Organic Materials Chemistry

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**Organic Materials Chemistry**

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**Approved for public release; distribution unlimited**
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BRIEF DESCRIPTION OF PORTFOLIO:
To exploit the uniqueness of organic/polymeric materials technologies for enabling future capabilities currently unavailable by discovering and improving their unique properties and processing characteristics

LIST SUB-AREAS IN PORTFOLIO:
Photonic Polymers/Organics
Electronic Polymers/Organics
Novel Properties Polymers/Organics
NanoTechnology
Organic Materials Chemistry

Research Objective and Challenges

To exploit the uniqueness of organic/polymeric materials technologies for enabling future capabilities currently unavailable by discovering and improving their unique properties and processing characteristics.

Challenges:
- Discover New Properties
- Control Properties
- Balance Secondary Properties

Approach:
- Molecular Engineering
- Processing Control
- Structure Property Relationship

- Program focused on developing new and controlled properties
- Not applications specific, but often use applications to guide the properties focuses

![Graph showing Tensile Modulus vs Compressive Strength for Pitch Based Carbon Fibers and PAN Based Carbon Fibers.](image-url)
<table>
<thead>
<tr>
<th></th>
<th>Small Molecule</th>
<th>Block CoPolymer</th>
<th>Star-Like Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au – Diameter (nm)</td>
<td>9 ± 0.44</td>
<td>13 ± 2</td>
<td>10.1 ± 0.3</td>
</tr>
<tr>
<td>Grams/L</td>
<td>5.11</td>
<td>0.56</td>
<td>20.2</td>
</tr>
<tr>
<td># Particles/L</td>
<td>6.9 × 10^{17}</td>
<td>2.5 × 10^{16}</td>
<td>2.0 × 10^{18}</td>
</tr>
<tr>
<td>Pt – Diameter (nm)</td>
<td>73 ± 5.74</td>
<td>6.0 ± 0.98</td>
<td>6.2 ± 0.2</td>
</tr>
<tr>
<td>Grams/L</td>
<td>4.86</td>
<td>0.86</td>
<td>26.3</td>
</tr>
<tr>
<td># Particles/L</td>
<td>1.1 × 10^{15}</td>
<td>3.6 × 10^{17}</td>
<td>1.1 × 10^{19}</td>
</tr>
<tr>
<td>Fe₂O₃ – Diameter (nm)</td>
<td>16 ± 1.49</td>
<td>10.8 ± 2.98</td>
<td>10.1 ± 0.5</td>
</tr>
<tr>
<td>Grams/L</td>
<td>2.94</td>
<td>1.81</td>
<td>36.2</td>
</tr>
<tr>
<td># Particles/L</td>
<td>2.6 × 10^{17}</td>
<td>6.552 × 10^{17}</td>
<td>1.3 × 10^{19}</td>
</tr>
<tr>
<td>Cd-Se-Diameter (nm)</td>
<td>8.5 ± 0.65</td>
<td>-----</td>
<td>9.9 ± 0.3</td>
</tr>
<tr>
<td>Grams/L</td>
<td>0.98</td>
<td>-----</td>
<td>22.8</td>
</tr>
<tr>
<td># Particles/L</td>
<td>5.2 × 10^{17}</td>
<td>-----</td>
<td>7.5 × 10^{18}</td>
</tr>
<tr>
<td>PbTiO₃ – Diameter (nm)</td>
<td>-----</td>
<td>50 ± 4.9</td>
<td>9.7 ± 0.4</td>
</tr>
<tr>
<td>Grams/L</td>
<td>-----</td>
<td>2.12</td>
<td>31.2</td>
</tr>
<tr>
<td># Particles/L</td>
<td>-----</td>
<td>4.1 × 10^{15}</td>
<td>7.5 × 10^{18}</td>
</tr>
</tbody>
</table>
NPs Synthesis by Novel Amphiphilic Star-Like Block Copolymers as Template
Core/Shell Nanoparticles – with Large Lattice Mismatch

Core/shell nanostructures are conventionally obtained by dissimilar materials epitaxy, which requires moderate lattice mismatches (<2%) between the two different materials in order to obtain high-quality core/shell heterostructures, which would otherwise be difficult to obtain.

\[
\text{Fe}_3\text{O}_4/\text{PbTiO}_3
\]

\[
D_{\text{Fe}_3\text{O}_4} = 6.1 \pm 0.3 \text{ nm (core)}
\]

\[
D_{\text{PbTiO}_3} = 3.1 \pm 0.3 \text{ nm (shell)}
\]

➢ Despite more than 40% lattice mismatch between \(\text{Fe}_3\text{O}_4\) and \(\text{PbTiO}_3\), \(\text{Fe}_3\text{O}_4/\text{PbTiO}_3\) core/shell nanoparticles can be readily crafted by this approach!!!
Hollow noble metal nanoparticles are the subject of intense research for use in bioimaging, photothermal therapy, drug delivery, etc. The thickness of Au is $3.2 \pm 0.3\text{nm}$.

