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Direct Arylation Polymerization of Indophenine-Based Monomers

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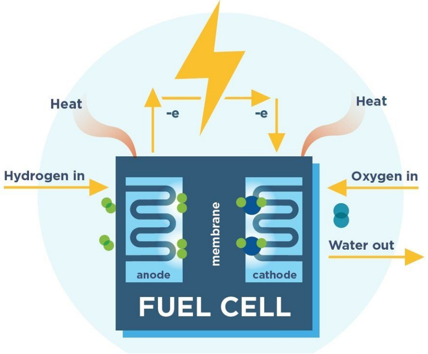
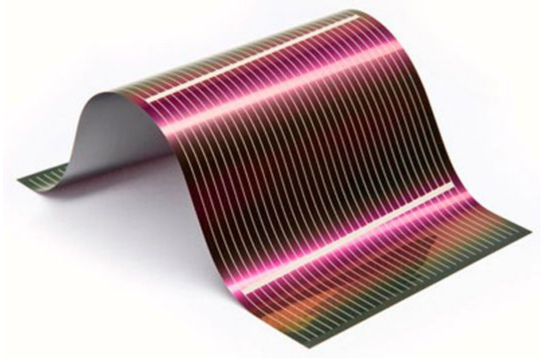
Spring 2020 UROP
Under the direction of Dr. Ted M. Pappenfus

Organic redox materials

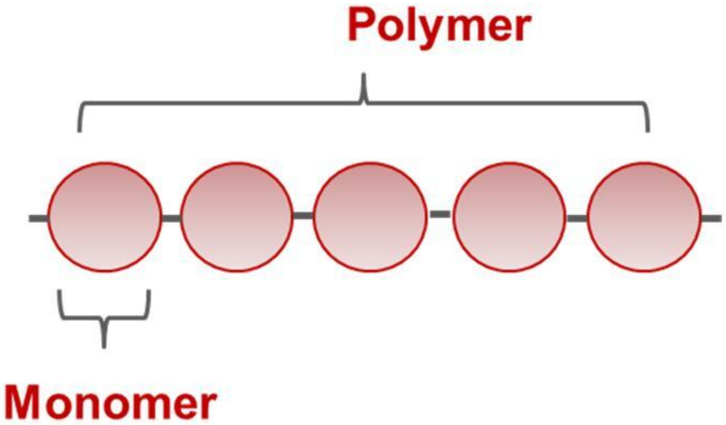
- Low-cost carbon materials
- Unique electronic properties
- High tunability/flexibility

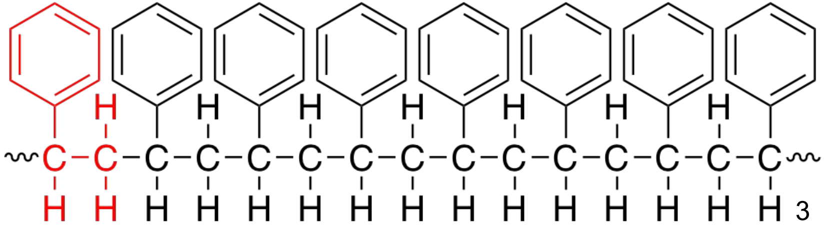




Solar Companies. http://www.solarcompanies.com/organic-solar-cells-thinner-lighter-and-printable/ (accessed Jan. 3, 2020). News wise. https://www.newswise.com/articles/scientists-create-thin-ilms-with-tantalizing-electronic-properties (accessed Jan. 3, 2020).

What do all these devices have in common?





