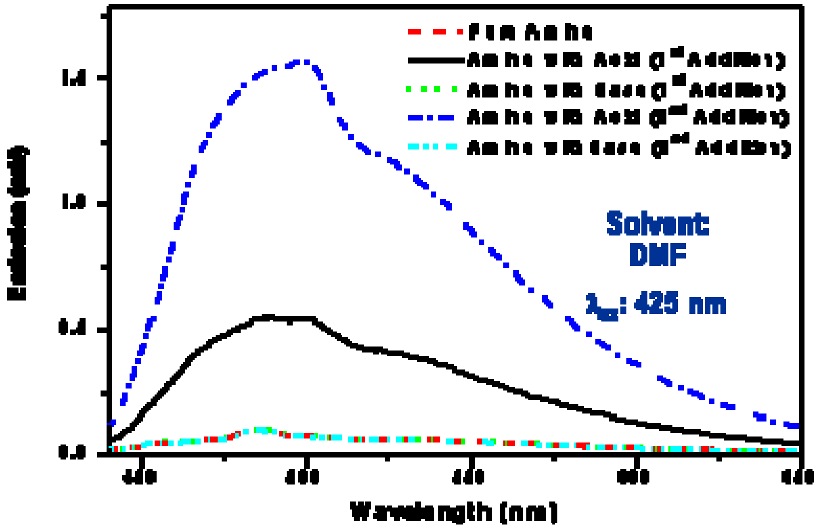


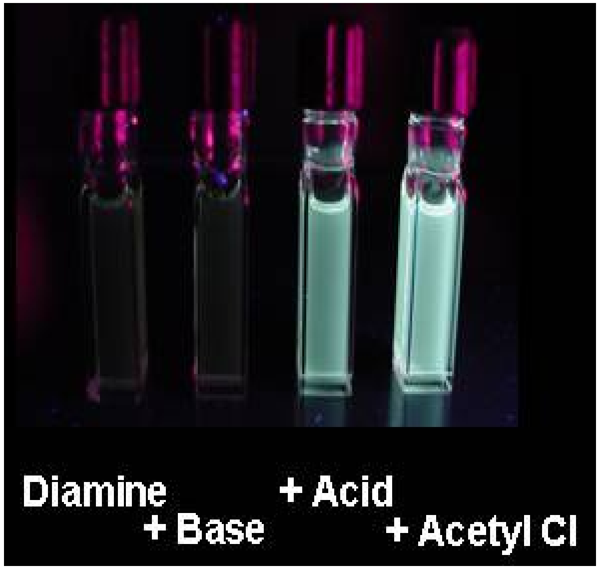
Electron donors that are tailored to interact with given analyte

Tune absorption and emission

New Anthracene Diimide Molecular Sensor



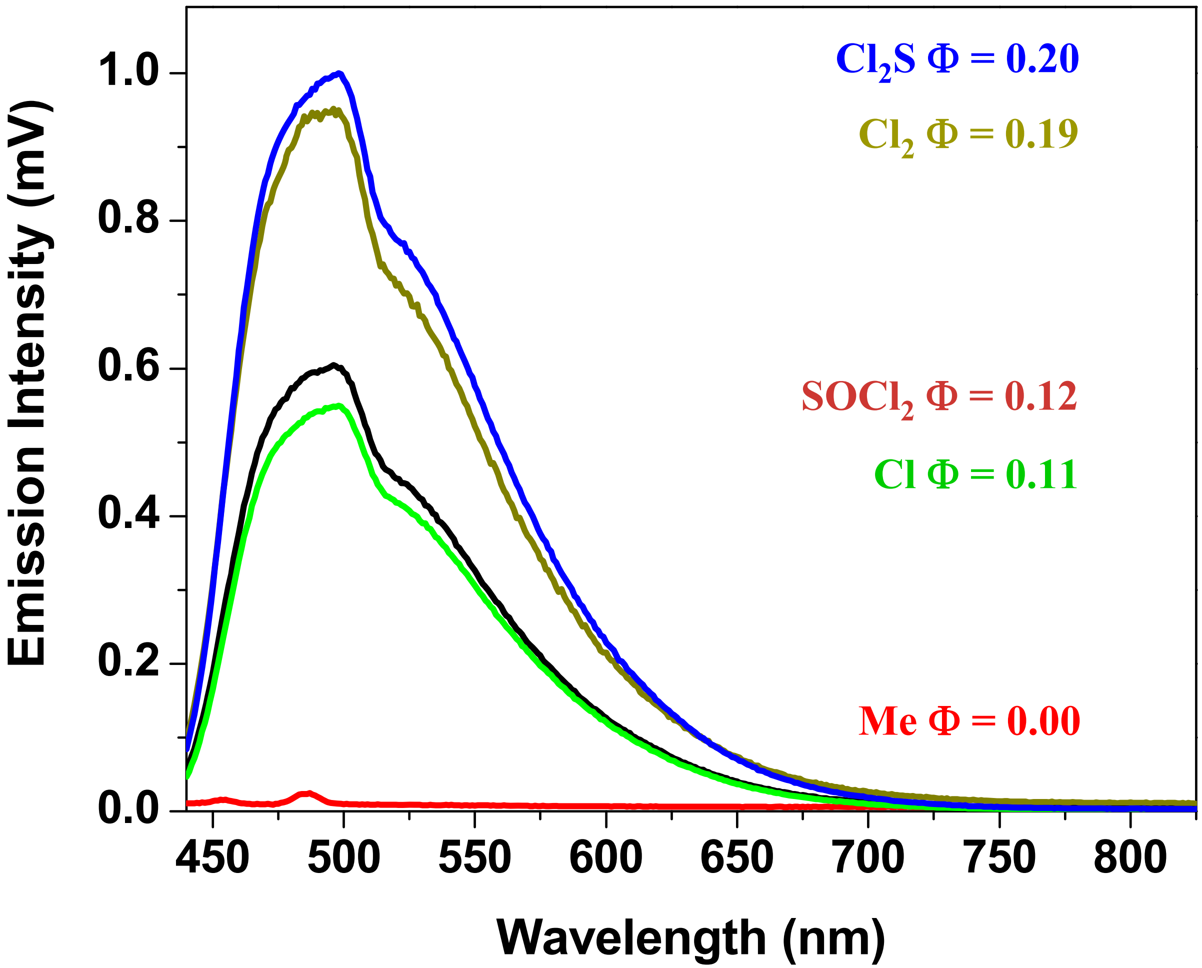


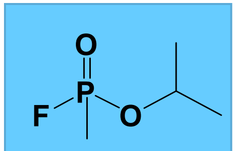


- **Charge Transfer from NH_2 quenches fluorescence**
- **Protonation or acetylation of the NH_2 prevents charge transfer, activates fluorescence**
- **Potential use as:**
    - ✓ **sensor for pH, chemical agents (nerve gas)**
    - ✓ **polymer cure monitoring**

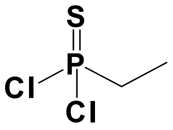
Ilhan, Tyson and Meador *Chem. Mater*. ***2004***

Diimide Can Detect Organophosphates

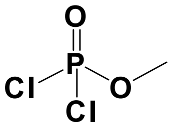




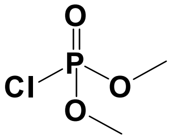
Sarin



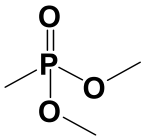
Ethyl dichlorothiophosphate (Cl_2S)



Methylphosphonic dichloride (Cl_2)

