MSE 207 RESEARCH ARTICLE PRESENTATION

TITLE: BIPHASE MICRO/NANOMETER SIZED SINGLE CRYSTALS OF ORGANIC SEMICONDUCTORS: CONTROL SYNTHESIS AND THEIR STRONG PHASE DEPENDENT OPTOELECTRONIC PROPERTIES

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THE CONTEXT

- **Organic Single-Crystal Devices:** These devices offer a "best of both worlds" approach, combining the advantages of single crystals and organic semiconductors.

- **Merits of Single Crystals:**
  - They have perfect molecular ordering.
  - They are free of "grain boundaries," which are defects that act as performance-killers in most devices.

- **Advantages of Organic Semiconductors:**
  - They are easy to modify and their properties can be "tuned."
  - They are inherently flexible, low-cost, and lightweight.

- **Why They are Scientifically Valuable:**
  - They provide an ideal platform to reveal the true, intrinsic properties of a material.
  - They are essential for understanding the link between a molecule's structure and its electrical properties.

PROBLEM

- **Device of Interest: The Photoswitch**
  - Definition: A photoswitch is a device that uses light to control the flow of electrical current, much like a switch on a wall.
- **Working Analogy:**
  - It's a "three-terminal" device, just like a standard Field-Effect Transistor (FET).
  - But instead of a physical gate, it uses light as an "unconventional gate" to turn the device ON and OFF.
- **The Problem: A Major Performance Gap**
  - The performance of organic photoswitches is "extremely lower" than devices made from traditional inorganic materials (like silicon).
- **The Quantitative Benchmark (The "Gap"):**
  - Inorganic Materials: Can have a light/dark current ratio (the ON/OFF ratio) as high as 10^3.
  - Organic Materials: Are typically limited to a ratio of only about 10^2.
- **The Goal:** To create an organic photoswitch that can close this 10x performance gap.

SUITABLE MATERIAL (BPEA)

- **The Molecule:** 9,10-bis(phenylethynyl)anthracene (BPEA).
- **What it is Known For:**
  - BPEA is famous for its strong fluorescent properties and high emission efficiency.
  - It's commonly used in things that create light, like fluorescent dyes and OLEDs.
- **Why We Chose It:**
  - BPEA is "biphase," or polymorphic. This means the same molecule can form single crystals in two different 3D structures, known as α phase and β phase.
  - This makes BPEA a perfect candidate to study the relationship between a crystal's structure and its performance.

PHASES OF BPEA

The two phases are made of the same molecule but have radically different 3D structures.

Phase α (Alpha):

- Conformation: The BPEA molecule itself is nearly planar (flat).
- Crystal System: Monoclinic (C_2/c).
- Packing: A typical “herringbone” pattern, with a wide angle of about 79.2°.

Phase β (Beta):

- Conformation: The BPEA molecule adopts a nonplanar (twisted) structure.
- Crystal System: Orthorhombic (Phen).
- Packing: Also a herringbone, but with a very sharp, acute angle of about 27.3°.

Key Structural Takeaway: The β phase's sharp angle means its molecules are packed "more close to face-to-face" or lamellar stacking. This is a crucial difference.

