Optimizing the Optoelectronic Properties of Conjugated Polymers Through Metal-Ligand Coordination

Anita Hu
University of Windsor, hu14l@uwindsor.ca

P. Blake J. St. Onge
University of Windsor, stongep@uwindsor.ca

Simon Rondeau-Gagné Dr.
University of Windsor, simon.rondeau-gagne@uwindsor.ca

Optimizing the Optoelectronic Properties of Conjugated Polymers through Metal-Ligand Coordination

Anita Hu, P. Blake J. St. Onge, Simon Rondeau-Gagné Dr.
(University of Windsor)

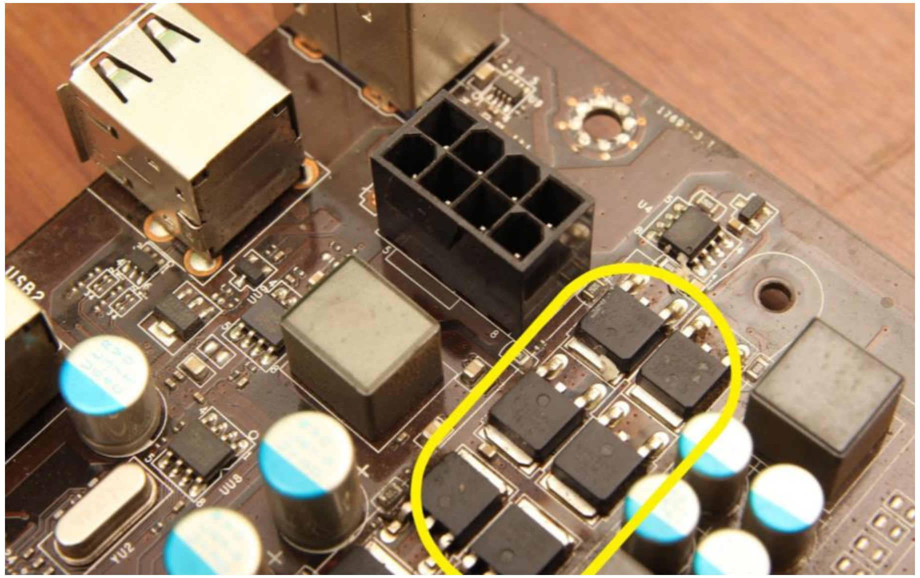
From work conducted by:

Langlois, A., St Onge, P., Karsenti, P. L., Younus, A., & Rondeau-Gagné, S. (2021). Modulating the Photophysical Properties and Electron Transfer Rates in Diketopyrrolopyrrole-Based Coordination Polymers. *The Journal of Physical Chemistry B*, *125*(33), 9579–9587. https://doi.org/10.1021/acs.jpcb.1c03177

Current Age of Electronics: Silicon Semiconductors

✓ Excellent conductors

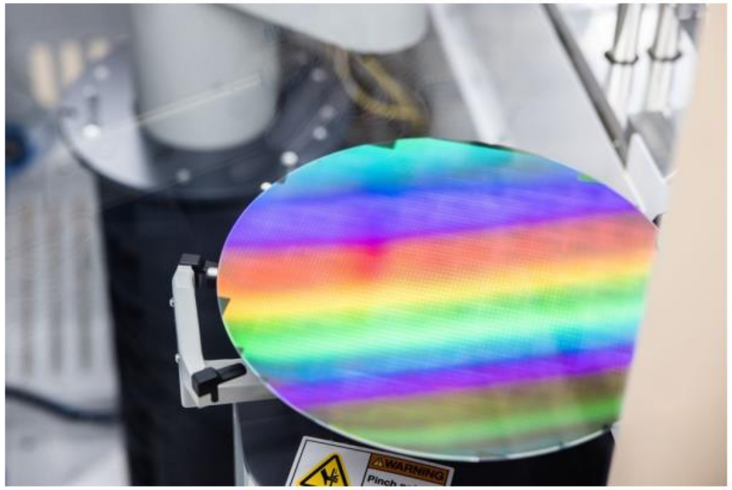
✗ Costly and difficult to manufacture



Technology

Key Supplier of Wafers for Chips Has Sold Out Through 2026

- Sumco expects supply-demand imbalance to last five years
- Silicon wafer maker sees little room for factory expansion



Manufacturing of semiconductors. *Photographer: Akos Stiller/Bloomberg*

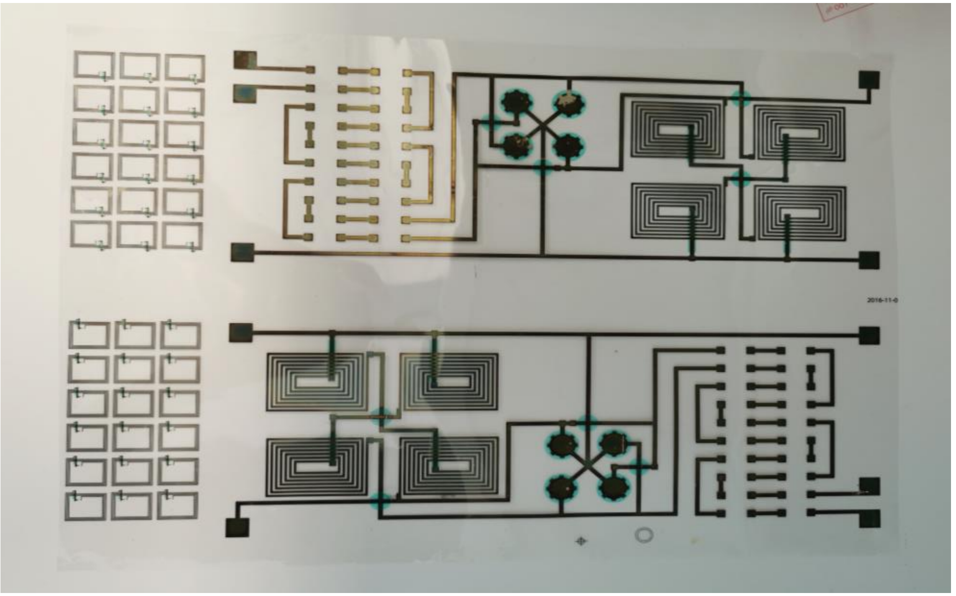
By Takashi Mochizuki and Vlad Savov
February 9, 2022, 7:42 AM EST *Updated on February 9, 2022, 8:01 PM EST*

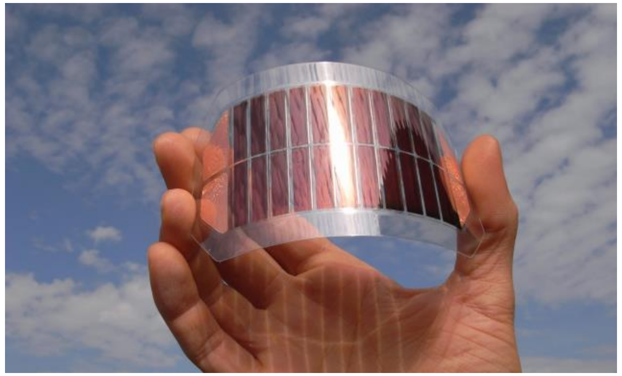
Sumco Corp., a key supplier of silicon wafers for the semiconductor industry, said it has already sold out its production capacity through 2026, a sign shortages in the industry may not abate for years.

(Bloomberg)

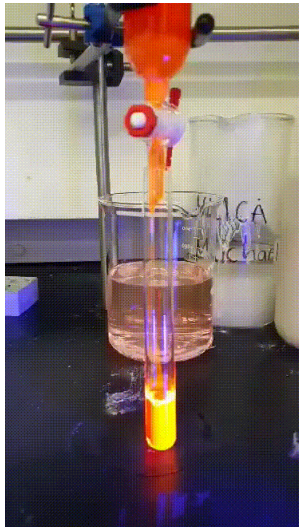
A New Age of Electronics: Organic Semiconductors

- ✓ Good conductors
- ✓ Less costly to manufacture





Organic Devices

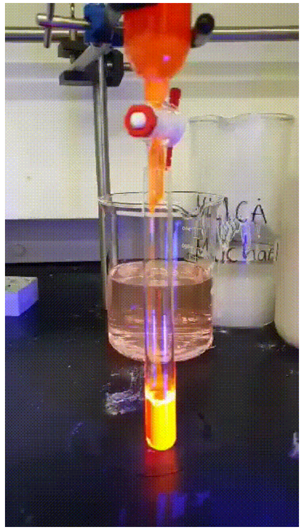


- Produced through the chemical synthesis of **organic** (containing Carbon, Oxygen, Nitrogen) molecules and monomers
- **Advantages:**
- **Disadvantages/Challenges:**
- **Opportunity:**

Kim, J., Kim, MG., Kim, J. *et al.* (2015). *Scientific Reports*, *5*, Article 14520.