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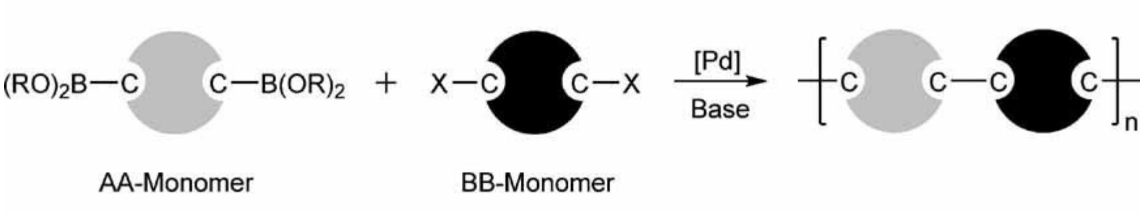
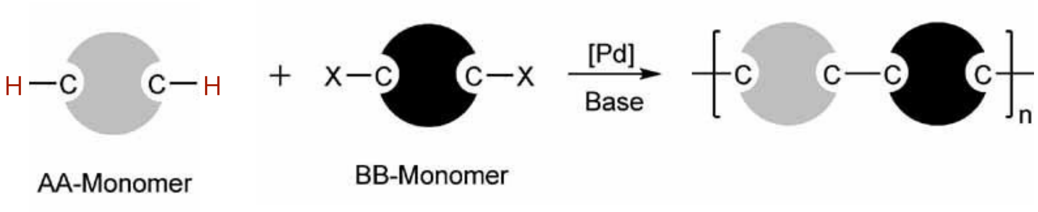
Polymerization methods

Step-growth polymerization via transition metal-catalyzed coupling (example: Stille)



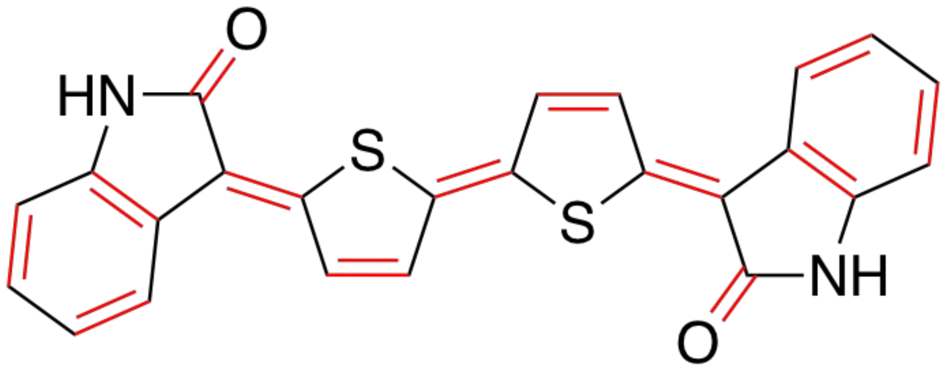
Step-growth polymerization via direct arylation polymerization (DArP)



Indophenine as a monomer for polymerization

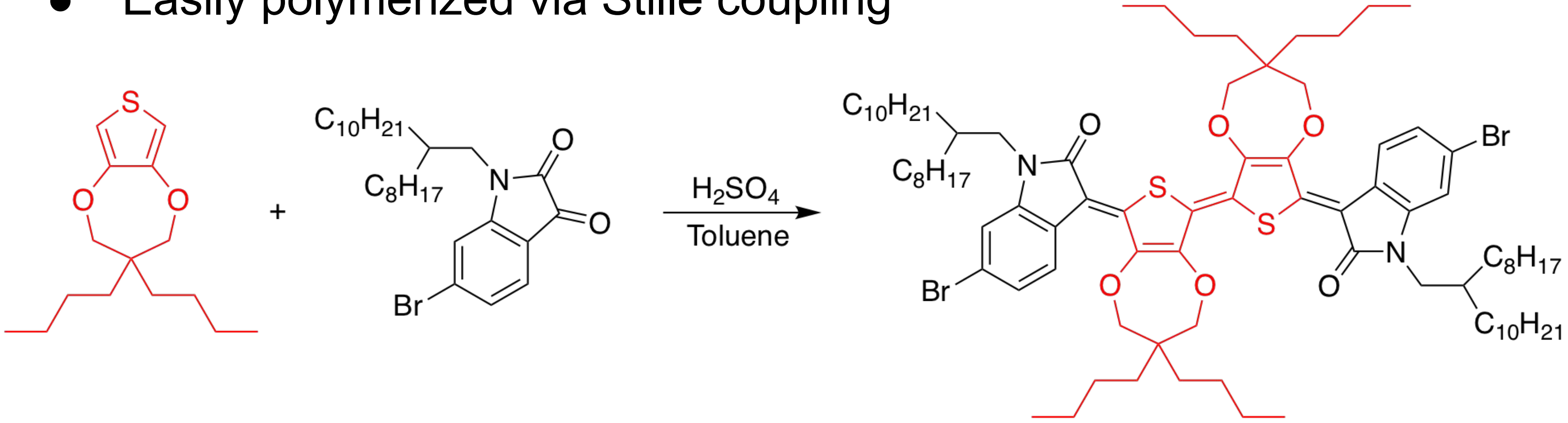
- History:
  - **1879:** indophenine was discovered by Alfred Baeyer
  - **1882:** indophenine is made from thiophene (Meyer et al.)
  - **1924**: correct structure identified (Heller et al.)