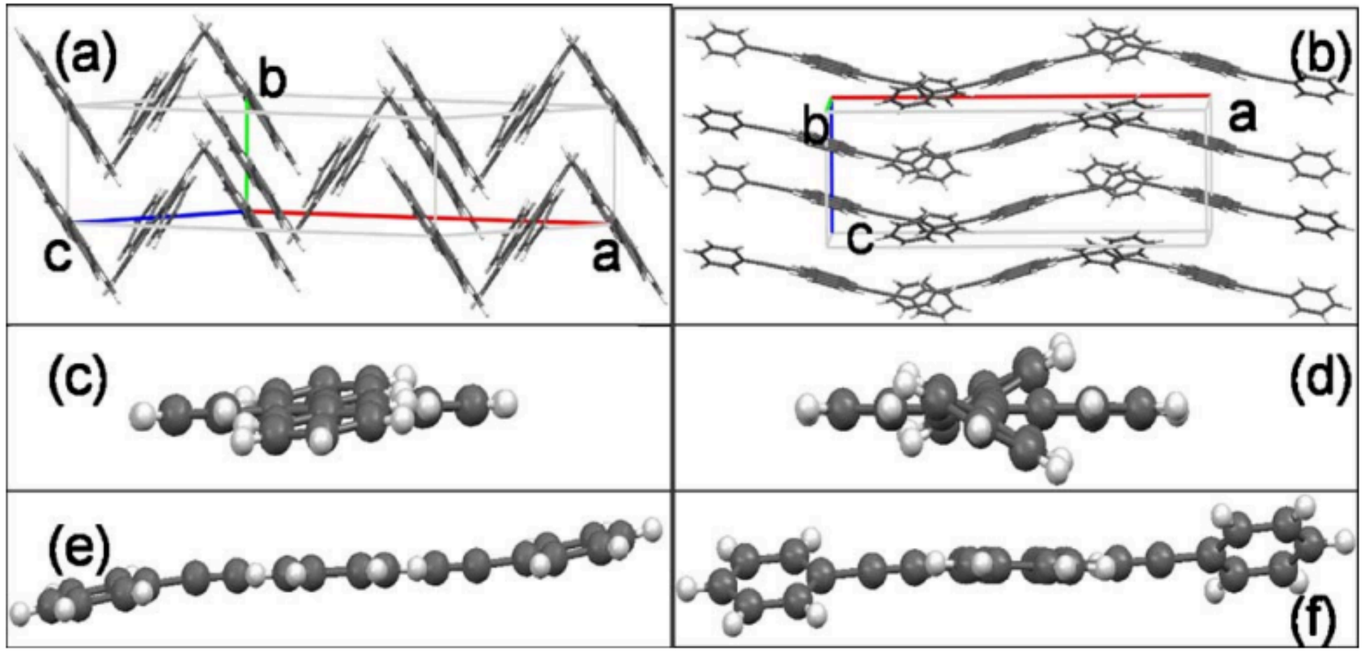


FIG. 1. (Color online) The single crystal diffraction results of α and β phase BPEA. (a) and (b) Packing diagram, (c) and (d) molecular structure viewed along the long axis, and (e) and (f) molecular structure viewed along the short axis. (a), (c), and (e) phase α; (b), (d), and (f) phase β.

THE BREAKTHROUGH (CONTROL SYNTHESIS)

The Method: We used a simple "drop casting" method. The choice of solvent acts as the "control knob" for the crystal phase.

Synthesizing Phase α (Rods):

- **Solvent:** Chlorobenzene.
- **Result:** This forms thick, rod-like microcrystals (a typical rod is ~440 nm thick).

Synthesizing Phase β (Ribbons):

- **Solvent:** Dichloromethane.
- **Result:** This forms very thin, wide ribbons (a typical ribbon is only ~60 nm thick).

The Proof:

- Selected Area Electron Diffraction (SAED) patterns confirmed the rods and ribbons have "different structure and packing."
- SAED also confirmed the ribbons were single crystals and "belonged to β phase."

DIFFERENCE BETWEEN TWO DEVICES

We tested both phases as transistors (FETs) and as photoswitches, and found they have completely opposite properties.

- Phase α (Rods): The Good FET
  - Field-Effect Transistor (FET): High performance, with mobility up to 0.73 $cm^2/V \cdot s$.
  - Photoswitch: Poor performance, with a light/dark current ratio of ~10^2 (the original problem).
- Phase β (Ribbons): The Good Photoswitch
  - Field-Effect Transistor (FET): Very poor performance, with mobility less than 0.01 $cm^2/V \cdot s$.
  - Photoswitch: Record-breaking performance, with a light/dark current ratio up to 6×10^3.

THE SOLUTION

This slide highlights the main achievement and frames it against the initial problem.

- **Recall the Problem**:
  - Organic photoswitches were stuck at a ratio of ~10^2.
  - The inorganic benchmark to beat was ~10^3.
- **The Solution Delivered**:
  - The β-Phase BPEA device achieved a light/dark current ratio of 6×10^3.
- **The Significance**:
  - This result is 6 times better than the inorganic benchmark.
  - It is "one of the highest values reported for organic materials."
  - This high ratio was "even rarely obtained in inorganic materials."