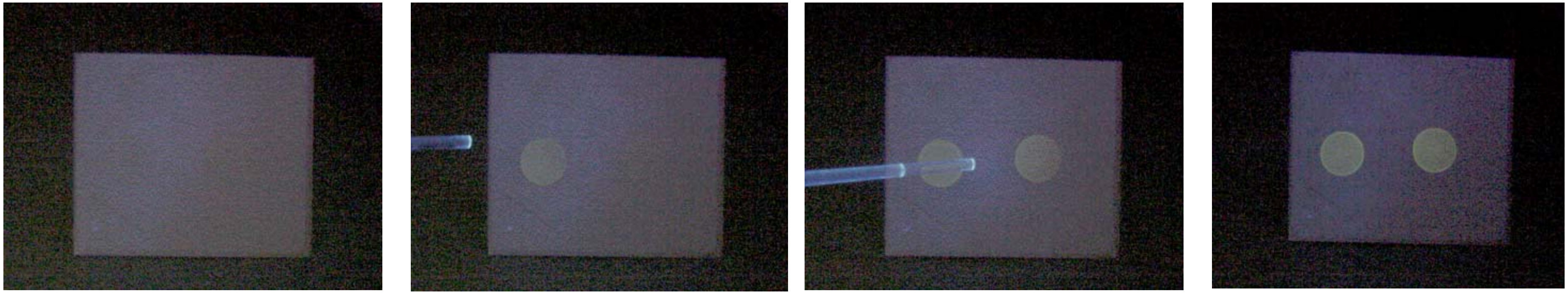


Dimethylphosphinic chloride (Cl)

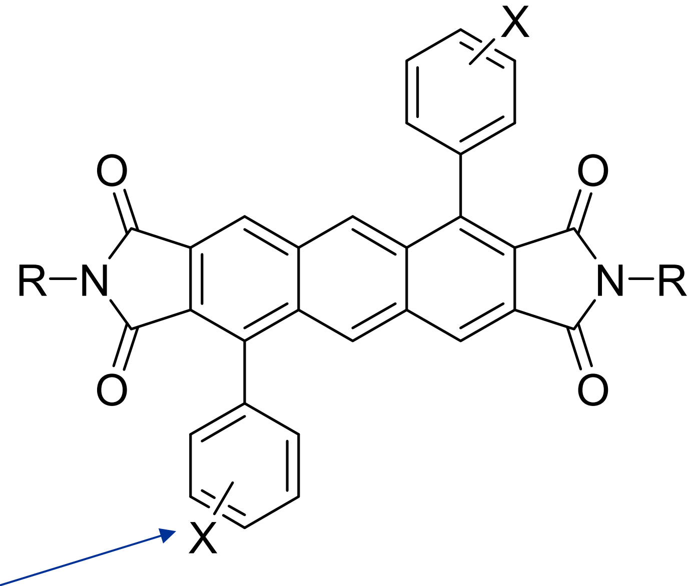


Dimethyl methylphosphonate (Me)

Sensor Effective for Both Liquids and Vapors



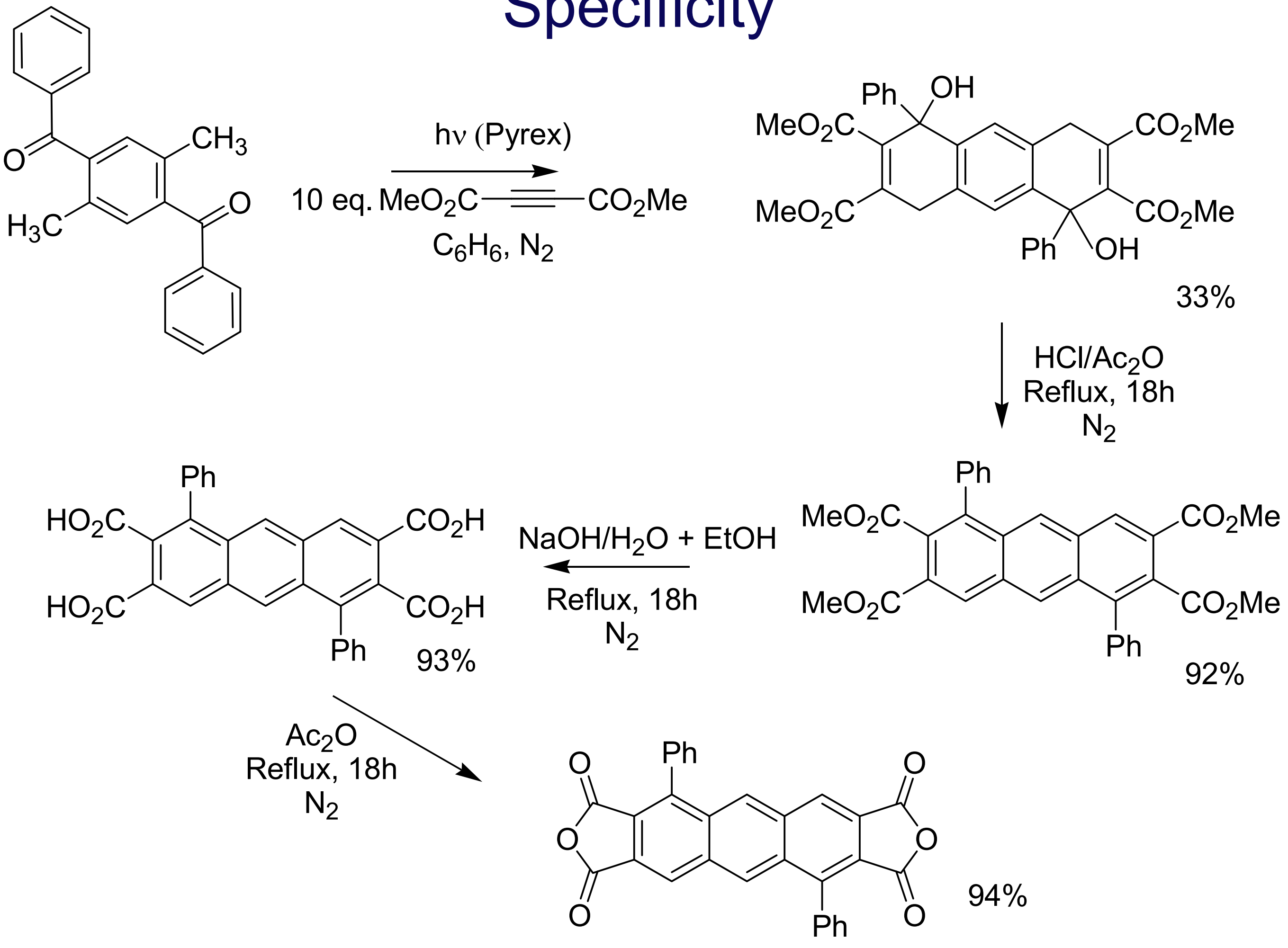
Anthracene Diimide Provides Platform for Charge Transfer Mediated Fluorescent Sensors