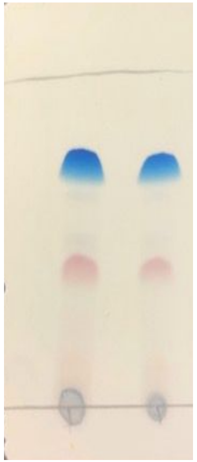
- Indophenine shows promise for electronic applications due to its…
  - Quinoidal structure
  - Conjugated character
  - Synthetic modifiability



Indophenine-based monomer

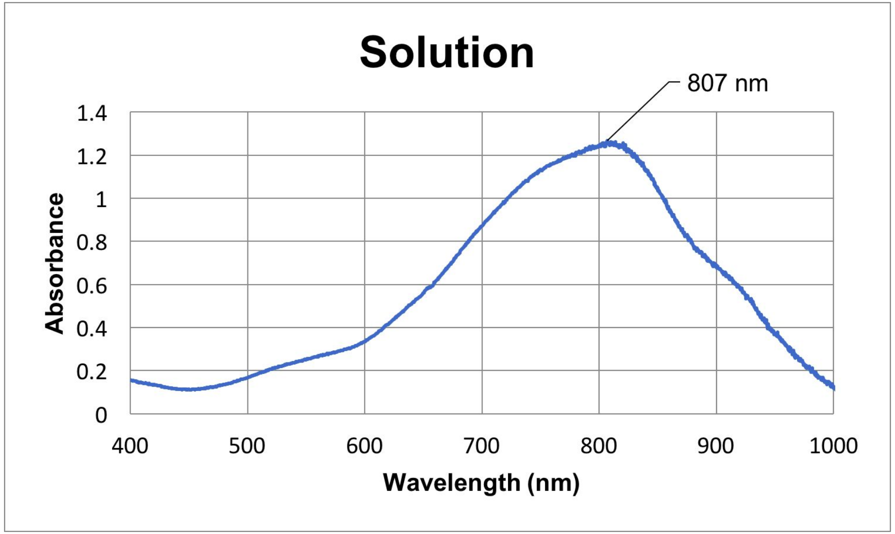
- Modified with ProDOT substituents to enhance solubility and eliminate isomerism (Pappenfus et al.)
- Facile synthesis with acid catalyst (Cava et al.)
- Easily polymerized via Stille coupling