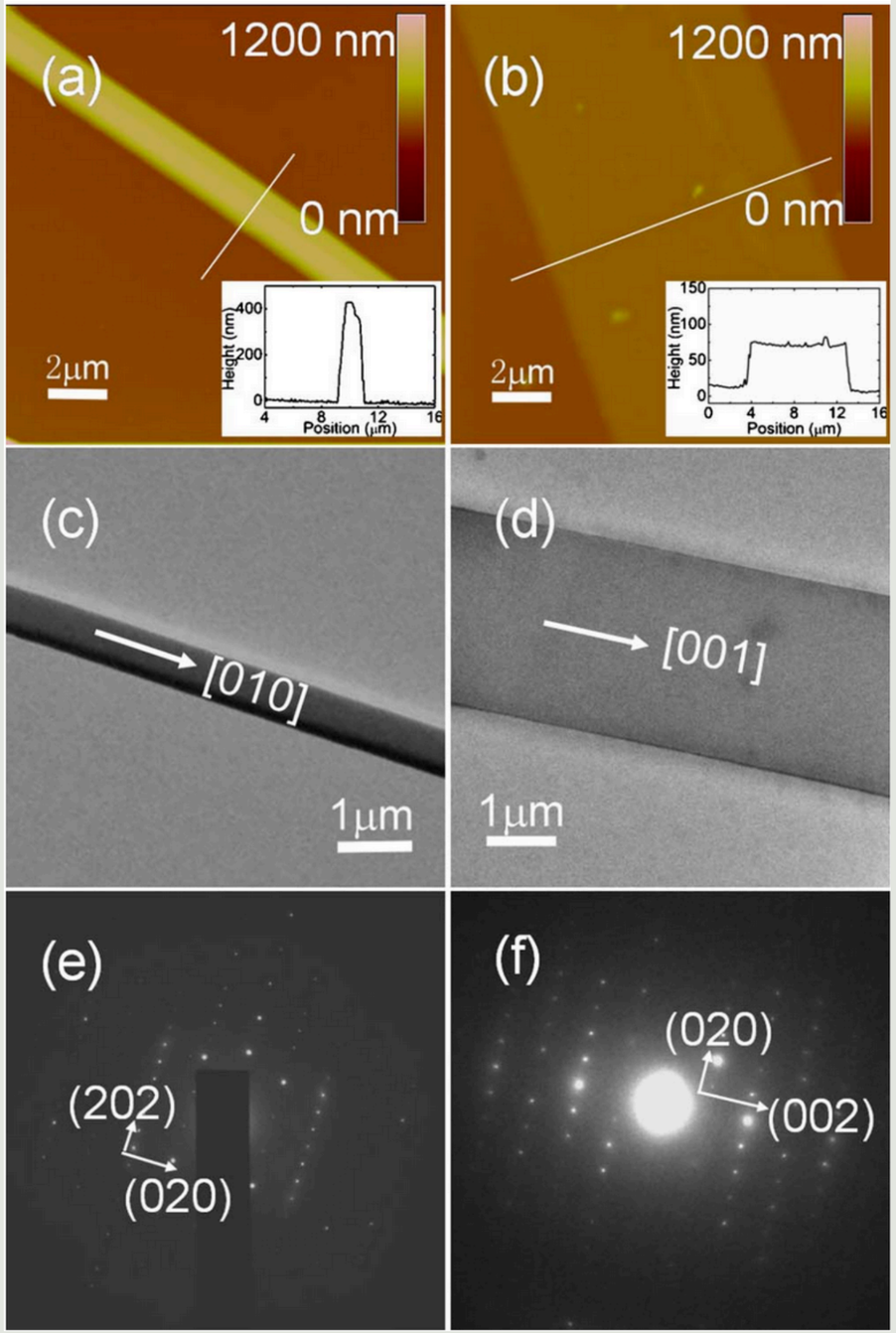
The "Why?"

The Core Reason: The huge difference in properties is due to two factors:

- The "different molecular conformations and arrangements" (Slide 5).
- The "different working mechanisms" of the two device types.

- Field-Effect Transistors (FETs) are "Injection-Limited":
  - An FET works when a gate voltage injects charge from the electrode into the material.
- Why β-Phase Fails:
  - Its twisted (nonplanar) structure disrupted the conjugation and lowered the HOMO energy level.
  - This created a larger mismatch with the electrodes, blocking charge injection and resulting in low mobility.

- Photoswitches are "Transport-Limited":
  - A photoswitch works when light creates carriers (excitons) inside the material, which then transport to the electrodes.
- Why β-Phase Succeeds:
  - In this mechanism, the low HOMO level (the injection problem) is not the main factor.
- The dominant factor is the nearly face-to-face packing, which acts like a "superhighway" and is more effective at transporting the generated carriers than the α-phase's packing.



- (a) AFM image of α-phase BPEA micro/nanorods grown from solution on OTS-modified SiO_2 substrate. Rods are about 440 nm thick and ~1.9 μm wide.
- (b) AFM image of β-phase BPEA micro/nanoribbons grown from dichloromethane solution. Ribbons are much thinner (~60 nm) and wider (~10 μm).
- (c) SEM image of an α-phase rod showing the crystal growth direction along [010].
- (d) SEM image of a β-phase ribbon showing the growth direction along [001].
- (e) SAED pattern of the α-phase rod, indexed to (020) and (202) planes.
- (f) SAED pattern of the β-phase ribbon, showing distinct diffraction spots (020), (002), confirming single-crystalline nature.

Conclusion & Impact

- **Synthesis**:
  - We successfully achieved the controlled synthesis of both α- and β-phase micro/nanosized single crystals of BPEA.
- **Performance**:
  - α-phase devices displayed high field-effect performance, making them excellent FETs.
  - β-phase devices exhibited very high photoswitch performance, with a record-breaking on/off ratio that surpassed the inorganic benchmark.
- **Scientific Impact**:
  - These quite distinct phenomena provide a deep and clear understanding of the structure–property relationship.
  - The results help explain the different working mechanisms of FETs (injection-limited) and photoswitches (transport-limited).
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Key Takeaway: Crystal packing is a powerful tool. By simply changing how a molecule is stacked, we can tune its function from a great transistor to a record-breaking photoswitch.

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Thank You

For your attention