Electron donors that are tailored to interact with given analyte

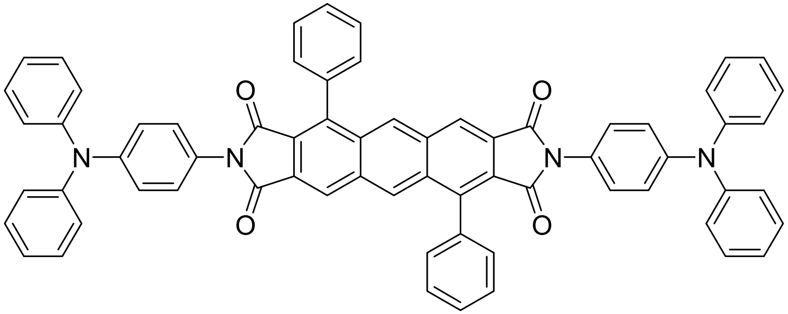
Tune absorption and emission

Anthracene Dianhydride is Key to Tailoring Sensor Specificity

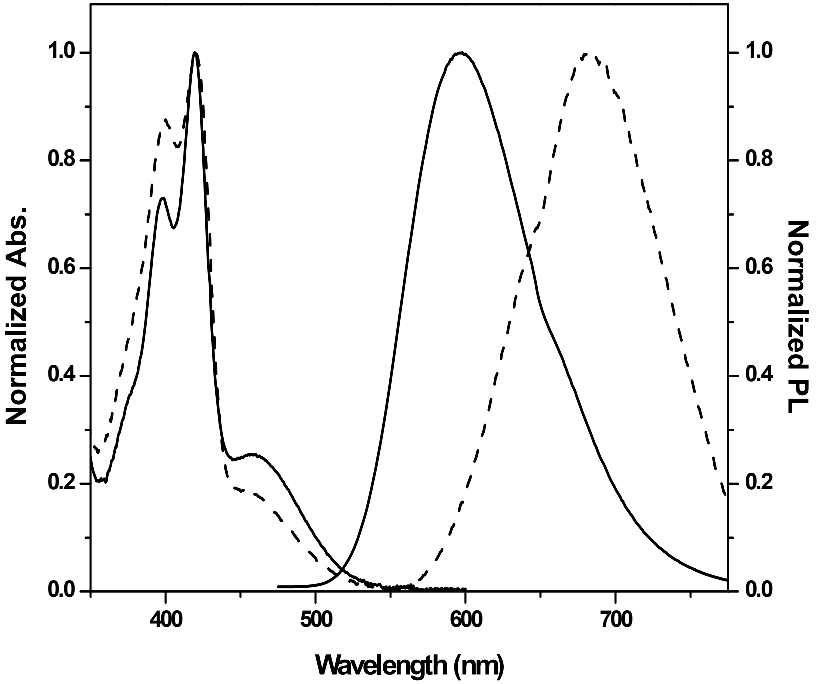


Enables attachment of substituents to imide N that might be photosensitive, e.g., pyridyl groups

Absorption and Emission Spectra



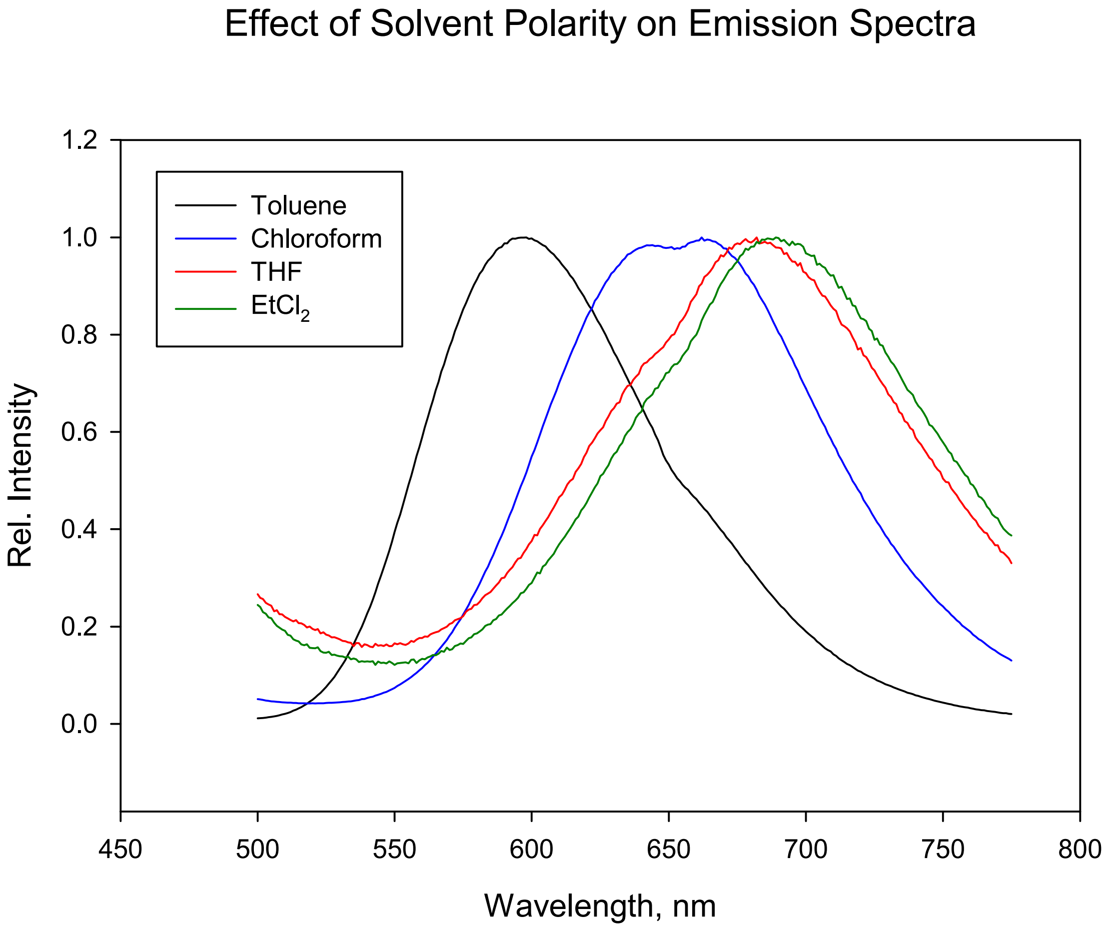
Absorption and Emission Spectra in Toluene and 1,2-Dichloroethane



Φ_f = 0.035 in Toluene

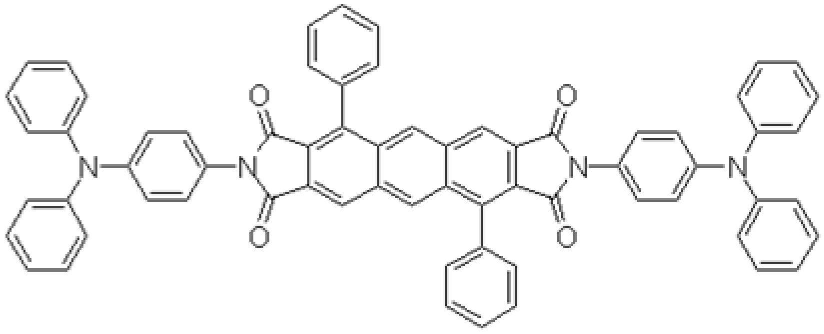
τ_f = 90ps

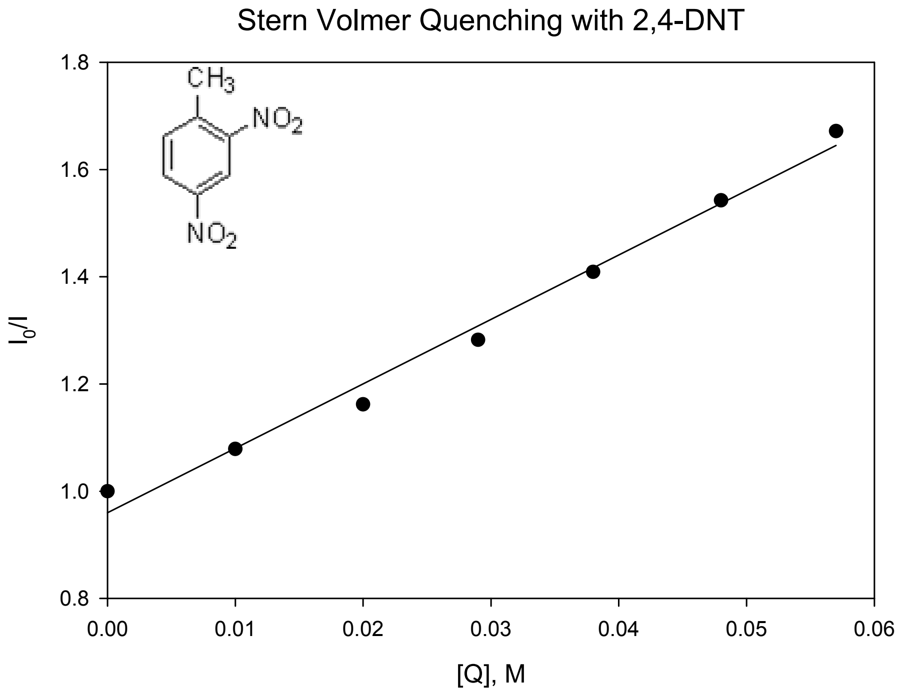
Diimide Fluoresence Shows Solvatochromic Behavior