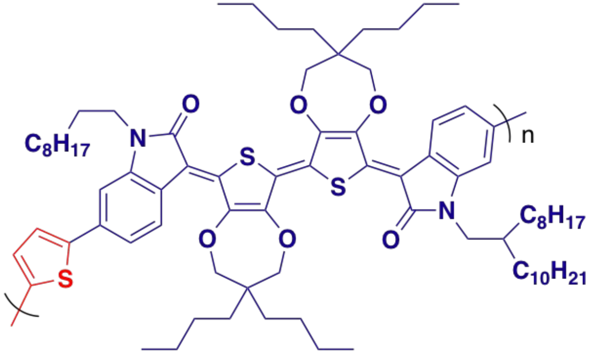


ProDOT **Alkylated-Isatin** **Monomer**
32% yield

Stille copolymer



Mw	7000 g/mol
Mn	5222
PDI	1.34

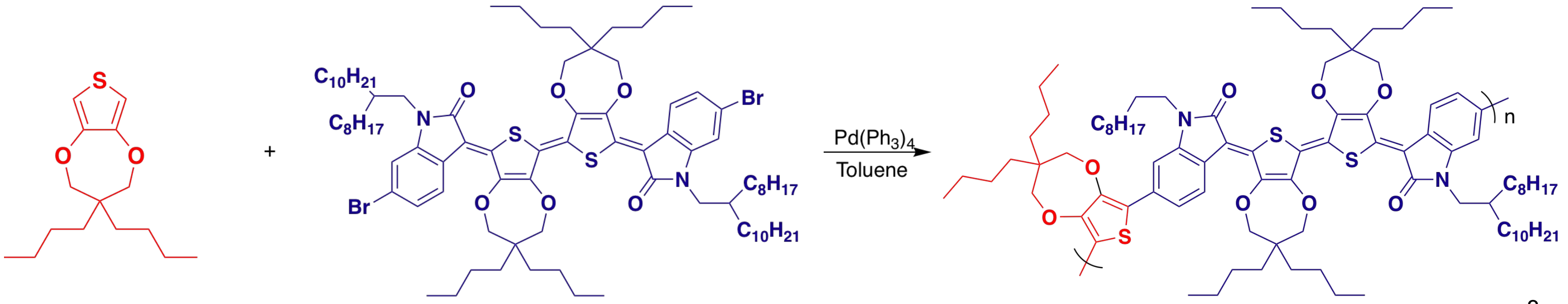


λmax (solution) = 807 nm
λmax (film) = 771 nm
Bandgap = 1.2 eV

Stille Copolymer
95% yield

A greener route: DArP

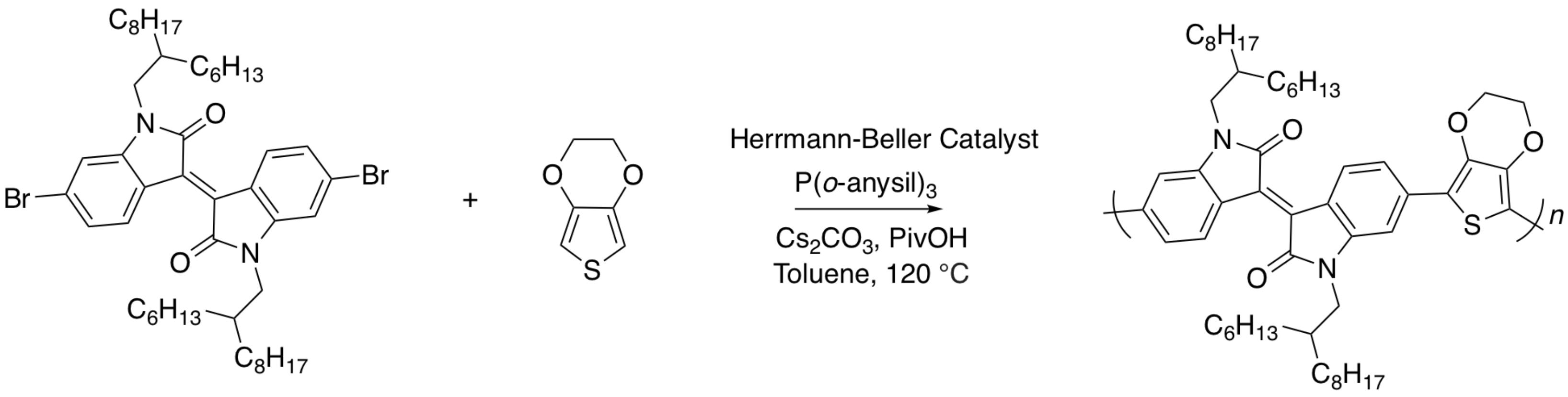
- Requires the functionalization of only *one* coupling site (halide)
- Other coupling site is a C-H bond that is “activated”
- DArP with indophenines has not been previously reported