St. Onge, P.B., Chen, T., Langlois, A., Younus, A., Jo Hai, I., Lin, B., Chiu, Y., & Rondeau-Gagné, S. (2020. *Journal of Materials Chemistry C, 8*, 8213-8223.

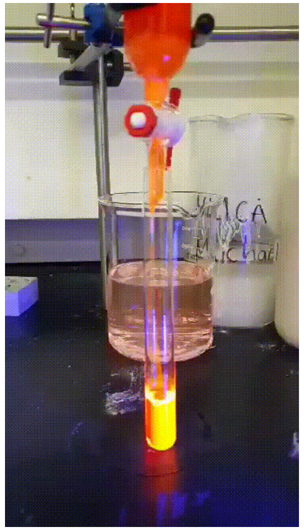
Organic Devices



- Produced through the chemical synthesis of **organic** (containing Carbon, Oxygen, Nitrogen) molecules and monomers
- **Advantages:** ✓ Good conductors comparable to silicon counterparts (Kim *et al.*, 2015)
  ✓ More flexible and easier to manufacture than silicon
- **Disadvantages/Challenges:**
- **Opportunity:**

Kim, J., Kim, MG., Kim, J. *et al.* (2015). *Scientific Reports*, *5*, Article 14520.
St. Onge, P.B., Chen, T., Langlois, A., Younus, A., Jo Hai, I., Lin, B., Chiu, Y., & Rondeau-Gagné, S. (2020. *Journal of Materials Chemistry C, 8*, 8213-8223.

Organic Devices

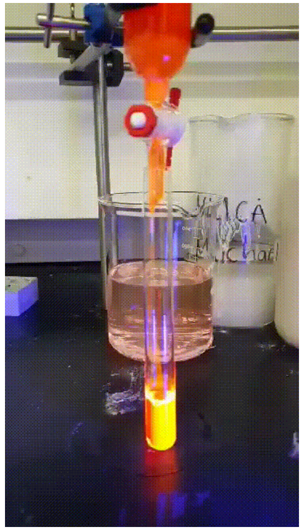


- Produced through the chemical synthesis of **organic** (containing Carbon, Oxygen, Nitrogen) molecules and monomers
- **Advantages:**
  - ✓ Good conductors comparable to silicon counterparts (Kim *et al*., 2015)
  - ✓ More flexible and easier to manufacture than silicon
- **Disadvantages/Challenges:** ✗ Difficult to fine-tune their mechanical and optoelectronic properties
- **Opportunity:**

Kim, J., Kim, MG., Kim, J. *et al.* (2015). *Scientific Reports*, *5*, Article 14520.

St. Onge, P.B., Chen, T., Langlois, A., Younus, A., Jo Hai, I., Lin, B., Chiu, Y., & Rondeau-Gagné, S. (2020. *Journal of Materials Chemistry C, 8*, 8213-8223.

Organic Devices



- Produced through the chemical synthesis of **organic** (containing Carbon, Oxygen, Nitrogen) molecules and monomers
- **Advantages:** ✓ Good conductors comparable to silicon counterparts (Kim *et al.*, 2015)
  ✓ More flexible and easier to manufacture than silicon
- **Disadvantages/Challenges:** ✗ Difficult to fine-tune their mechanical and optoelectronic properties

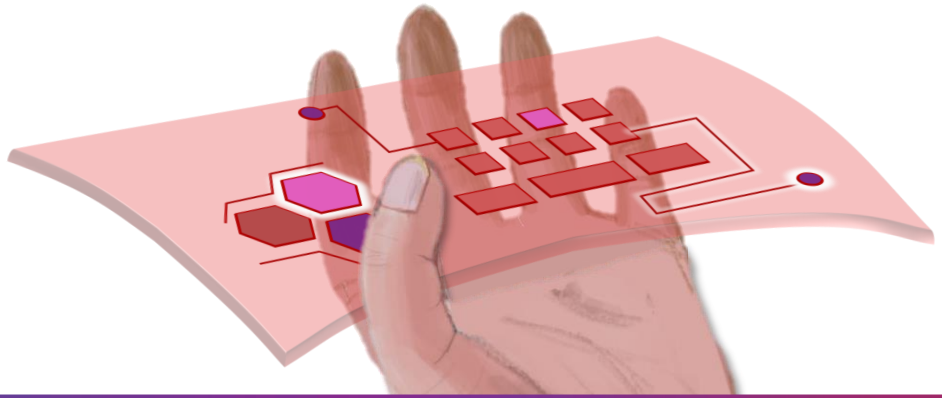
↓

- **Opportunity:** Research has shown that incorporating **Metal-Ligand (M-L) interactions** into semiconducting polymers can help control device properties (St. Onge *et al.*, 2020). *Can M-L interactions be used to control optoelectronic changes?*

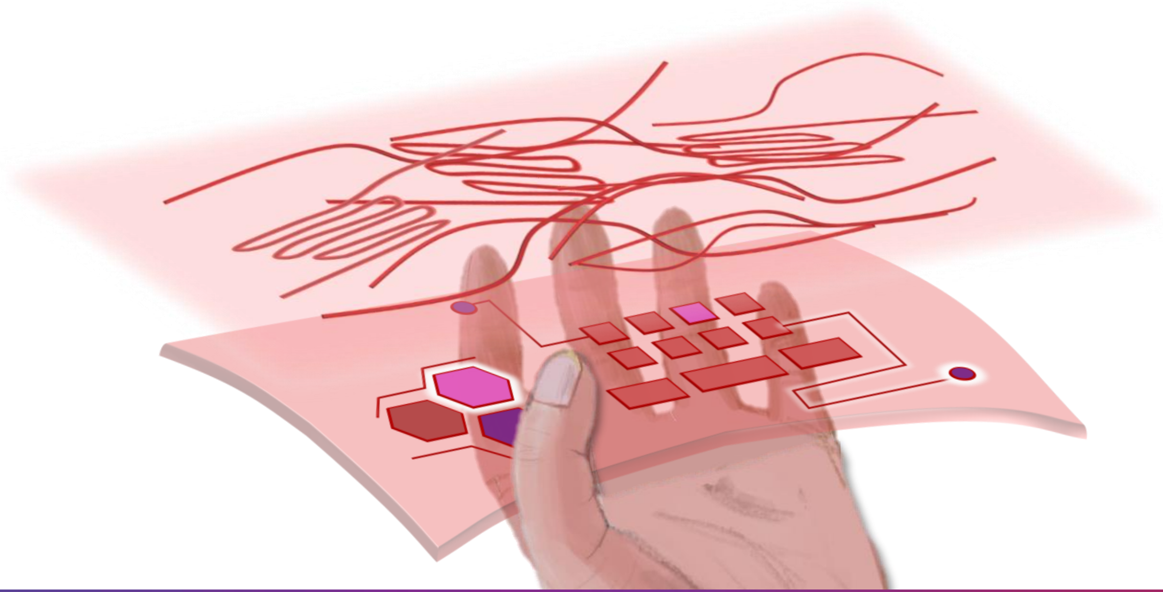
Kim, J., Kim, MG., Kim, J. *et al.* (2015). *Scientific Reports*, *5*, Article 14520.

St. Onge, P.B., Chen, T., Langlois, A., Younus, A., Jo Hai, I., Lin, B., Chiu, Y., & Rondeau-Gagné, S. (2020). *Journal of Materials Chemistry C, 8*, 8213-8223.