The diameter of hollow core is $5.6 \pm 0.4\text{nm}$. Janus Nano-Particles
Phototropic liquid crystals
Tim White, Tim Bunning, AFRL/RX

“Phototropism”: A term used to describe light induced phase changes in liquid crystals.

An example of light induced order-disorder:

“Negative” phototropism – S (order parameter) decreases with light
In this case of “positive” phototropism, illumination increases the compatibility of the naphthopyran as the molecular shape becomes planar and quasi-rod like aligning favorably with the liquid crystalline phases.
AMI15/8CB Mixture Shows Additional Transition

AMI15/8CB shows Photoinduced
- Isotropic to Nematic Transition
- Nematic to Smectic A Transition

“Positive” phototropism – S (order parameter) increases with light

Different Phase Change with Chiral Dopant

AMI15/5CB/R1011 Mixture shows Photoinduced:
- Isotropic to Cholesteric Phase Transition

R1011 – a chiral dopant from Merck

5CB

Before irradiation – sample completely transmissive in VIS and NIR

After irradiation – sample becomes both absorptive and reflective

Data collected at AFRL/RX
Naphthopyran Phototropic Mixtures
Unprecedented “Photo-dichroism”

For the Isotropic to Nematic Transition in AMI15/5CB Mixtures,
Dramatic light induced changes in dichroic ratio from ~0 to 0.722

The mixture changes color and becomes polarized at the same time
(Plain Glasses become Polarized Sunglasses)
To craft novel *organic-inorganic nanocomposites* composed of Superparamagnetic Iron Oxide Nanoparticles (SPION) *intimately* and *permanently* connected with nematic liquid crystals (LCs) and chiral azo molecules with high helical twisting power (HTP) for many potential applications.

Potential for application in *communication devices, molecular devices, light-controllable devices, optical display system, optical data recording, photo-optical triggers, polarizers, and reflectors, and electromagnetic sensors, etc.*


**Light–induced liquid crystallinity**

**Color switching**
Background on 1-D Metal Chains:
- Solid-state mixed-valence 1-D chains with Metal–Metal bonds
- Aqueous mixed-valence oligomers

There are a few reports of infinite 1-D chains in the solid state with Metal–Metal bonds.
- Not solution stable; Solid-state syntheses take several days or weeks
  - low yield (usually 50% or less)
  - small scale (< 100 mg)

Chosen (d⁷-d⁸) oligomers: Pt blues, Ir blues, Rh oligomers.


New Chemistry – Solution Processible Palladium Wires

From Dimers to Wires:
- Infinite Pd chains in solid state revealed by X-ray crystallography
- Rapid, High-Yielding, Gram-Scale, Solution Phase Synthesis

Oxidation of dipalladium (III) complexes with coordinating anions (Cl–) leads to Pd dimers with covalent bond between the metal atoms.

The polymerization occurs in solution in less than 5 minutes, giving pure material on large scale.
Solution Stable 1-Dimensional Palladium Wire

1-D metal wires are predicted to display room temperature superconductivity

- Lengths up to 750 nm (>1,300 Pd atoms) observed in solution
- The longest solution-stable metal–metal bonded chain previously reported with assigned length contains 12 metal atoms‡.
- Choice of counter-Anion controls chain length
- Enabled efficient device fabrication, not possible with previous 1-D wires

Thin-Film Conductivity:

- Solution processing capabilities allow for thin-film coating
- Four-point probe device used to measure conductivity of 1-D wire polymers film

Devices were fabricated using thin films of the 1-D wire polymers, which could be deposited from dichloromethane solutions either by drop casting or spin coating.

Tuning of Electronic Properties

Tuning Flexibility:
- Side Group Solubility
- Counter Ion
- Pd Oxidation State

Films based on Pd(2.5) display the first example of a transition to a metallic state observed at ambient pressure for a polymer based on 1-D metal wires.