Preparation of indophenine-based polymer using DArP

Related DArP polymers

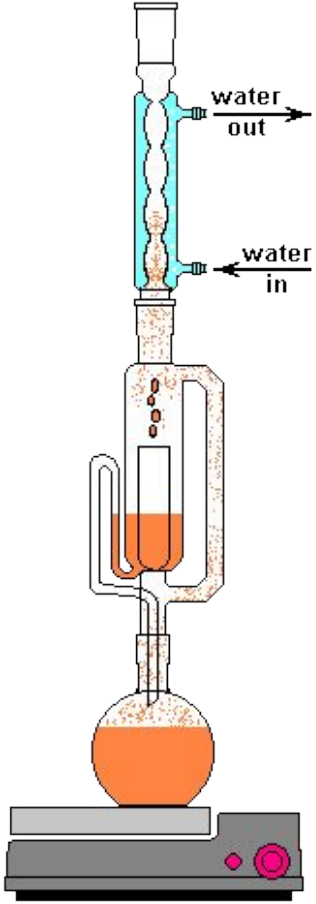
- Grenier et al. (2015) synthesized a similar polymer via DArP with:
  - 95% yield, *Mw* = 210,000 g/mol, PDI = 2.31



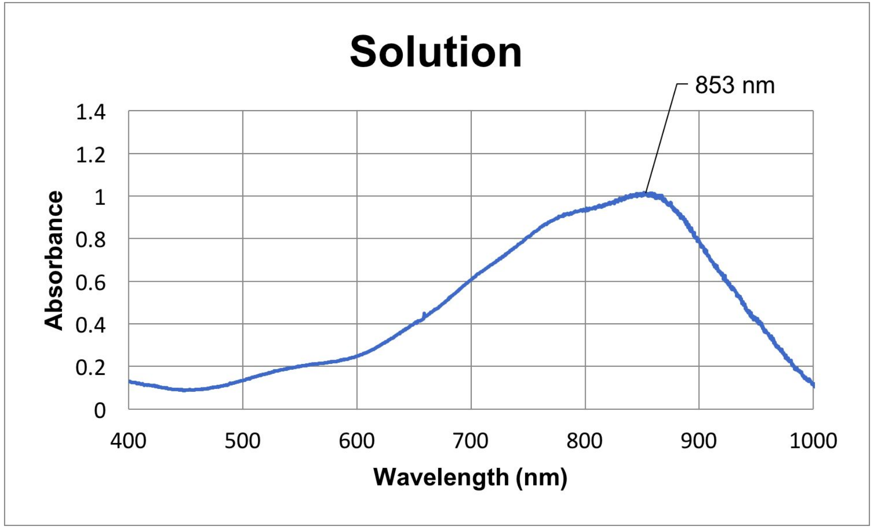
DArP polymer: purification

Methanol
Acetone
Hexanes (33%)
Chloroform (62%)
Combined yield of 95%

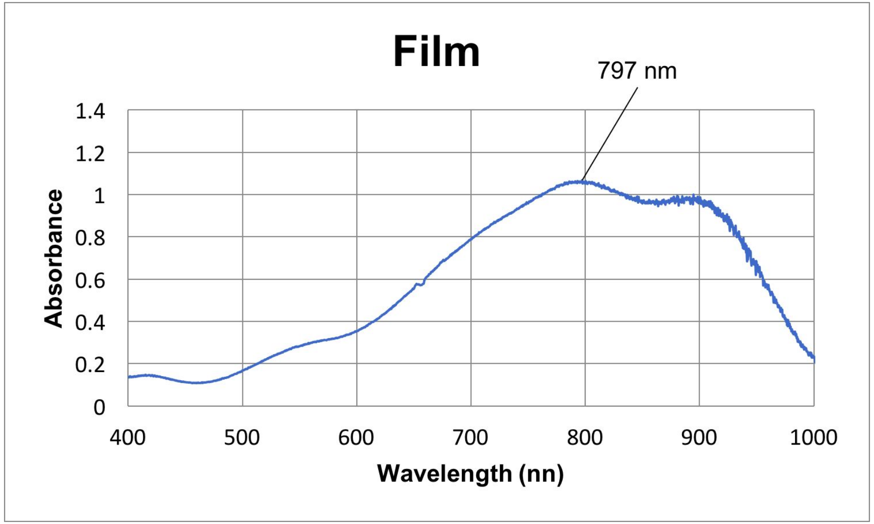
Mw	6047
Mn	5287