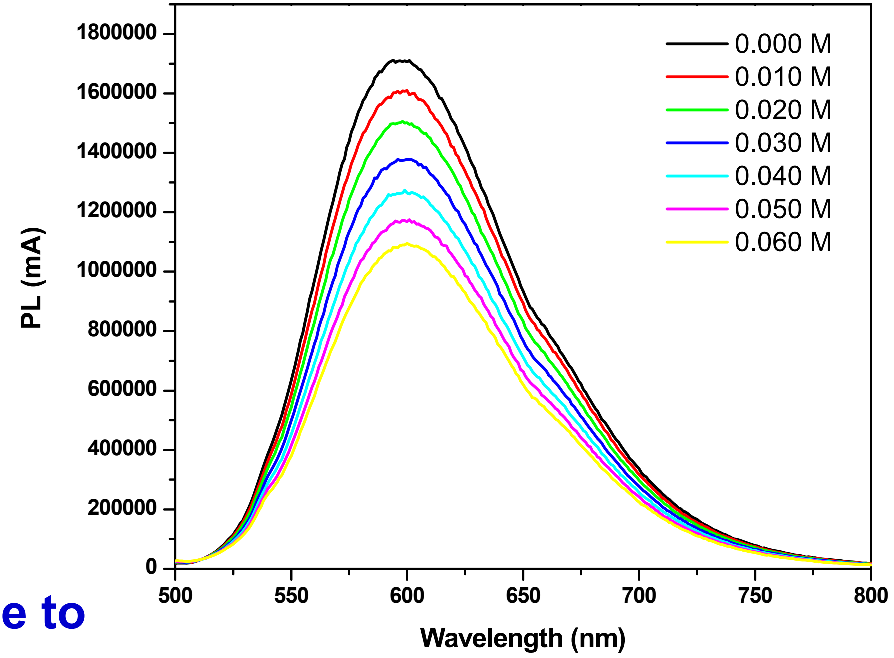


400 nm excitation

Diimide Fluorescence Quenched by Nitroaromatics

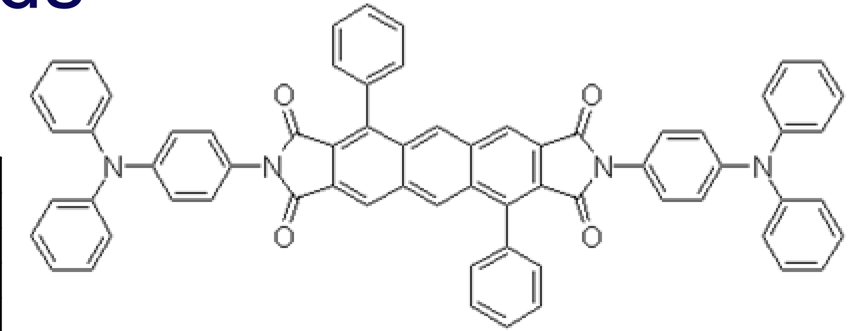


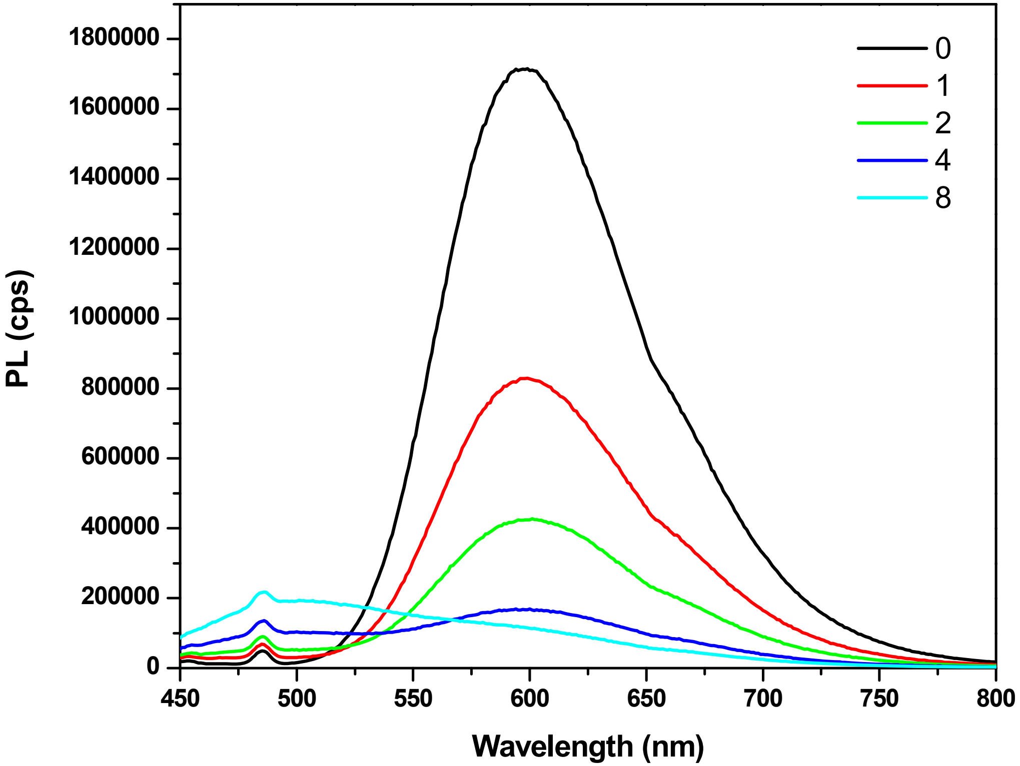




Excited state charge transfer from dye to nitroaromatics quenches fluorescence

Fluorescence Inhibited by Addition of Acids

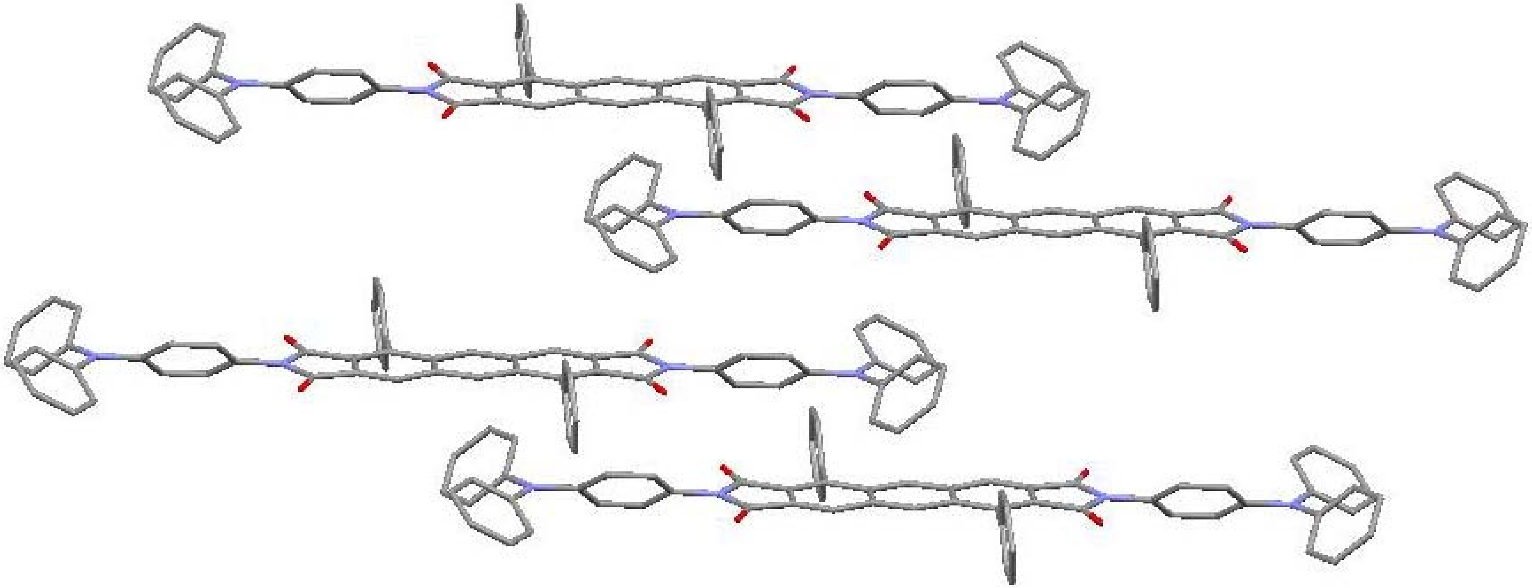




Addition of TFA protonates amine and inhibits charge transfer

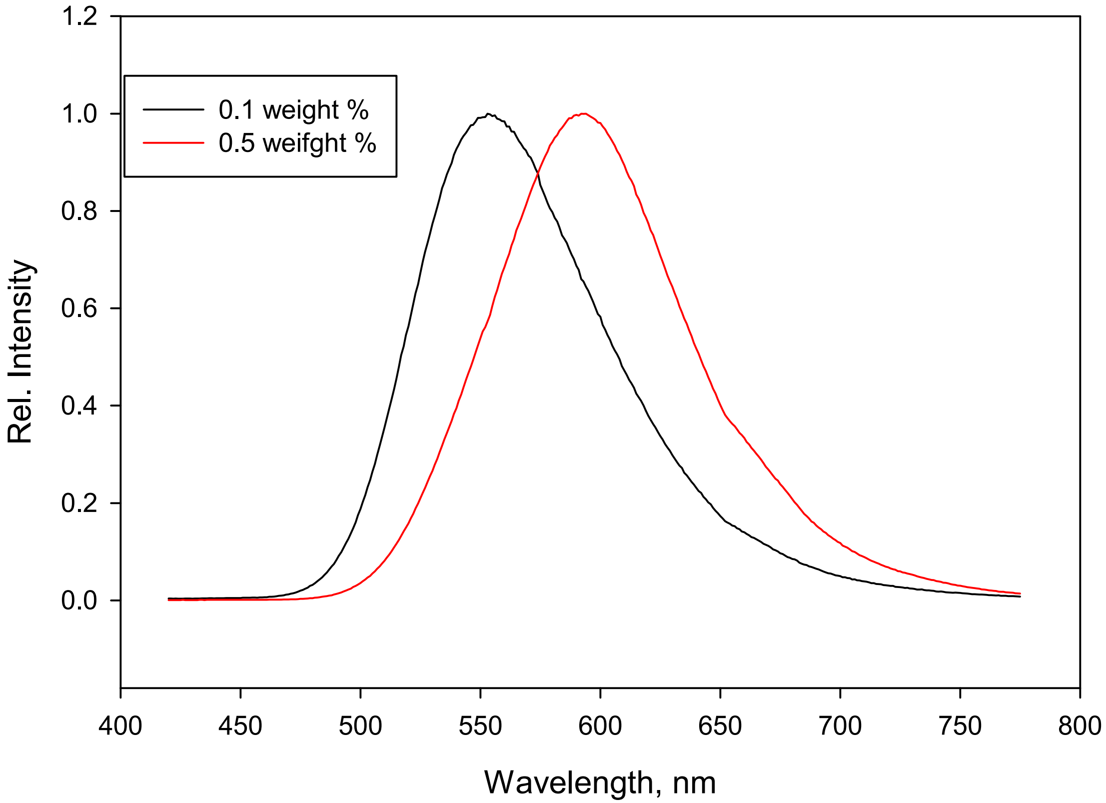
Excitation at 400 nm

Aggregate Formation in Solid State is Evident in X-Ray