Solution-stable 1-D metal wires with tunable conductive properties may have an impact on areas such as:

- Next-Generation Solar Cells
- Molecular Sensors
- Molecular Wires for Nanoscale Circuits

Nature Chem. 2011, 3, 949–953
First demonstration of electricity generation from polymeric materials.
Air-stable fabric thermoelectric modules made of n & p-type composites

Objective: Demonstrate power generation & cooling with organic composites

(1) Flexible composite

(2) Module fabrication

(3) Multiple junctions in series

Voltage output vs Temperature

Power output vs Temperature

Voltage and power are being increased by:
(a) stacking more layers;
(b) connecting more modules
Improving Power Factor by Tuning P-type composites with multiple CNT stabilizers

Objective: Produce the highest possible power factor (PF) for fully organic, flexible composites

- Double-walled carbon nanotubes (DWNT) are stabilized with two different molecules in poly(vinyl acetate) latex:
  - PEDOT:PSS (conductive)
  - TCPP (semi-conductive)

Electrical conductivity increases with DWNT concentration; while the Seebeck coefficient remains relatively insensitive.

The power factor \((S^2\sigma)\) increases with DWNT concentration and is within an order of magnitude of traditional inorganics (maroon shaded region).

Highest PF ever reported for fully organic composite at \(~500\ \mu\text{W(m\cdot K}^2)\)!
Different Module Design Concept
David Carroll, Wake Forest U.

Using Different CNT Compositions and TE Module Concept

The garment has recently been shown on CNN International, CNBC, and the Discovery Channel.
Photorefractive Polymers
Multi-TD’s Interests

- Laser Refraction
- Optical Signal Processing
- Wave Front Correction
- 3D Holographic Display
- Image Correlation

Earlier Results
<table>
<thead>
<tr>
<th></th>
<th>Earlier</th>
<th>Now</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminance</td>
<td>350Cd/m²</td>
<td>1000Cd/m²</td>
</tr>
<tr>
<td>Image Holding</td>
<td>&lt;50Cd/m²</td>
<td>&gt;200Cd/m²</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>200mW</td>
<td>1W</td>
</tr>
</tbody>
</table>

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Cross Correlation in Signals with Cluttered Background and Poor Discrimination are Issues in Target Recognition Applications

Breakthrough in Correlation Filter Success due to Two Efforts

1. The holographic, dynamic range compression developed by AFRL/RY (Jed Khoury)

2. Organic photorefractive material that was developed by University of Arizona/Nitto Denko

Both efforts funded by AFOSR
No correlation filter in the last 50 years, since the first correlation invented by Vander Lugt (1963), have been designed that can improve simultaneously the discrimination, the signal-to-noise ratio, and the peak-to-noise ratio.

Using input that has a lot of background noise, Two Beam Coupling Correlation is:

- 1.5X better than Yaroslavsky Optimal filter
- 10X better than Phase-only filter
- superior to Matched filter (failed to recognize target)

But the scheme will require very large beam ratio, that will require a photorefractive material that has very high diffraction efficiency.
Arcs instead of full rings due to asymmetric dephasing.

Thick arc line due to broad impulse response.

Only first order correlation peaks.

**Bulk photorefractive**

**Thin film photorefractive polymer**

Many orders.

Sharp, narrow, symmetric.

**Asymmetric**

**Thick**

**One**

**broad**

**Input Image**

Full rings, nearly symmetric due to negligible dephasing factor in thin film polymer.

Narrow ring lines due to narrow impulse response with thin photorefractive polymer.

Very narrow and sharp correlation peak due to narrow impulse response.

Numerous correlation orders due to very small dephasing.

**A Thick BSO Crystal**

Point source (δ-function input)

Thick diffracted beam (Broad impulse response)

**A Thin Nitto Denko Organic Material**

Point source (δ-function input)

Thin diffracted beam (Narrow impulse response)

Dephasing Factor is small in thin film holographic materials.
Two Beam Coupling Experiment with PR Polymer Thin Film (1)

Input Data

Dynamic range compression increases
Two Beam Coupling Experiment with PR Polymer Thin Film (2)

Dynamic range compression increases

Input Data

Dynamic range compression increases
Applied to Synthetic Aperture Radar Data

Dynamic range compression increases

The first correlation filter that can improve simultaneously the
- SNR (100X)
- PNR,
- Discrimination (3 orders of Magnitude)

Material Chemistry Makes It Possible!!!

Correlation filter that outperforms optimal digital correlation filters
Portfolio Trends

Decreasing Emphases:
- Organic Solar Cells
- Organic Transistors

Increasing Emphases:
- Self Assembly in Solid State
- Radical, Spin and Excited State Controlled Properties
Summary

- Program Focused on developing New and Controlled Properties
- Not applications specific, but often use applications to guide the properties focuses
- Scientific Challenges
  - Discover New Properties
  - Control Properties
  - Balance Secondary Properties
- General Approaches
  - Molecular Design
  - Processing Control
  - Establish Structure Properties Relationship