PDI	1.13



DArP polymer: UV-Vis



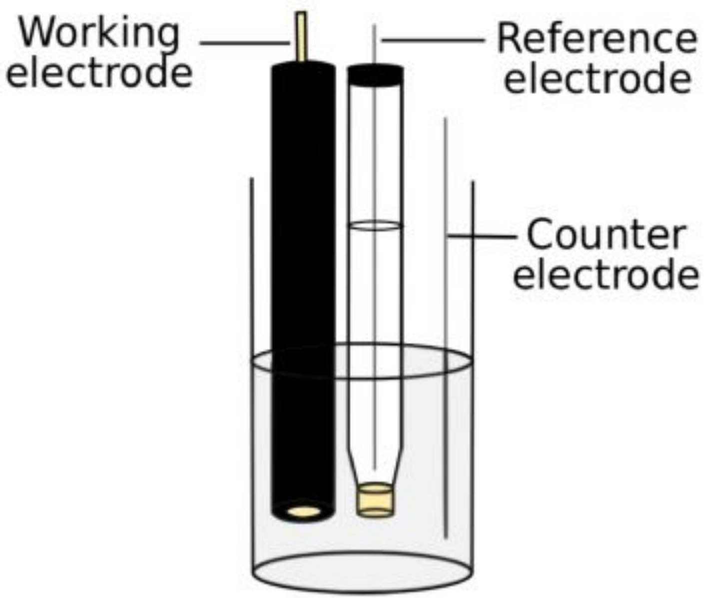
λmax = 853 nm

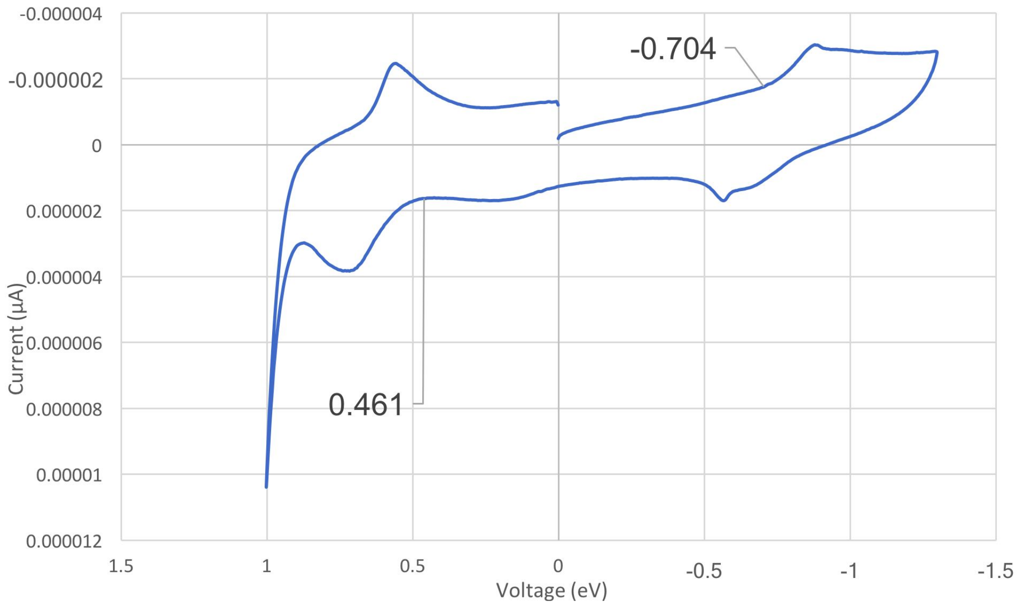


λmax = 797 nm

Band gap = 1.22 eV

Cyclic voltammetry of DArP polymer





Electronic Band Gap = 1.17 eV

DArP versus Stille Coupling

	Stille polymer	DArP polymer
Yield	95%	95%
Solution λmax	807 nm	853 nm
Solution Bandgap	1.2 eV	1.2 eV
Mw	7000 g/mol	6047 g/mol
Mn	5222 g/mol	5287 g/mol
PDI	1.34	1.13