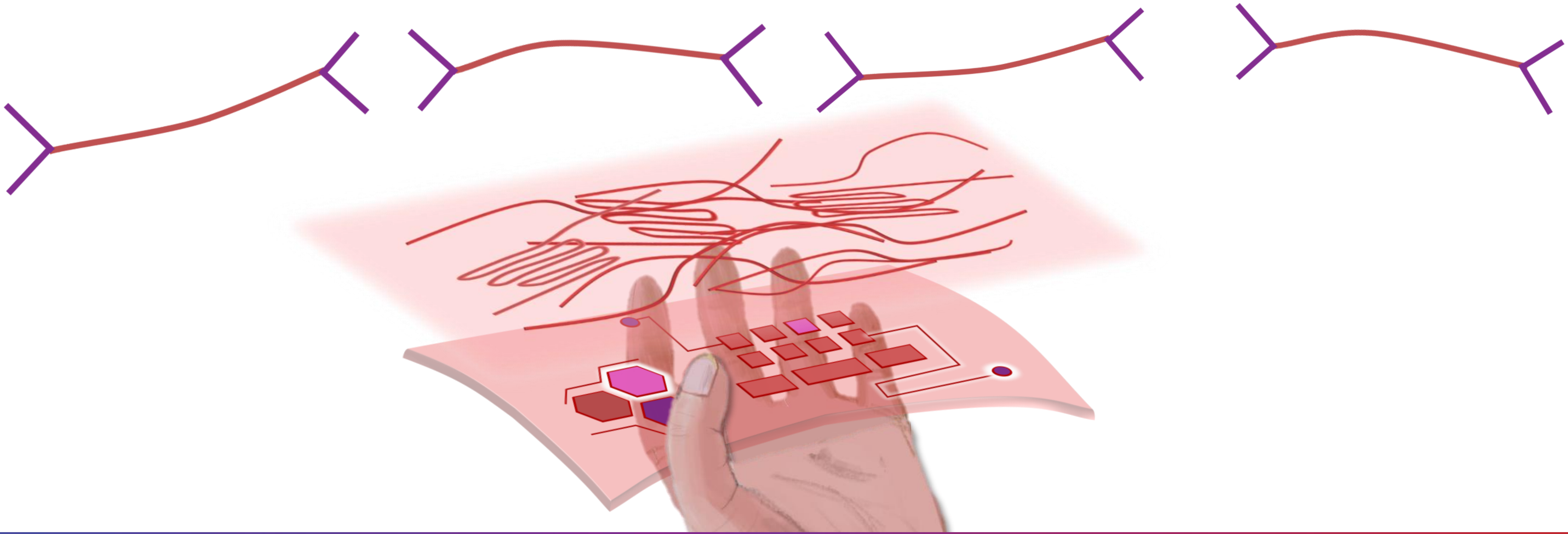
Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?



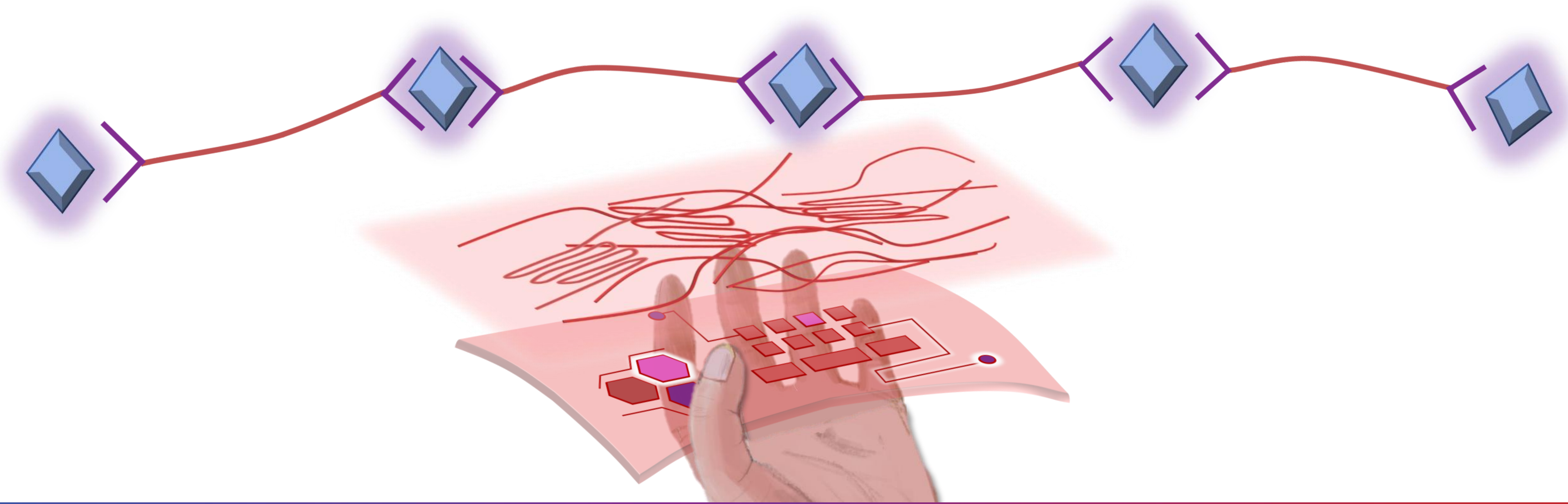
Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?



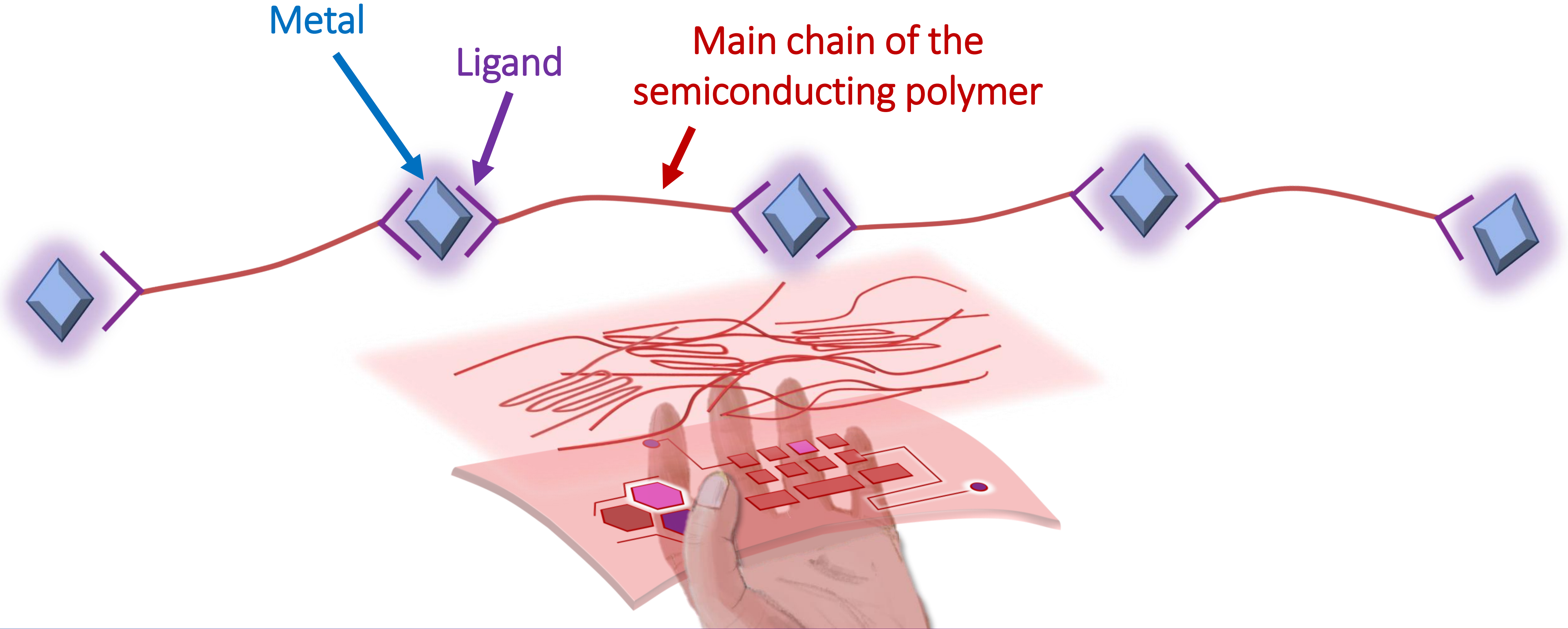
Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?