Increased Loading Levels Lead to Red Shifted Emission

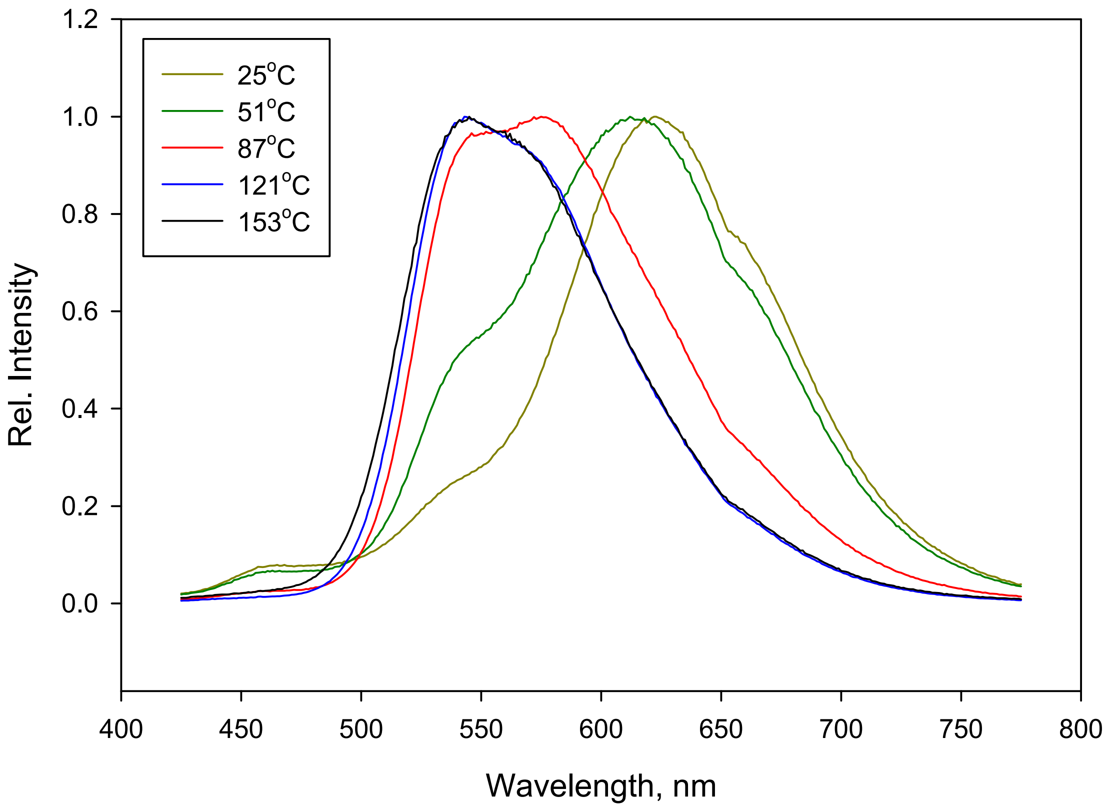
Emission Spectra in Polystyrene

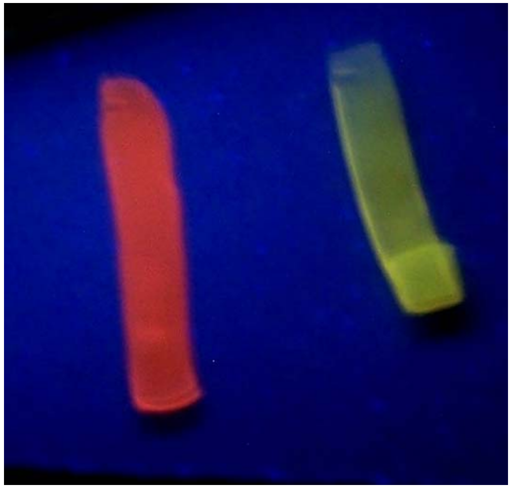


Suggests formation of dye aggregates in the polymer

TPAA Doped Films Exhibit Thermochromic Behavior

Effect of Temperature on Emission Spectra of Dye Doped LLDPE

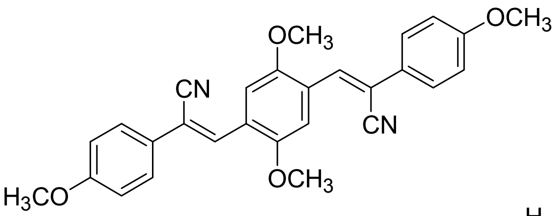




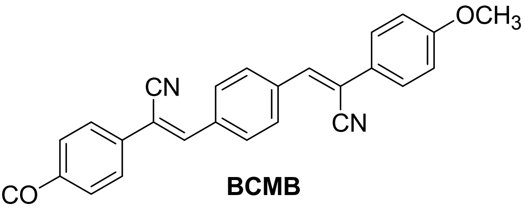
- Aggregation disrupted at higher temperatures – blue shift
- Process is reversible