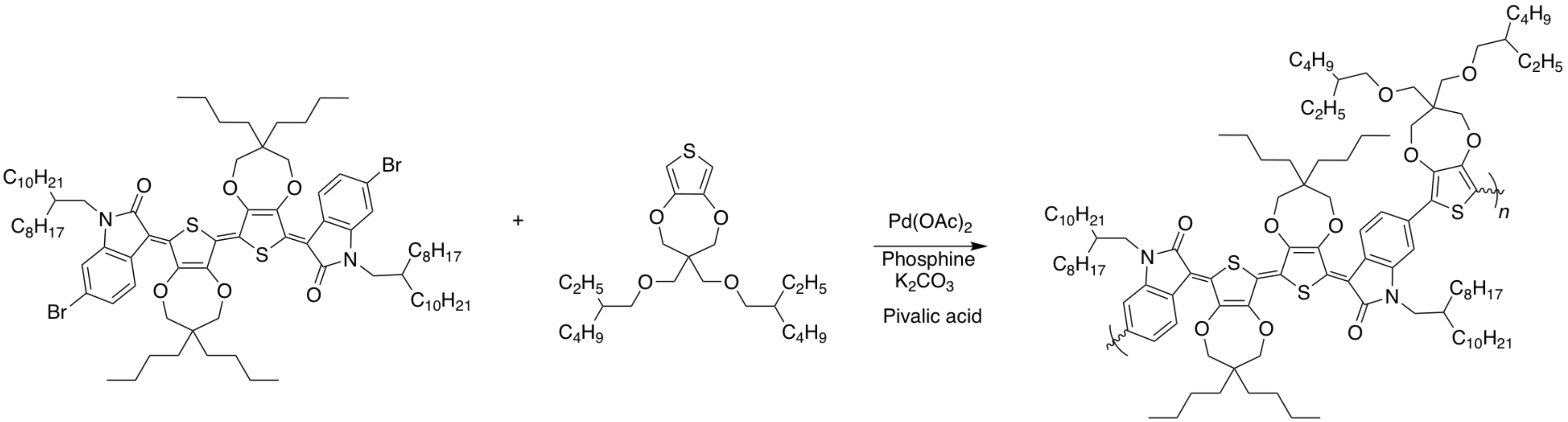
Direct arylation polymerization is a viable route to produce indophenine polymers with desirable electronic properties.

Optimization

- Improving molecular weight by:
  - Enhancing solubility to prevent premature polymerization termination
  - Using already-synthesized alternative monomers with improved solubility
  - Designing new monomers with enhanced solubility
- Increasing sustainability by using alternative solvents
- Exploring new catalytic systems

Enhancing solubility: thiophene monomer

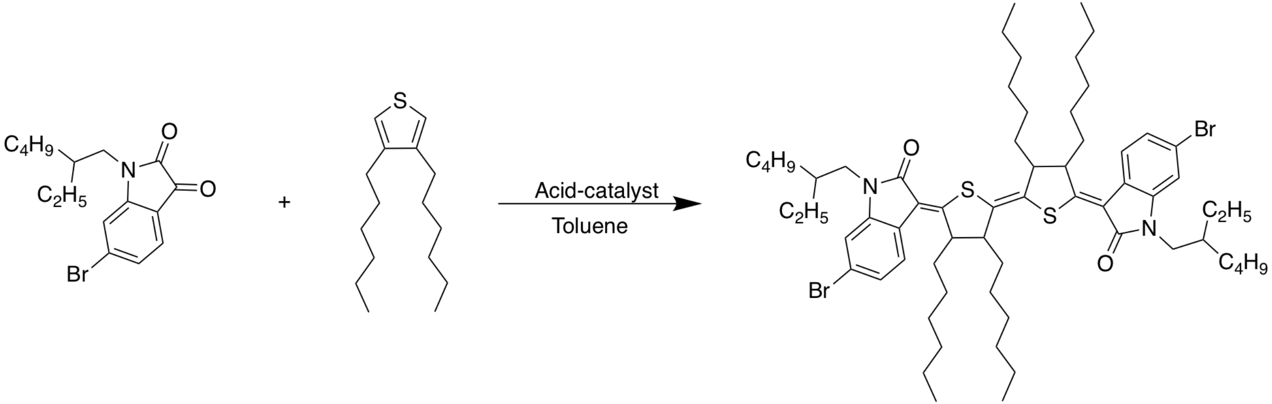
- Replace ProDOT monomer with a more soluble thiophene monomer
- Used optimized conditions proposed by Meyers et al.