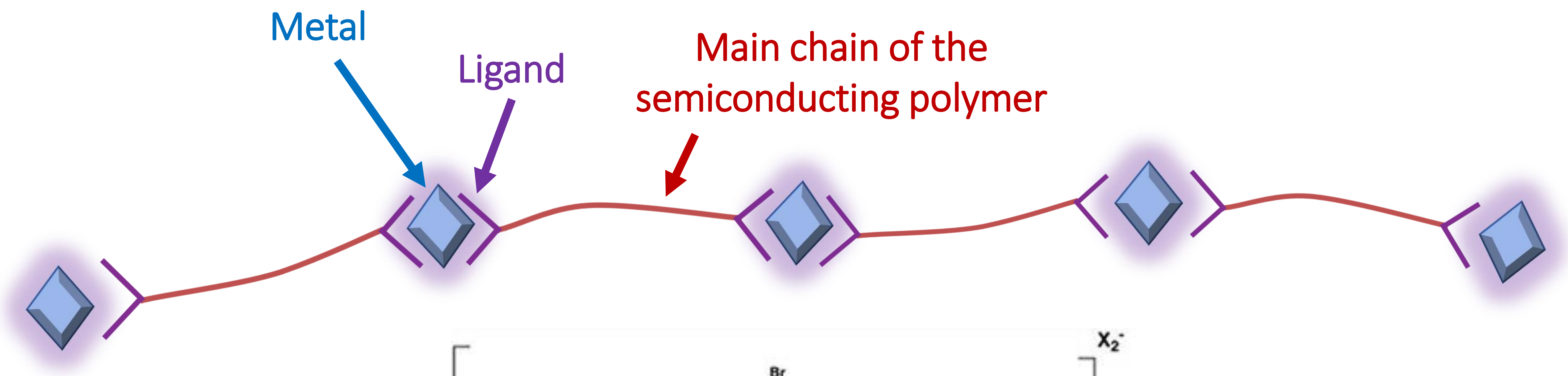
Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?

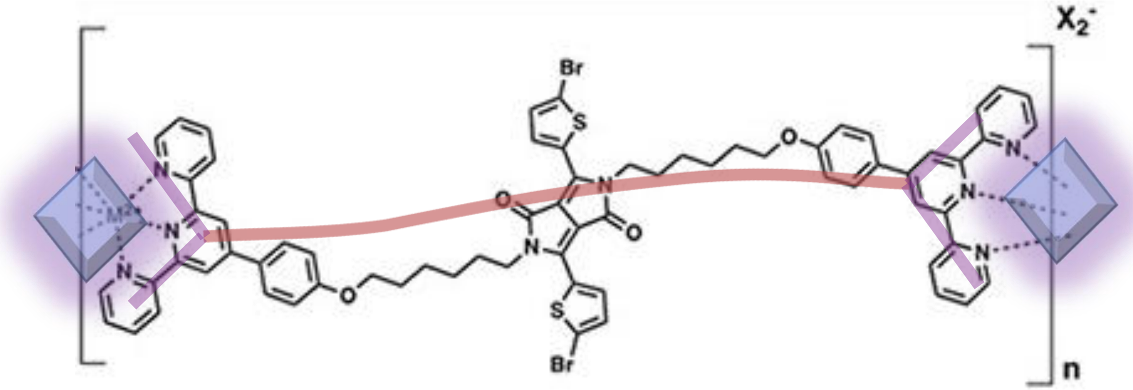


Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?

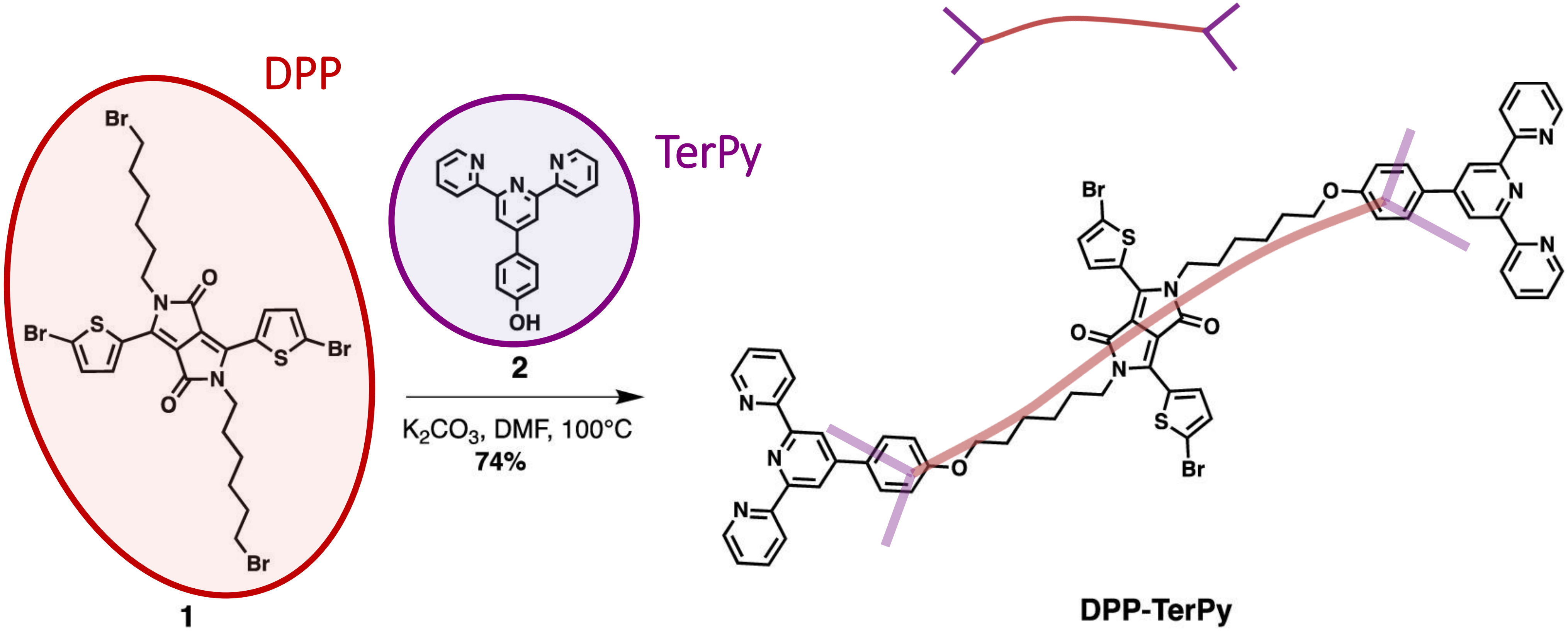


Study Objective: Can M-L interactions alter the light emission of semiconducting polymers?