Mechanochromic and Themochromic Polymers

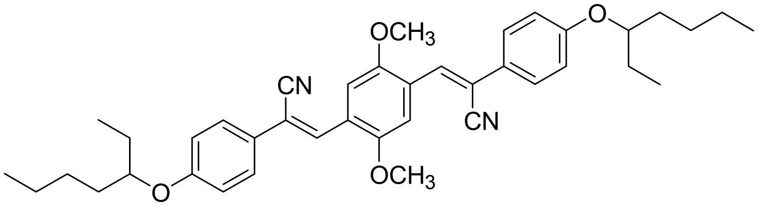
Crenshaw, B.R. and Weder, C. *Macromolecules* **2003**, *15*, 4717-24



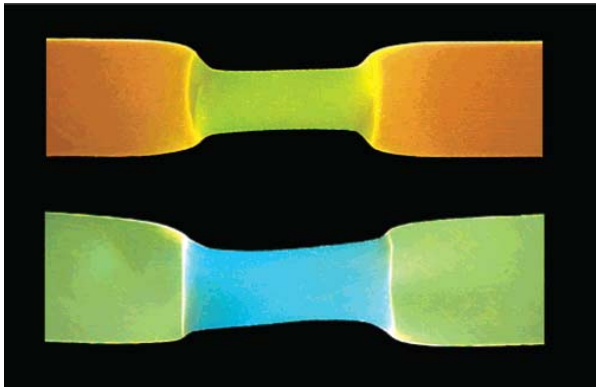
BCMDB



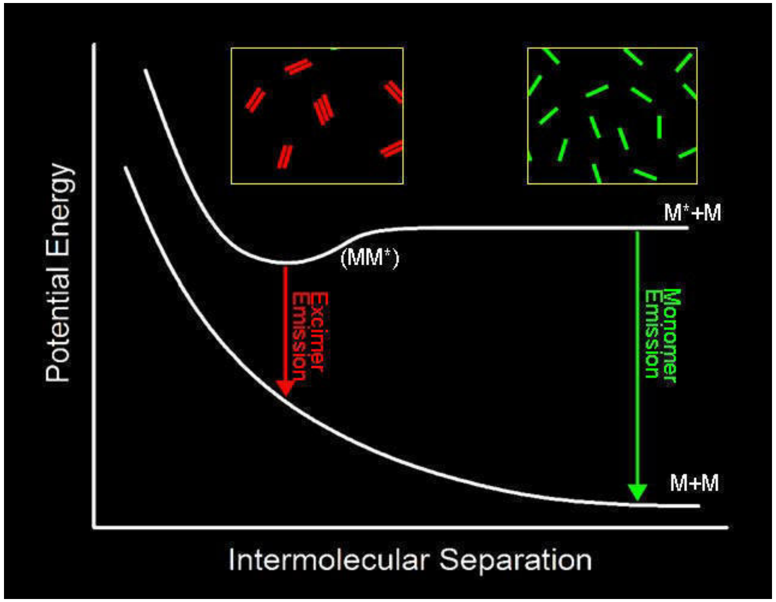
BCMB

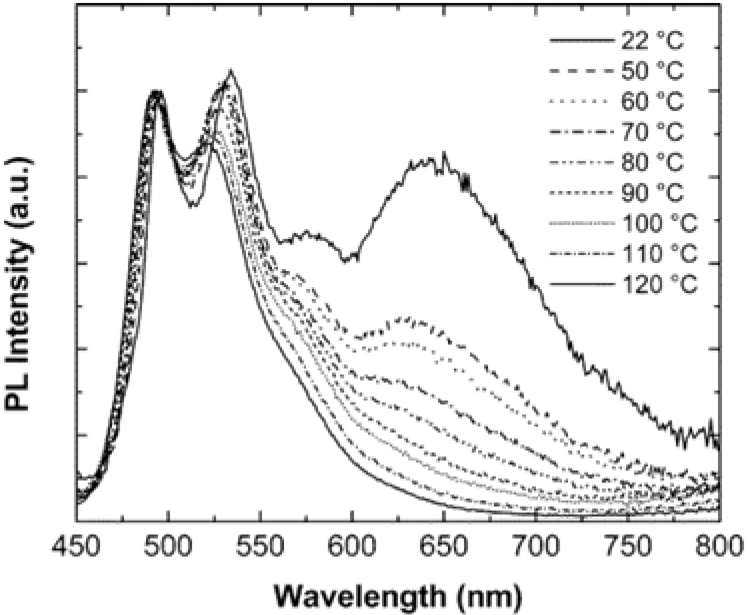


BCEDB



Stretched Films of 0.18 wt. % BCMDB and BCMB in LLPE



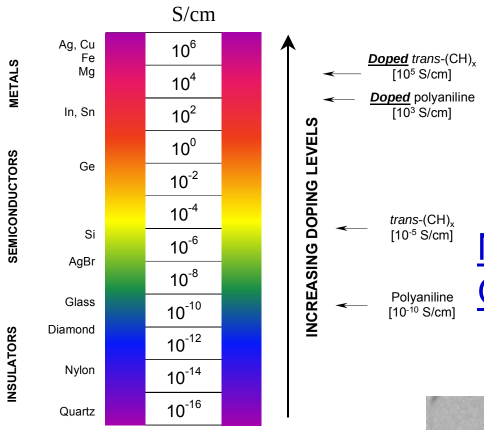


PL Spectra of 0.2 wt. % BCDMB/LLPE Film as a Function of Temperature

Polymer Films and Nanowires for Field Effect Transistors

Applications:

- Small size, power-efficient flexible electronic circuitry for space exploration applications
- Communications and data storage circuitry that can be interwoven into clothing and other surfaces
- Active matrix light emitting diodes, RF identification cards



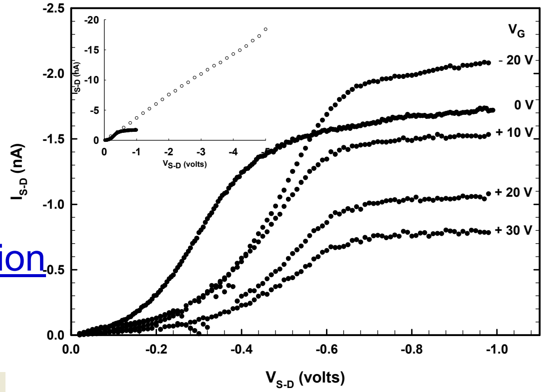
The electrical conductivity of bulk polyaniline can be varied From 10^{-10} to 6×10^{3} siemens per centimeter

Technology development requires interdisciplinary collaboration

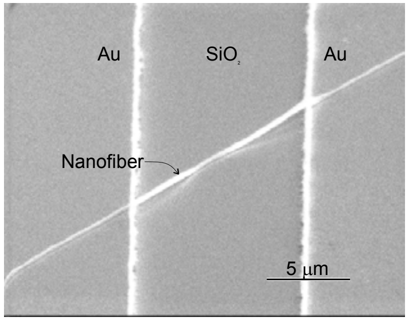
Materials Optimization

Nano-metrology

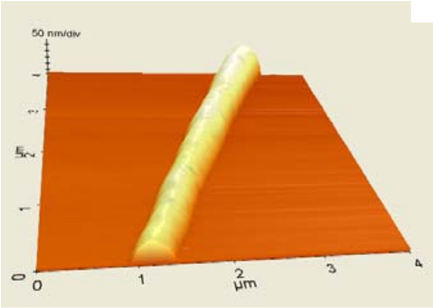
Device Characterization



Current- voltage characteristics of nanofiber FET



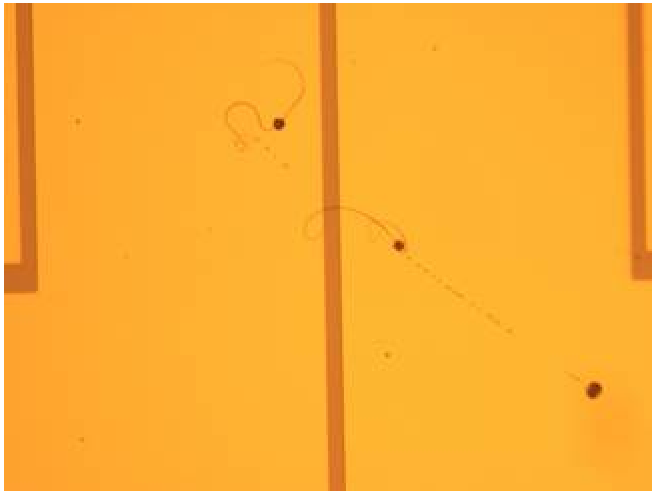
SEM image of nanofiber Deposited on metallized SiO_2/Si substrate