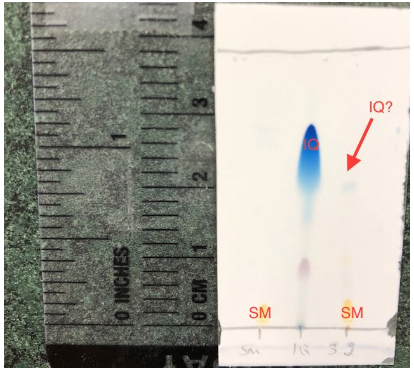


No visible color change occurred and TLC indicated formation of no product.

Enhancing solubility: indophenine monomer

- Design a new indohenine monomer with hexyl substituents rather than ProDOT subsitutents.

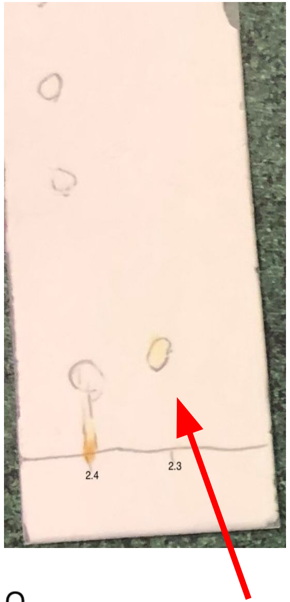




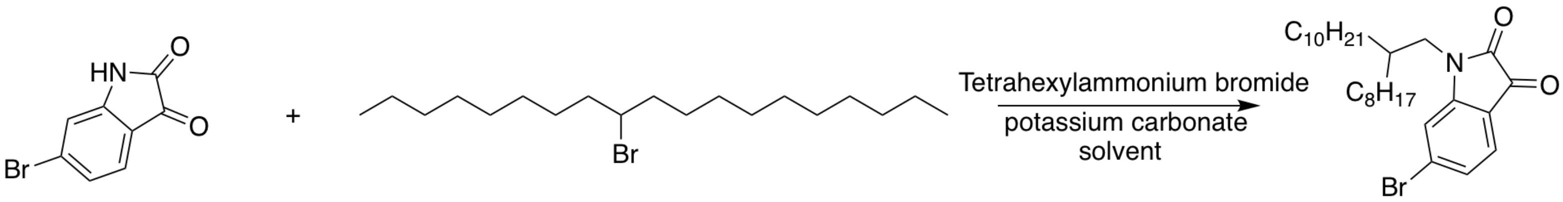
No visible color change occurred and TLC indicated formation of almost no product. Steric and/or electronic effects likely make the reaction less favorable.

Enhancing sustainability: solvent

- A key starting material is an alkylated isatin.
- The conventional reaction uses DMF as a solvent, which…
  - Complicates purification
  - Reduces sustainability
- Attempt same reaction with acetone as solvent



Only starting material in acetone



In DMF, the reaction formed the desired product in 60% yield. In acetone, no product formed.

Conclusions and Future Work

- Direct arylation polymerization is a sustainable and effective route toward indophenine polymers with desirable electronic properties
- Further optimization needed to:
  - Increase the molecular weight of indophenine polymers
  - Enhance the solubility of indophenine monomers and polymers
  - Improve the sustainability of the synthesis of starting materials
- Future work includes:
  - Theoretical calculations to understand energy barriers of failed reactions
  - Continued exploration of more soluble indophenine monomers
  - Continued testing of different catalytic systems

Acknowledgements

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