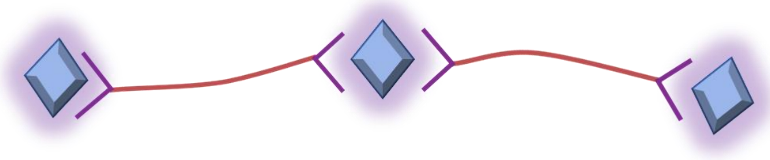


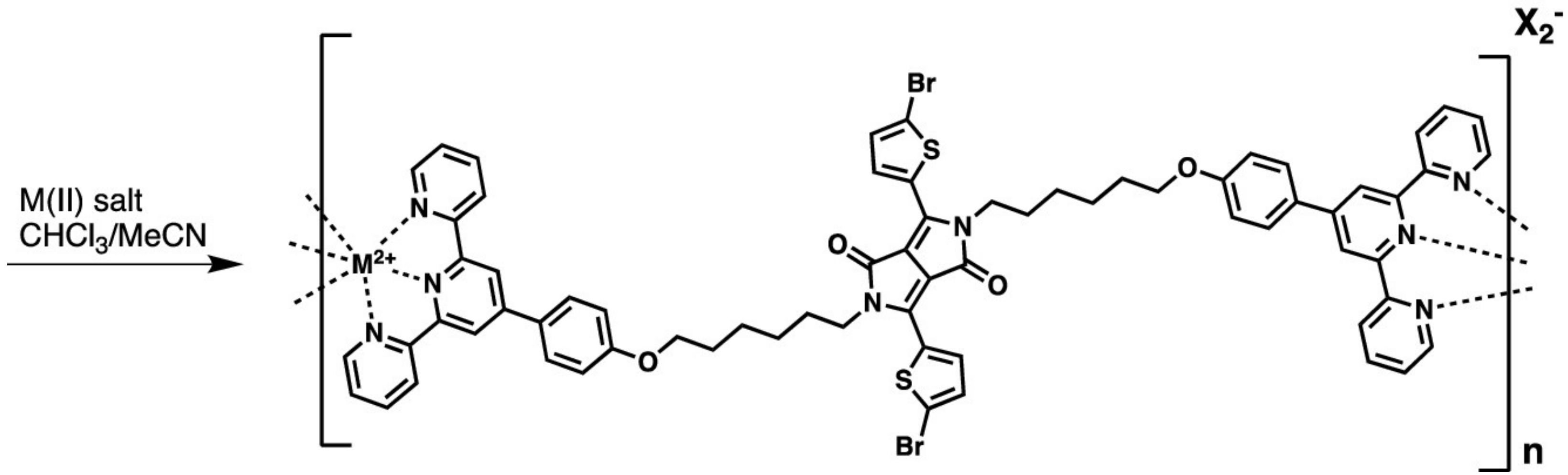


Step 1: Polymer Synthesis –Diketopyrrolopyrrole (DPP) Core



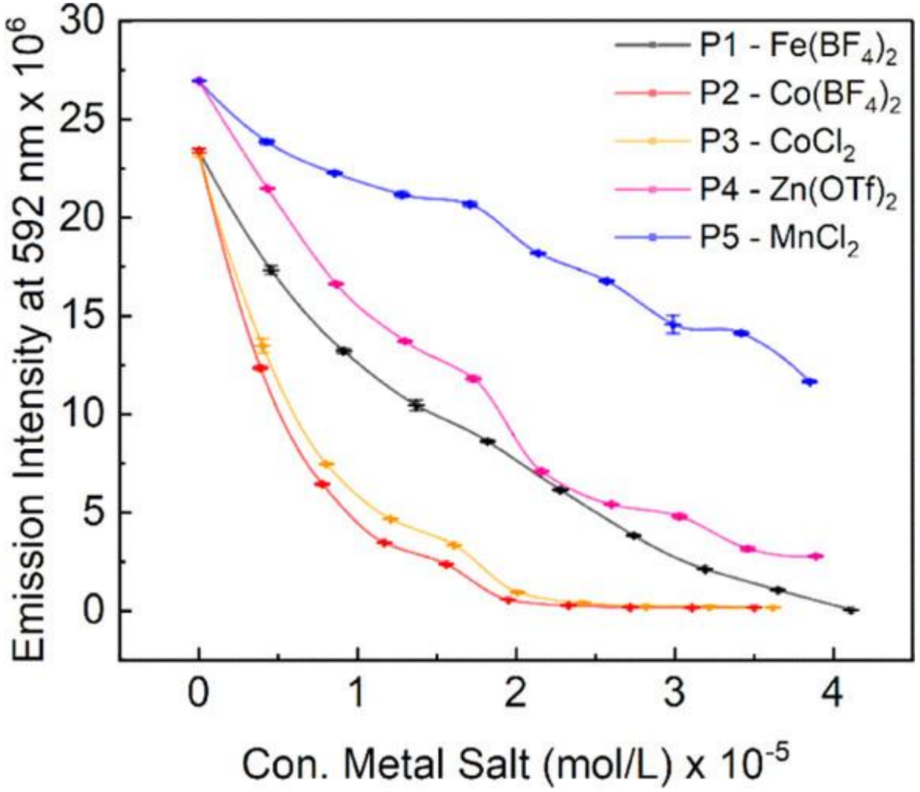
Step 1: Polymer Synthesis – M-L Coordination





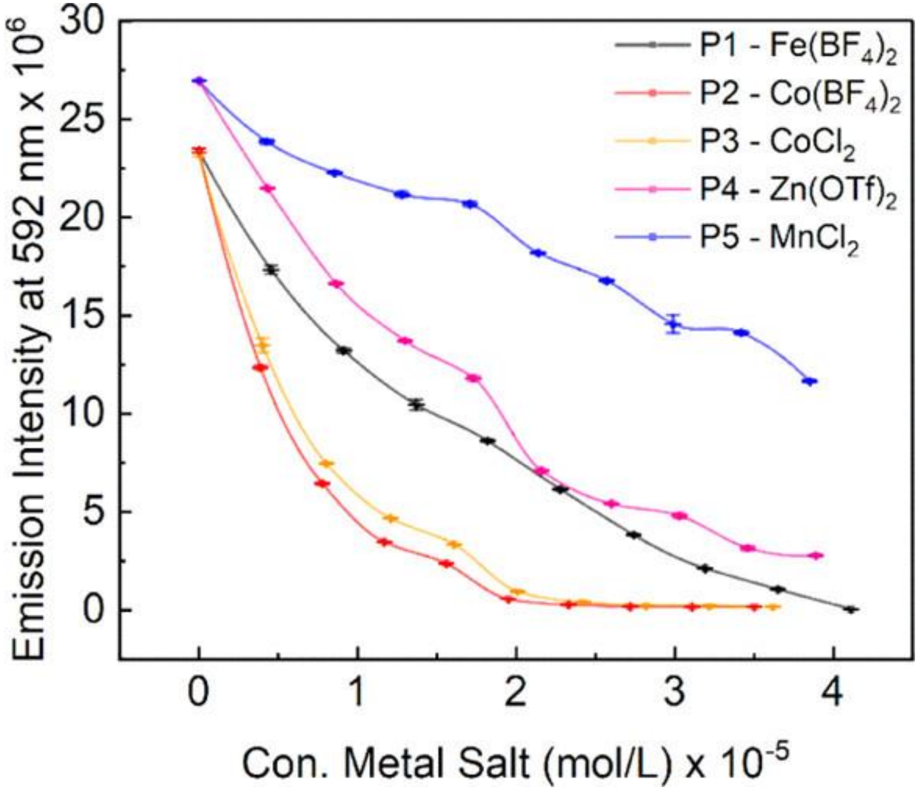
P1, M = Fe, X = BF_4
P2, M = Co, X = BF_4
P3, M = Co, X = Cl
P4, M = Zn, X = OTf
P5, M = Mn, X = Cl

Step 2: Observing Changes in Emission Intensity



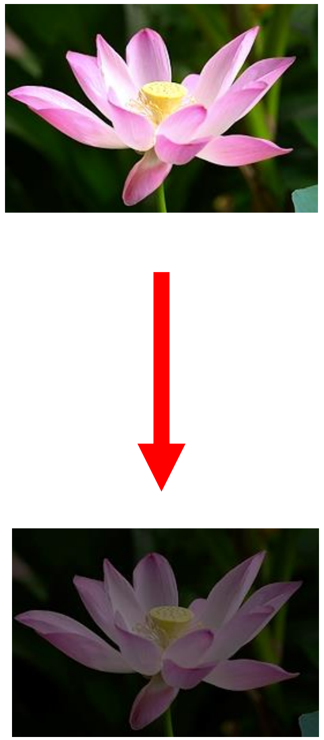
Decreased emission intensity suggests <u>fluorescence quenching</u>

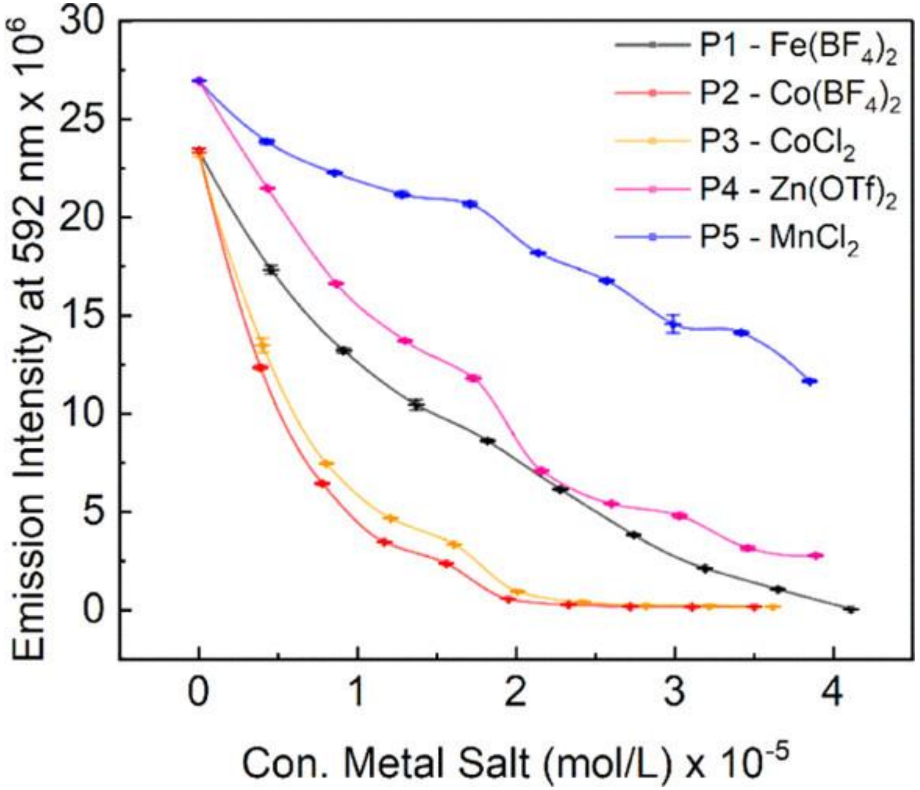
Step 2: Observing Changes in Emission Intensity



