Biopolymers assume structural and functional roles in nature and in commercial applications. The ability to organize other molecules is an underutilized function that will be discussed in the context of two different biopolymers. Cellulose nanocrystals (CNCs) align in parallel fashion to produce liquid crystals. The potential exists for semiconducting polymers to follow CNCs into the aligned state, thereby leading to materials with enhanced optoelectronic performance. Having achieved their organizational objective, the CNCs will remain to confer mechanical strength. A different route to organization uses biosurfactant proteins known as hydrophobins. Produced by fungi in the forest and on the farm, these small proteins assemble into strong films that can encapsulate many fluids, including semiconducting polymer solutions. Improved alignment and attendant performance gains may be realized as the solvent leaks out of the capsules, progressively concentrating the polymers into waterborne latex particles for easy and environmentally friendly application.
Some pairings are particularly powerful organizers.

Pairing #1: Cellulose nanocrystals and polythiophenes.

![CNC](Fleming, Gray, Prasannan & Matthews JACS 2000 (10.1021/ja000764e))

Sigourney Weaver as Gatekeeper
Rick Moranis as Keymaster
(Ghostbusters, 1989)

Together they organized the spirit world.


Maybe together they can organize electron flow.
We are having trouble with hydrocarbon-soluble CNCs, so we have begun with this water-soluble semiconducting polymer.

\[
\text{poly[3-(potassium-4-butanoate)thiophene-2,5-diyl]} \]

\[
M=16,000 \text{ g/mol polymer} \\
M_o = 206 \text{ g/mol monomer} \\
N \approx 80 \\
L \approx 300 \text{ Å} \equiv 30 \text{ nm}
\]
Mix 3 mg/mL PPBT in aqueous CNCs at 5%. After one week, liquid crystal domains appear under Polarized Optical Microscopy.

3 mg/mL PPBT + 5 wt% CNCs

Average Pitch = 4.36 ± 0.27 μm
Water-soluble PPBT polythiophene does not alter CNC phase transition points.

X marks the spots when we mixed 3 mg/mL PPBT (structure below) with varying amounts of CNCs (0, 2, 5, 8 wt%).

X

Volume Fraction Anisotropic Phase

Total CNC Concentration (wt%)

poly[3-(potassium-4-butanoate)thiophene-2,5-diyl]
Solution UV-Vis shows increased ordering with addition of CNCs.

3 mg/mL PPBT
Same thing at higher PPBT loading.

5 mg/mL PPBT

![Absorbance vs Wavelength Graph](image)
A model by Spano correlates increase in effective conjugation length of the semiconducting polymer with addition of CNCs.

\[
\frac{A_{0\ 0}}{A_{0\ 1}} = \left( \frac{1 - 0.24W / E_p}{1 + 0.73W / E_p} \right)^2
\]

\( W = \) free exciton bandwidth

\( E_p = \) energy of main intra-molecular transition

(0.18 eV for symmetric C=C stretch = 4.5 \( \times \) \( k_B \) \( T \))

** Decrease in \( W \) represents an increase in conjugation length**
PSE Fellow Bailey Risteen’s future work:

- Time dependence of PPBT/CNC pitch, compare with pure CNC pitch
- Depletion studies: maintain CNC wt% but increase PPBT concentration to see if it induces LC phase
- UV-Vis of PPBT/CNC films (spin coating, blade coating)
- Make/test devices?
Part I Conclusion:
It does seem that CNC Liquid Crystals improve alignment of PPBT.
Some pairings are so crazy they just have to be tried.

Pairing #2: Fungal hydrophobins and P3HT.

$\leftarrow$ Hydrophobin HFBII

$\leftarrow$ P3HT in pi-stacks

Spano & Silva
Annu. Rev. P. Chem. 2014
10.1146/annurev-physchem-040513-103639

Again, the idea is to organize electron flow.
Hydrophobins are nature’s most surface-active proteins.

↓ Sequence for Cerato ulmin


Nature’s Janus particle.