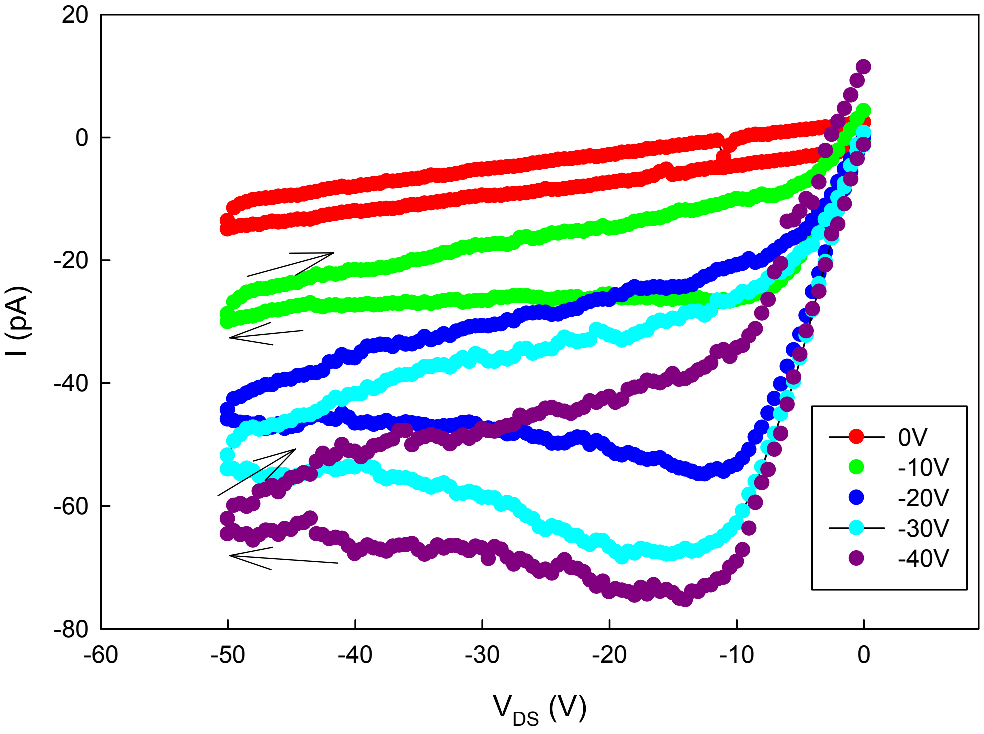
AFM image of polyaniline/ polyethylene nanofiber

Point of Contact:
Dr. Félix A. Miranda, RCA
216-433-6589

Pentacene/PEO Nanofiber FETs



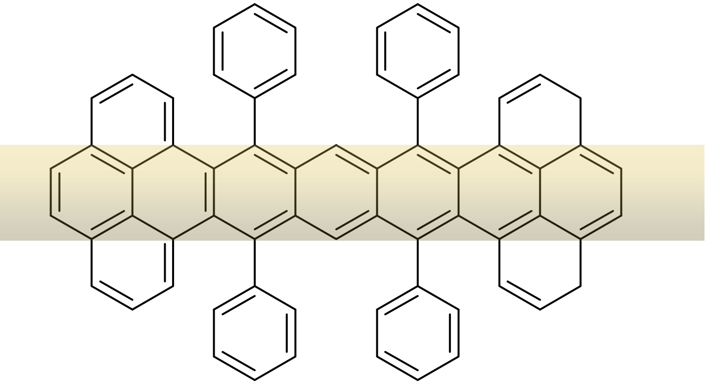
Electrospun Pentacene/PEO Fiber (vacuum)
20 August 2007

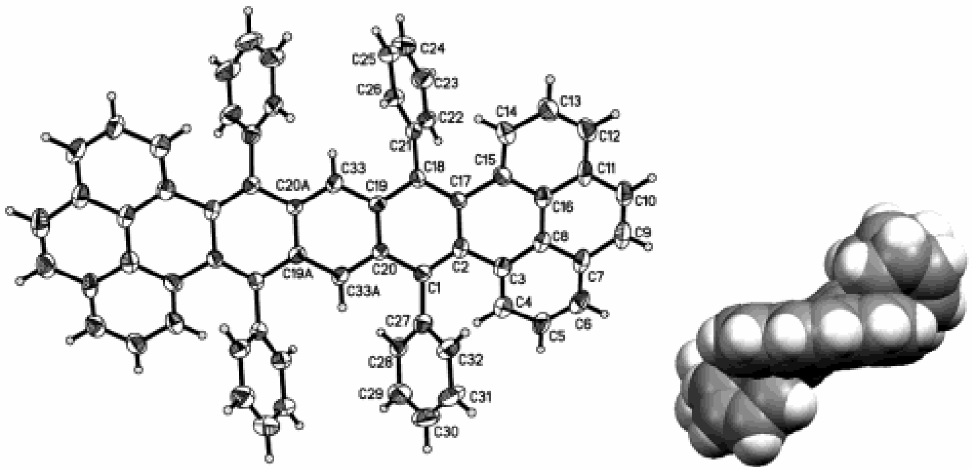


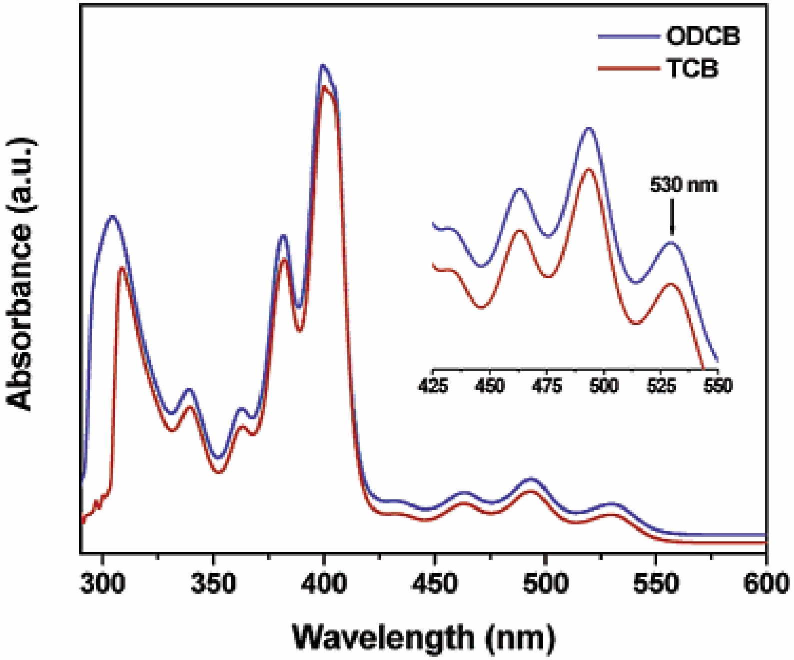
Pentacene/PEO nanofibers grown by Prof. Nicholas Pinto, U of Puerto Rico- Humacao