Decreased emission intensity suggests <u>fluorescence quenching</u>

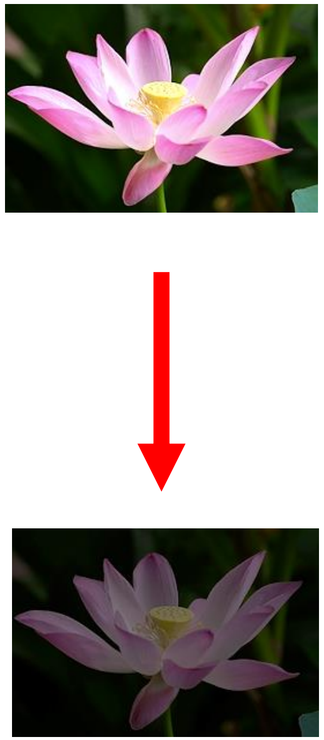
Step 2: Observing Changes in Emission Intensity

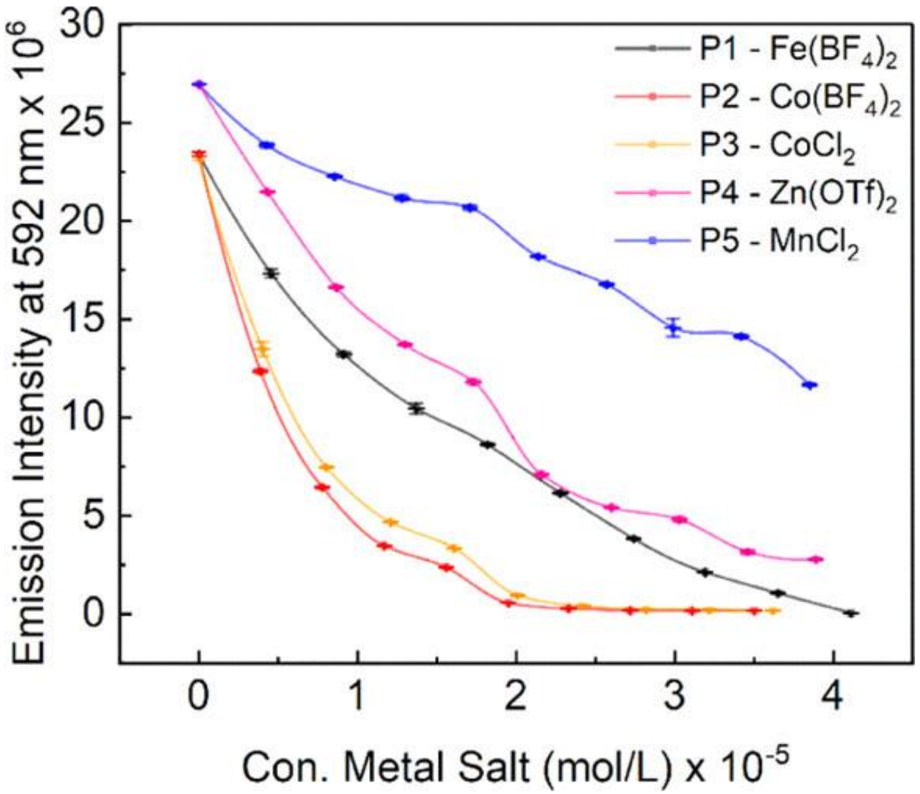




Decreased emission intensity suggests <u>fluorescence quenching</u>

Step 2: Observing Changes in Emission Intensity

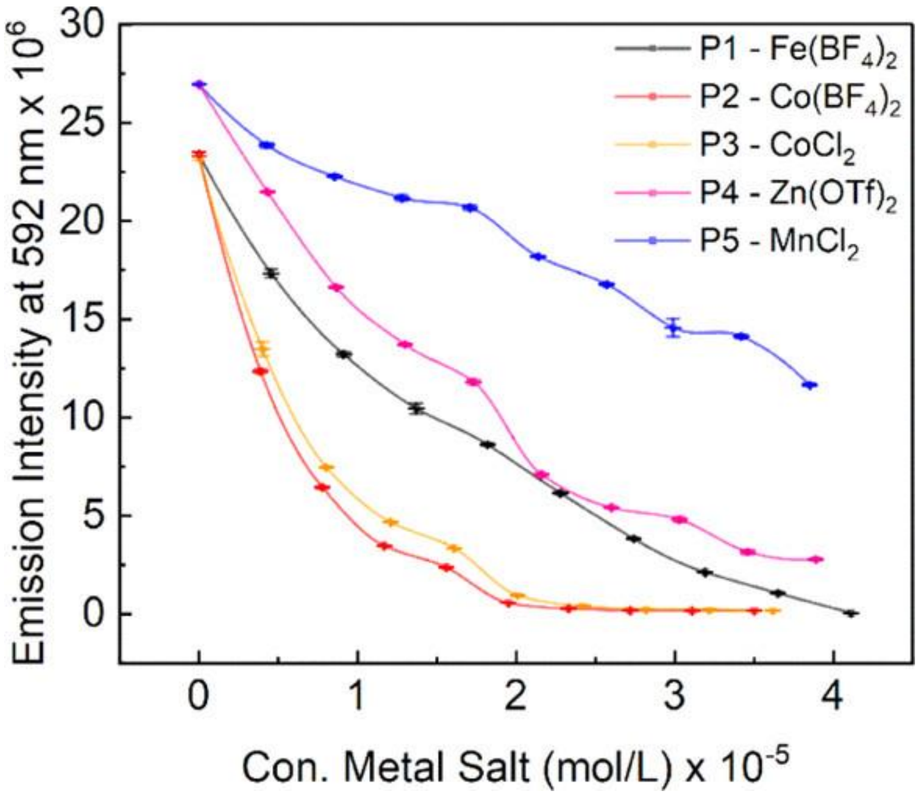




Decreased emission intensity suggests <u>fluorescence quenching</u>

Mn requires large changes in concentration to lower emission intensity
→ Inefficient quencher

Step 2: Observing Changes in Emission Intensity



Decreased emission intensity suggests fluorescence quenching

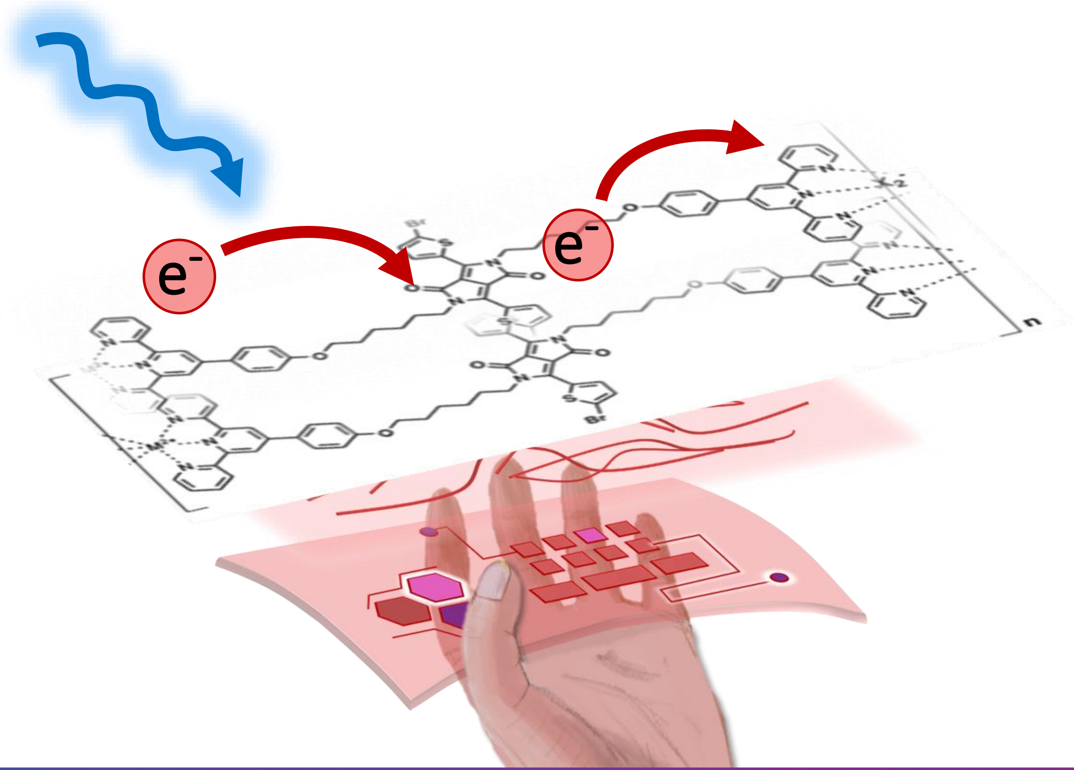
Mn requires large changes in concentration to lower emission intensity
→ Inefficient quencher