↔ Hydrophobin HFBII

green = hydrophobic

Temple B, Horgen PA
Biological roles for cerato-ulmin, a hydrophobin secreted by the elm pathogens, *Ophiostoma ulmi* and *O-novo-ulmi*

*Mycol* 2000;92:1-9
Hydrophobins are secreted by fungi; no one knows why, but yesterday here at RBI Gregg Beckham from NREL demonstrated that fungal enzymes have a role in converting biomass. Those fungi will also be producing hydrophobins.

Edible ‘shrooms in a Manhattan Market

Giant mushroom found under a tree at Georgia Tech!!!

Aspergillus niger

←photo is 5 inches (12.5 cm) across.
Hydrophobins have 8 crosslinked cysteine residues.

L-Cysteine: \[
\text{HS} - \text{CH}_3 - \text{C} - \text{NH}_2
\]

virtually insoluble

slightly more soluble
Dutch elm disease
a.k.a. Elm wilt

Thousands of these beautiful shade trees die each year.

The particular hydrophobin called cerato ulmin has been implicated in the death of American elm trees (Dutch elm disease).
CU traps air and oil into stable (but not equilibrium) cylindrical structures.

Fibrillar air bubbles: rocking

Tubular oil blobs: rocking

Half-moon polymer gel drops (PSLG/dodecane): Sonication
Sample prep determines the shape of the bubbles.

CU aqueous solution
In this video, cylindrical bubbles fatten under tension, then go spherical. They crinkle on reducing the pressure.
A slide showing unusual structures was removed here:
contact
paul.russo@mse.gatech.edu
If CU captures air, it should capture oils.
CU Biofilms must be strong! Let’s begin with how surface tension is determined.

Single hydrophobin

Grey: Hydrophilic patch
Green: Hydrophobic patch

Schematics of CU molecules at air/water or oil/water interface at a capillary tip.

$$\gamma(t) = \frac{(P_T - P_H) R(t)}{2}$$

$$\frac{R_j P_{T,i} - R_i P_{T,j}}{R_j - R_i} = P_H$$

P1: PT (transducer)
P2: PH (hydrostatic)
In this case, the microtensiometer is not oscillating...just watching bubble radius with time. CU takes about one hour to lower air/water surface tension from 72.8 mN/m to 53 mN/m at 1 μg/mL.
Walker-Anna dynamic tensiometer oscillates bubble.
The CU membrane at air/water interface becomes solid-like and more rigid.

where \( \phi \) is the phase difference between the area and surface stress, \( E' \) is the in-phase (elastic) contribution, and \( E'' \) is the out-of-phase (viscous) contribution.
How do cylindrical bubbles form?

We don't know, but….
We can polymerize styrene in CU blobs.

CU hydrophobin aqueous solution
Styrene
Azobisisobutyronitrile (AIBN)
$C_{18}$ coated $SiO_2$ tracer particles
70 oC, 14h

scale bars: 200 $\mu$m
Biofilm bag (it’s a biomaterial!) securely contains spill oil.

Macondo spill oil

Magnetic field is applied
Hydrophobins have captured rodlike poly(3-hexylthiophene) semiconducting polymer in benzene. What happens to the polymer if the solvent evaporates?

Control experiment: Toluene escapes with time.
Click to add results, patents, $$$
We have a little bit more complete results on NON-volatile solvents, such as trichlorobenzene (TCB).

Protein-Assisted Assembly of π-Conjugated Polymers
Cornelia Rosu, Nabil Kleinhenz, Dalsu Choi, Christopher J. Tassone, Xujun Zhang, Jung Ok Park, Mohan Srinivasarao, Paul S. Russo, and Elsa Reichmanis
DOI: 10.1021/acs.chemmater.5b04192
Huge 640-nm shoulder bespeaks exceptional alignment.

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It’s huge!
Grazing incidence SAXS confirms excellent alignment.
In time, blobs evolve into dendritic structures that “bleb out” bits of CU-encapsulated P3HT…a latex-like route to processing P3HT?
Part II Conclusion:
Again, we see an altogether different biopolymer organize a different functional polymer, P3HT.

We are chasing a feather, and it seems to be leading somewhere.
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