N-Type Materials for Organic Thermoelectrics: High electron mobility polymers and fullerenes

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Compelling properties of organic materials

Inexpensive
• Solution processable
• Mechanically flexible
• Earth-abundant elements

Low thermal conductivity
• Typical $\kappa < 1 \text{ W/m-K}$

Fundamental challenge: maximize the power factor

$$ZT = \frac{S^2 \sigma}{\kappa}$$
Challenge: stable extrinsic doping

\[ ZT = \frac{S^2 \sigma}{T} \]

Why so few prior results for n-type organics?

\[ n \text{-type PANI (unstable)} \]
High LUMO makes $n$-doping unstable

Stability is a challenge for $n$-type charge transfer doping

Can we choose a stable polymer-donor pair that will donate upon activation?
Reactive Dopants for Electron Conduction

N-DMBI
dihydro-1H-benzoimidzol-2-yl

P. Wei et al., JACS 2010

P(NDIOD-T2)

Z. Chen et al., JACS 2008
H. Yan et al., Nature 2009

Energy levels preclude charge transfer doping of P(NDIOD-T2)

Hydride transfer reactions

A. Colter et al., JACS, 1976
N-DMBI dopes P(NDIOD-T2) n-type
N-DMBI dopes P(NDIOD-T2) n-type

Carrier concentration increases to $\approx 6 \times 10^{17} \text{ cm}^{-3}$
Consistent with ESR data
N-doping of P(NDIOD-T2) is stable

Dopant still active after one month under N₂
PANI reported to p-type in minutes!
Thermoelectric Power Factor

$N$-type P(NDIOD-T2) follows same trend as $p$-type

$P(NDIOD-T2) + N$-DMBI

Prior Studies (PANI)

$N$-type P(NDIOD-T2) follows same trend as $p$-type
Effects of increasing dopant load

Conductivity saturates at a moderate doping load
Estimate < 1% of N-DMBI active
Why so few dopants active?

Neat P(NDIOD-T2)

N-DMBI + P(NDIOD-T2) (10:1)

Solubility issue: dopants segregate out
Spin density persists after washing aggregates.

N-DMBI + P(NDIOD-T2) (10:1)

After Wash with H₂O

No detectable change in spin density after washing with H₂O
A new DMBI derivative: FB8

N-DMBI + P(NDIOD-T2) (10:1)

FB8 + P(NDIOD-T2) (10:1)

Is morphology change indicative of doping efficiency?
Comparison of N-DMBI & FB8

FB8 is comparable to N-DMBI

Synthetic expertise to increase solid-solid solubility
P(NDIOD-T2) tracks same trend as p-type

Result of similar electronic structure?
What about other candidate organics?

Can fullerenes be doped with fullerenes?

Fullerenes

Energy (eV)

Thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

PCBM-SC

PCBM-EVP

PCBNB
“Self” Doping of Fullerenes

- High mobility (1-10 cm²/Vs) n-type semiconductors
- Wide selection of solution processable structures

Charge-transfer compound

1,3-bis(diisopropylphenyl)imidazol-2-ylene-C₆₀
H. Li, ... G. Bazan, JACS 2011

Dopants with similar structures offer potential to harness exceptional thermal properties of fullerenes
Novel Fullerene Dopant!

PCBM:IDIPP power factor is about 10x that of P3HT at a similar conductivity!
Conclusions

• N-DMBI dopes P(NDIOD-T2) $n$-type
  – Maximum $\sigma$ achieved: $\sim 10^{-3}$ S/cm
  – Solubility limits doping efficiency

• Fullerene charge transfer compound dopes PCBM $n$-type
  – Power factor 10x P3HT at a similar conductivity!

• N-doped and p-doped polymer follow similar trend
Acknowledgments

- **Synthetic Collaborators (MURI)**
  - Fulvio Brunetti, Craig Hawker
  - Andreas Lorbach, Gui Bazan

- **Chabinyc Group at UCSB**

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  - Anne Glaudell
  - Gregory Su
N-Type Materials for Organic Thermoelectrics: Water Soluble Dicationic Perylene Diimides

Boris Russ

University of California, Berkeley
N-type organic materials are scarce and have limited performance.
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Perylene diimides (PDI’s) also have potential as n-type materials.

Are stable electron doping strategies possible with PDI’s?
Self-doping PDI material system


- Water soluble
- Conductivity tunable by orders of magnitude (as high as $10^{-3}$ S/cm)

Provides an intriguing system for investigation

- N-type
- Electronic conductivity can be broadly tuned
- Long-term potential for investigating structure-property relationships through chemical design
Probing the impact of charge separation on TE properties through synthetic design

Charged perylene diimide electron density distribution

Comparing cationic perylene diimide variants with ethyl, butyl, and hexyl chain charge spacers

Fulvio Brunetti (Hawker)
Remarkably high n-type thermoelectric performance observed

Modification of charge separation leads to 100X increase in conductivity without significant change in thermopower.
Dihexyl perylene diimide is best-in-class n-type small molecule thermoelectric material.
Both electronic and structural modifications can impact electrical transport. Tuning charge concentration and tuning morphology can change electrical conductivity by 2-3 orders of magnitude. Che et al. (2007) and Rivnay et al. (2009) have studied these changes. Are these changes electronic or structural in nature?
Optical insight into electronic properties

Controlling properties through annealing

Tunable electrical conductivity

Ongoing studies are probing the effect of annealing temperature on thermoelectric properties
Optical insight into modifications of electronic properties - annealing

Spectra as temperature ramped from RT to 120 °C under N₂

Polaron peaks grow in with increasing temperature
Optical insight into modifications of electronic properties – air exposure

Exposure to air at RT over 15 hours

Polaron peaks decrease with increased air exposure
Electron spin resonance studies are underway to probe role of charge carrier concentration in observed modulation of TE properties.

All variants display similar optical features.

How does the morphological packing of these variants compare?
Increased side chain length alters the packing morphology.

Synthetic design and molecular simulation efforts are underway to probe the impact of structure on TE properties.
Developing design principles to push organic n-types to a new frontier

Strategic Vision
- Tuning Electronics Properties
  - Synthetic Design
  - Molecular Doping
- Tuning Morphological Assembly
  - Synthetic Design
Acknowledgments

• Collaborators (MURI)
  Fulvio Brunetti, Max Robb, Craig Hawker

Segalman Group at UC Berkeley

Levi Miller, Shrayesh Patel, Michael Chabinyc

Funding Support
• MURI-AFOSR
• NDSEG Graduate Research Fellowship
Present novel design strategies to radically tune thermoelectric properties in multiple n-type systems

Demonstrate best-in-class n-type performance

Great opportunity to make further advances through strategic synthetic design and in-depth characterization

Opens pathway for highly tunable all solution-processed green thermoelectrics