Zn, **Fe**, Co are efficient quenchers ✓

Step 3: Measuring Electron Transfer Rates

Femtosecond Transient Absorption Spectroscopy

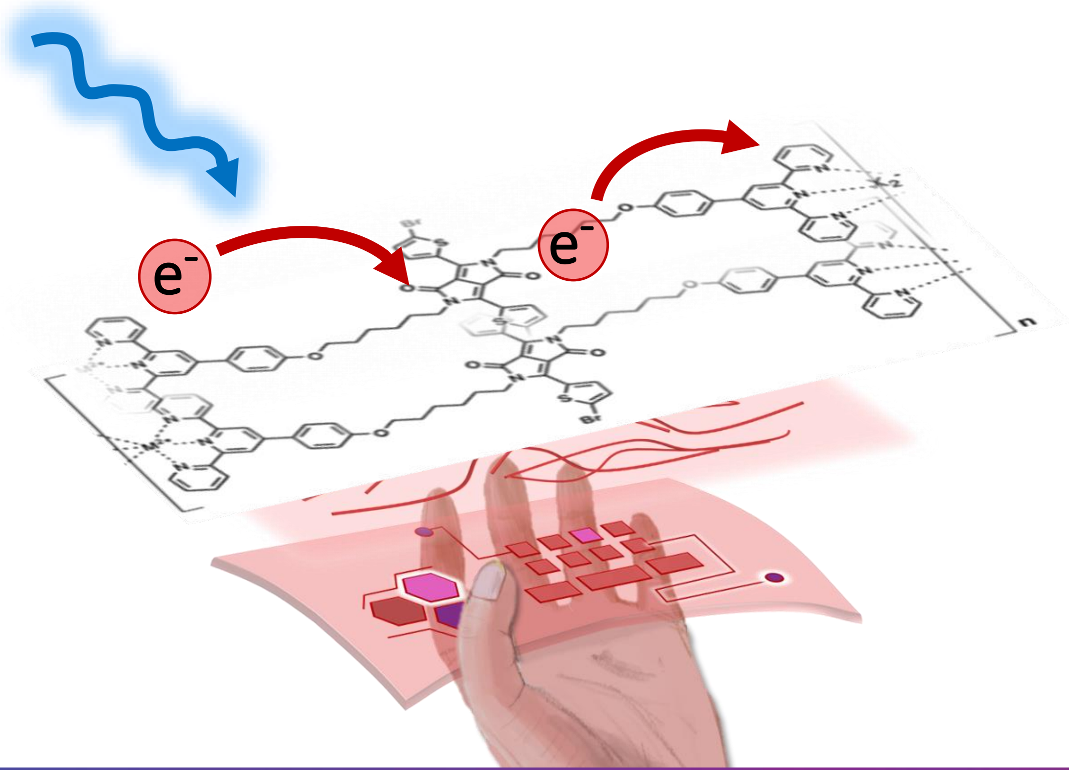
Electron Transfer Rate: An indication of electron transport efficiency;
the faster the transfer rate, the quicker electron conduction occurs through the polymer



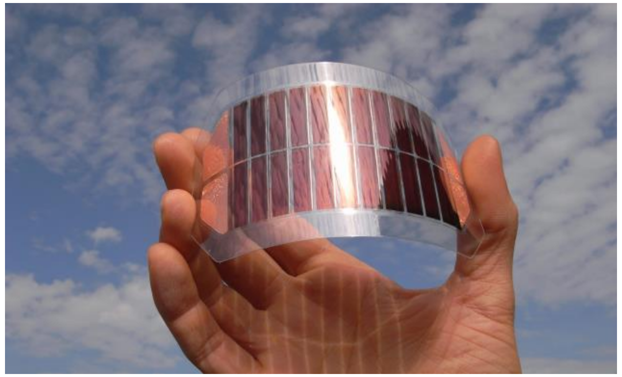
Step 3: Measuring Electron Transfer Rates

Femtosecond Transient Absorption Spectroscopy

Electron Transfer Rate: An indication of electron transport efficiency;
the faster the transfer rate, the quicker electron conduction occurs through the polymer



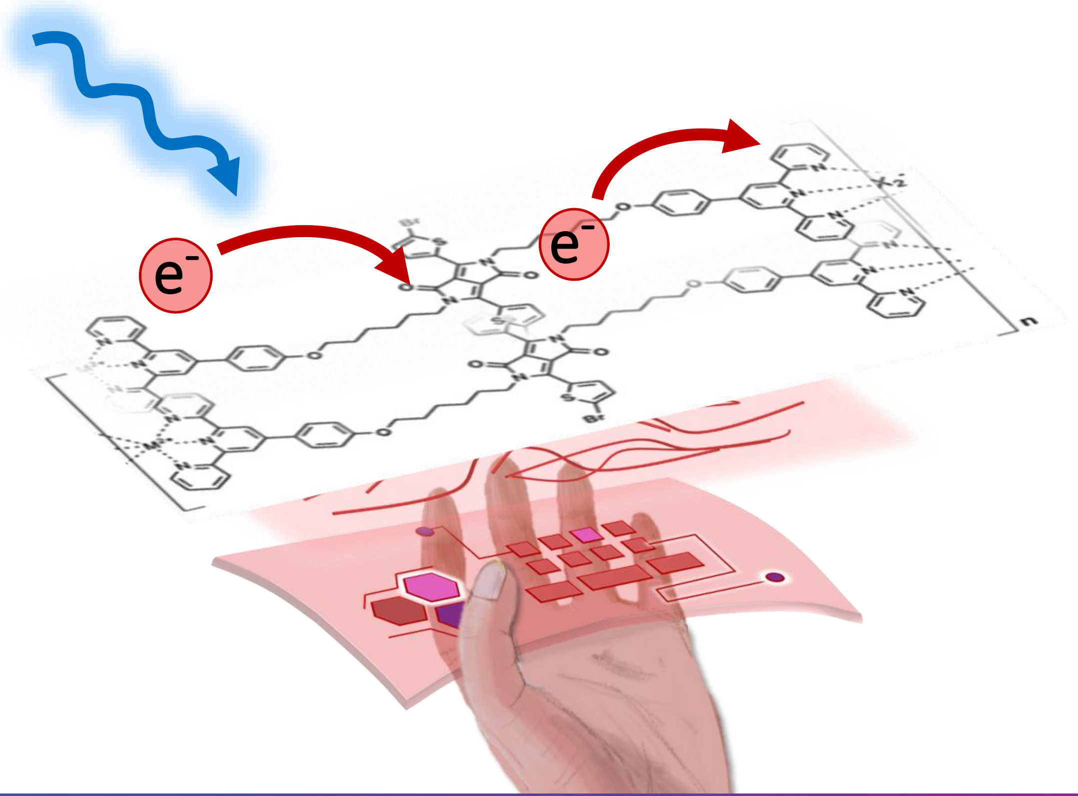
Direct application to organic solar cells!