Twistacenes

Wudl, F. *et al Org. Lett.* **2003**, *5*, 4433-36

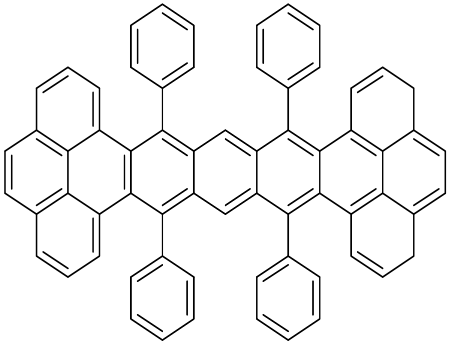


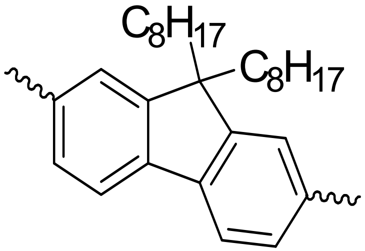


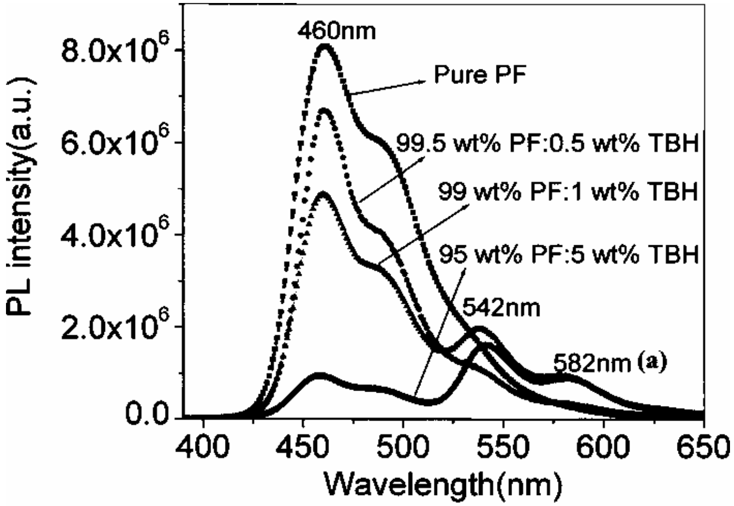


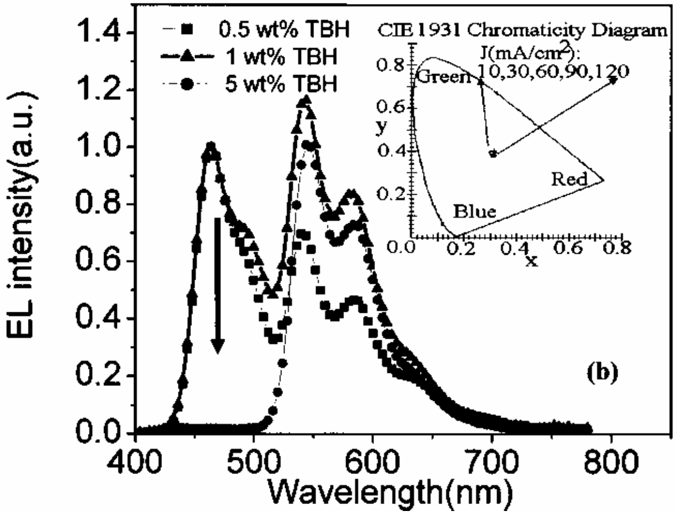
- Addition of pendant phenyls adds steric bulk-enhances photooxidative stability, prevents quenching
- Addition of perylene endgroups enhances Φ_f

Twistacenes





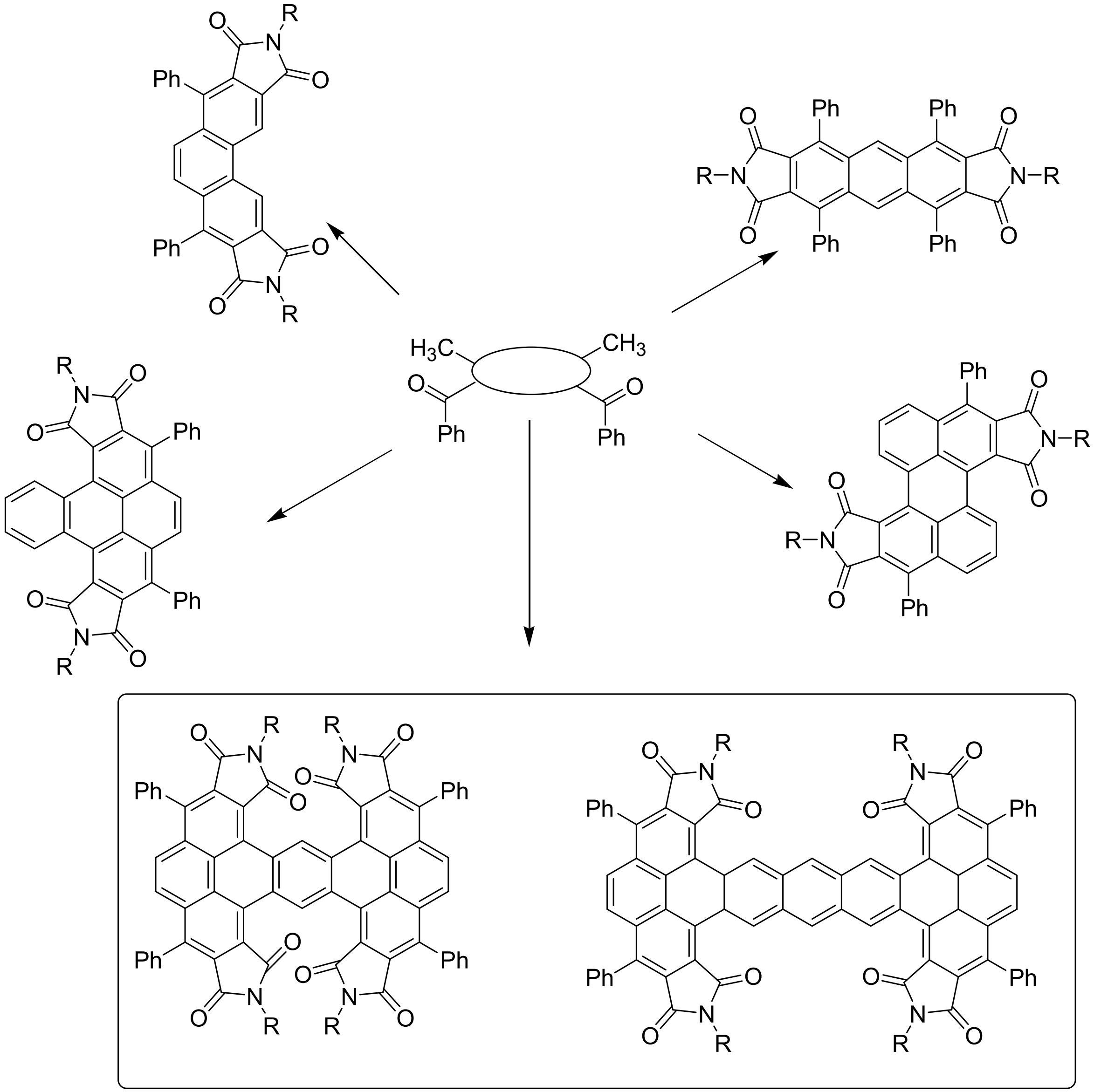




Xu, Q.; Duong, H.M.; Wudl, F.; Yang, Y. *Appl. Phys. Lett.* **2004**, *85*, 3357-59

Effect of added TBH on intensity of PL and EL of poly(fluorene films)

Beyond Anthracenes and Perylenes



- **Increasing number of benzene rings (conjugation) makes the molecule more polarizable**
- **Adding pendant groups improves stability and solid state fluorescence efficiency**
- **Flexible chemistry enables tailoring of electronic properties**
- **Potential for use in photovolatics, molecular electronics and photonics**

Summary

- Developed new route to highly substituted aryl diimides
  - Anthracenes
  - Perylenes
  - Pyrenes
  - Higher homologues
- Exploited excited state behavior to develop fluorescent sensors
  - Chemical species
  - Warfare agents
  - Temperature
- Incorporation of these dyes into polymers has the potential for making “smart” films, fibers, and composites

Acknowledgements

- NASA Undergraduate Student Research Program
- NASA Grant NNC07BA13B
- Funding from the Fundamental Aeronautics Program and the Glenn Innovative Research and Development Fund