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
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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

**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

**Functional Polymers**
- Adaptive polymers
- Fluorescent sensors
- Conductive membranes

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

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

Novel Perylene Diimide Has Potential as Strain Sensor

Red Luminescence 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

\[
\begin{align*}
\text{CH}_3 \text{O} & \quad \text{Ph} \\
\text{CH}_2 \text{OH} & \quad \text{Ph} \\
\text{HO} & \quad \text{Ph}
\end{align*}
\]

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

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

![Chemical Structure](image)

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Reaction Progress Can Be Monitored by $^1$H nmr
Mono- and Bisadduct Quantum Yield Effected by Extent of Diketone Conversion

\[ \Phi = \frac{\text{moles of photoprodudt}}{\text{Einstein of light}} \]

E/Z photoenol formation is 1:1 → Maximum theoretical quantum yield for monoadduct formation is 0.5
Bisadducts are Readily Converted into Anthracenes

\[
\begin{align*}
2 & \xrightarrow{\text{HCl/\text{Ac}_2\text{O}}} \text{Reflux, 3h} \rightarrow 3 \\
& \xrightarrow{\text{DDQ/\text{PhCl}}} \text{Reflux, 18h} \rightarrow 4
\end{align*}
\]

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Versatile Route to Arenes

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

$\Phi_f (\text{CH}_2\text{Cl}_2)$
Octyl = 0.67
$p$- Hexyloxyphenyl = 0.031
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

\[
\begin{align*}
\text{Ph}_2\text{C} & \quad \text{hv} \\
\text{Ph}_2\text{C} & \quad \rightarrow \\
\text{N} & \quad \text{R} \\
\text{N} & \quad \text{R} \\
\text{Ph}_2\text{C} & \quad \rightarrow \\
\text{Ph}_2\text{C} & \quad \rightarrow \\
\text{S}_8/\text{Ph}_2\text{O} & \quad \text{Reflux, 4h} \\
\text{R} & = \text{n-C}_8\text{H}_{17} \\
\text{R} & = \text{n-C}_8\text{H}_{17} \\
\text{R} & = \text{n-C}_8\text{H}_{17} \\
\end{align*}
\]
Absorption and Emission of Phenanthrene and Benzo[e]pyrene Bisimides and Benzo[e]pyrene

Spectra and quantum yields measured in CH$_2$Cl$_2$
Synthesis of Anthracene Diimides

\[
\begin{align*}
&\text{X} = \text{H}, \text{ OCH}_3, \text{ CN} \\
&R = \text{n-C}_8\text{H}_{17}, \text{Ph}, 4\text{-MeOPh}, 4\text{- (C}_6\text{H}_{13}\text{O})\text{Ph}, 4\text{-NO}_2\text{Ph}
\end{align*}
\]
Synthesis of Tetraaryl Diimides – Trapping Unaffected by Steric Hindrance

\[
X = H, \text{OCH}_3, \\
Y = H, \text{OCH}_3, \text{CN} \\
R = \text{n-C}_8\text{H}_{17}, \text{p-}(\text{C}_6\text{H}_{13}\text{O})\text{Ph}
\]
Substituent and Solvent Effects on Photophysics of Anthryl Diimides

Effect of Solvent on Fluorescence Quantum Yields

Effect of Solvent on Nor. PL (mV)

Wavelength (nm)

R = Octyl

R = Aryl

R = Aryl, X=OMe R = Aryl, X=CN

Tol

CHCl3

EA

THF

DCE

ACE

ACN

Wavelength (nm)

Nor. PL (mV)
Substituent and Solvent Effects on the Photophysics of Diimides

Fluorescence Quantum Yields

\[ \Phi_f \]

\( \Phi_f \) vs. Solvent and Substituent Effects

Wavelength (nm) vs. Nor. PL (mV)

\( X, Y = H \)

\( X, Y = \text{OMe} \)
Twisting of N-Aryl Group Inhibits Charge Transfer

- For R = \text{N-OH}_3
- For R = \text{N-C}_8H_{19}

Graphs showing normalized PL (mV) vs. Wavelength (nm) for different solvents and R groups.
Low Temperature Emission Spectra

Spectra measured in MeTHF at 77°C

Reducing temperature:
- Reduces rotational motion
- Inhibits charge transfer
Steric and Electronic Effects Regulate Excited State Photophysics

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

\( e^- \) Acceptor R’s
Restricted Rotation
\( e^- \) Donor R’s
Polar Solvents

\( e^- \) Acceptor X’s
\( e^- \) Donor X’s
LW
SW
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

- **Cl₂S** \( \Phi = 0.20 
- **Cl₂** \( \Phi = 0.19 
- **SOCl₂** \( \Phi = 0.12 
- **Cl** \( \Phi = 0.11 
- **Me** \( \Phi = 0.00 

Diagram shows emission intensity vs. wavelength for various organophosphates:
- Sarin (Sarin)
- Ethyl dichlorothiophosphate (Cl₂S)
- Methylphosphonic dichloride (Cl₂)
- 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 Fluorescence Shows Solvatochromic Behavior

Effect of Solvent Polarity on Emission Spectra

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

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 $6 \times 10^3$ siemens per centimeter.

Technology development requires interdisciplinary collaboration

Materials Optimization

Device Characterization

Nano-metrology

Current-voltage characteristics of nanofiber FET

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

Antenna, Microwave and Optical Systems Branch (RCA); Polymers Branch (RMP)
Electrospun Pentacene/PEO Fiber (vacuum)
20 August 2007

Pentacene/PEO nanofiber FETs

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

- Addition of pendant phenyls adds steric bulk-enhances photooxidative stability, prevents quenching
- Addition of perylene endgroups enhances $\Phi_f$
Twistacenes

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 photovoltaics, 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
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