Step 4: Measuring Electron Transfer Rates

Femtosecond Transient Absorption Spectroscopy

Electron Transfer Rate: An indication of electron transport efficiency;
the faster the transfer rate, the quicker electron conduction occurs through the polymer

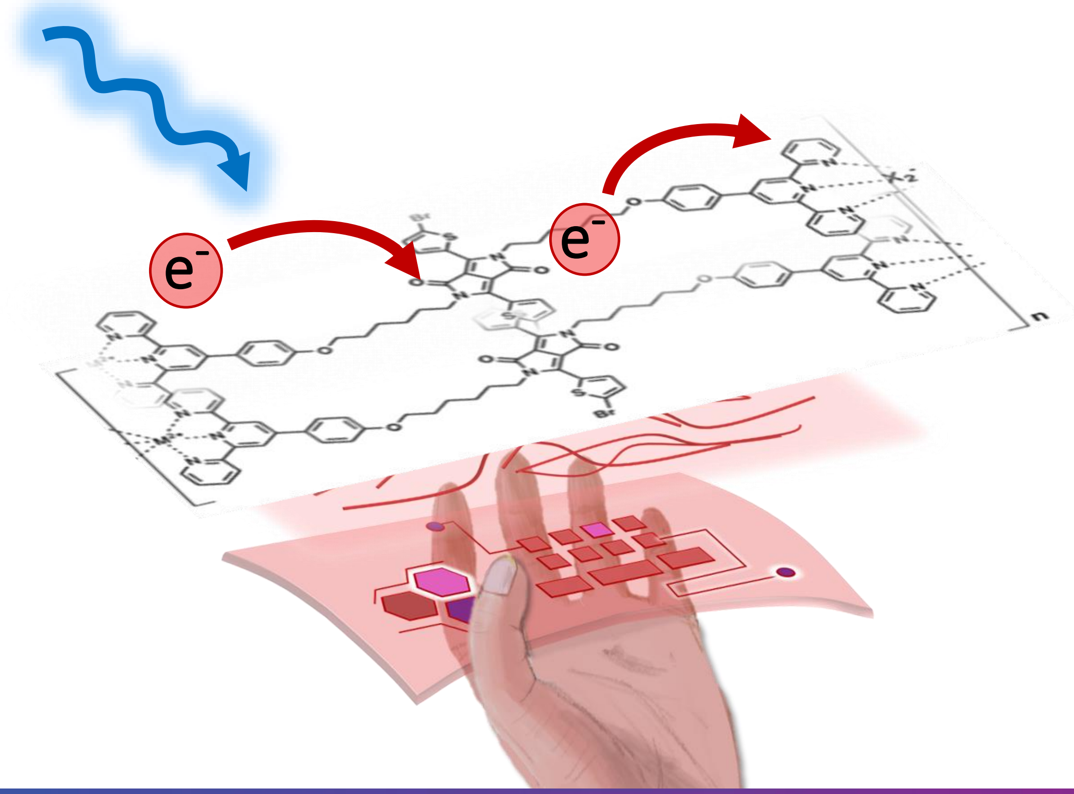


	Electron Transfer Rate (electrons/s)	Transfer Efficiency (%)
$Fe(BF_4)_2$	2.86×10^{11}	99.9
$Co(BF_4)_2$	1.51×10^{10}	98.7
$CoCl_2$	1.98×10^{10}	99.0
$Zn(OTf)_2$	7.82×10^{9}	97.5
$MnCl_2$	8.34×10^{9}	97.6

Step 4: Measuring Electron Transfer Rates

Femtosecond Transient Absorption Spectroscopy

Electron Transfer Rate: An indication of electron transport efficiency;
the faster the transfer rate, the quicker electron conduction occurs through the polymer



	Electron Transfer Rate (electrons/s)	Transfer Efficiency (%)
$Fe(BF_4)_2$	2.86×10^{11}	99.9
$Co(BF_4)_2$	1.51×10^{10}	98.7
$CoCl_2$	1.98×10^{10}	99.0
$Zn(OTf)_2$	7.82×10^{9}	97.5
$MnCl_2$	8.34×10^{9}	97.6

Fe and Co allow for the fastest photo-induced electron transfers ✓

Conclusions

✓Part 1: Successfully **synthesized and coordinated** new supramolecular DPP polymers with M-L interactions

✓Part 2: **Emission intensity varies** depending on the coordinated metal

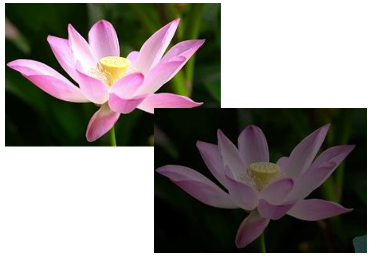
✓Part 3: Fe and Co metal ions allowed for the most **efficient electron transfer** upon interaction with light

Therefore, M-L coordination provides a mechanism to generate soft and tunable optoelectronics. This design should further be explored for a new generation of devices!

Conclusions

✓**Part 1:** Successfully **synthesized and coordinated** new supramolecular DPP polymers with M-L interactions

✓**Part 2:** **Emission intensity varies** depending on the coordinated metal

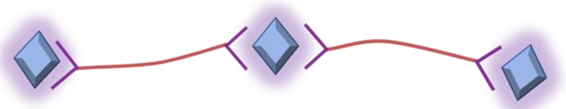


- Fe, Co effectively alter the optoelectronic properties of the polymer
- Mn is an inefficient quencher

✓**Part 3:** Fe and Co metal ions allowed for the most **efficient electron transfer** upon interaction with light

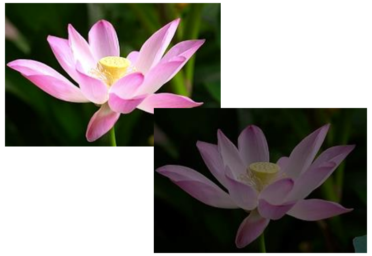
Therefore, M-L coordination provides a mechanism to generate soft and tunable optoelectronics. This design should further be explored for a new generation of devices!

Conclusions



✓**Part 1:** Successfully **synthesized and coordinated** new supramolecular DPP polymers with M-L interactions

✓**Part 2:** **Emission intensity varies** depending on the coordinated metal



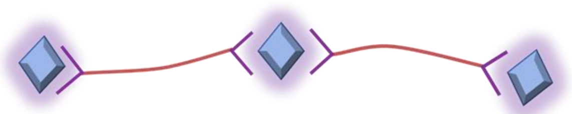
- Fe, Co effectively alter the optoelectronic properties of the polymer
- Mn is an inefficient quencher

✓**Part 3:** Fe and Co metal ions allowed for the most **efficient electron transfer** upon interaction with light

- Femtosecond Transient Absorption Spectroscopy

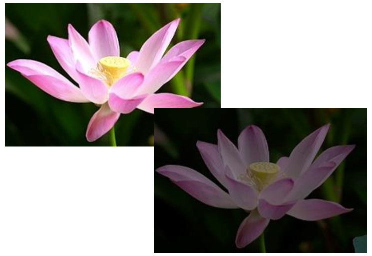
Therefore, M-L coordination provides a mechanism to generate soft and tunable optoelectronics. This design should further be explored for a new generation of devices!

Conclusions



✓**Part 1:** Successfully **synthesized and coordinated** new supramolecular DPP polymers with M-L interactions

✓**Part 2:** **Emission intensity varies** depending on the coordinated metal



- Fe, Co effectively alter the optoelectronic properties of the polymer
- Mn is an inefficient quencher

✓**Part 3:** Fe and Co metal ions allowed for the most **efficient electron transfer** upon interaction with light

- Femtosecond Transient Absorption Spectroscopy

Therefore, M-L coordination provides a mechanism to generate soft and tunable optoelectronics. This design should further be explored for a new generation of devices!

Acknowledgements

Simon Rondeau-Gagné

Postdoctoral Fellows
Nastaran Yousefi, PhD
Adam Pollit, PhD
M. Nazir Tahir, PhD

PhD
Michael Ocheje

PhD Candidates
P. Blake J. St. Onge
Madison Mooney
Gage Mason
Adit Nyayachavadi

PhD Candidates
Angela Awada
Fatemeh Motaghedi

MSc Candidates
Susanna Vu
Piumi Kulatunga
Daniella Skaf

Undergraduate Researchers
Monika Kojic
Deanna Fisher
Robert Moy
Katerina Iakovidis
Megan Wan
Chloe Crep
Josie Teti
Amit Sur

Collaborators
Adam Langlois
Aneeta Younus
Paul-Ludovic Karsenti
Jean-François Morin
Pierre Audet

Funding

Thank you for listening!

Any questions?