Azo-dye Degradation with Electrochemical Method

-Supramolecular Metal-organic Frameworks as catalyst

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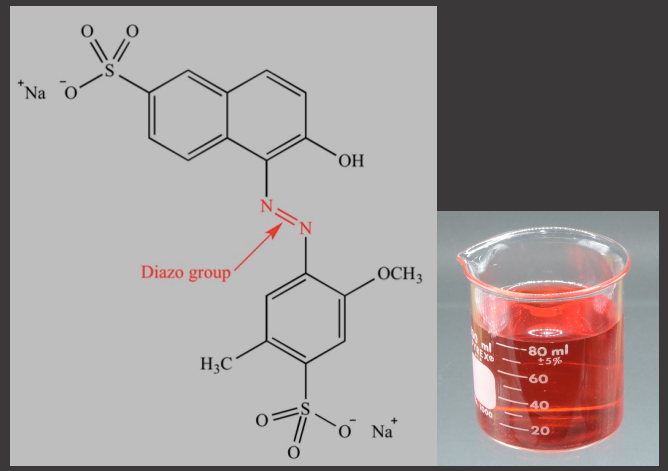
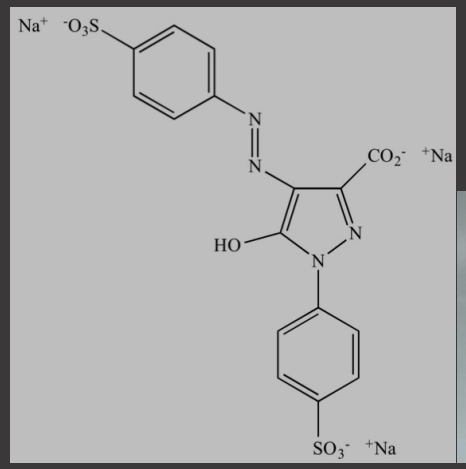
Azo-dye Degradation

FD&C Red 40



FD&C Yellow 5



Azo-dye Applications:

textile industry
paper production
food technology

Environmental issues:

damage aquatic lives
contaminate soil
effect human health

https://www.chem.ucla.edu/~harding/IGOC/A/azo_dye.html

Degradation methods

Biological Methods:

eg. enzymatic decomposition

-low efficiency

Chemical Methods:

eg. ozonation

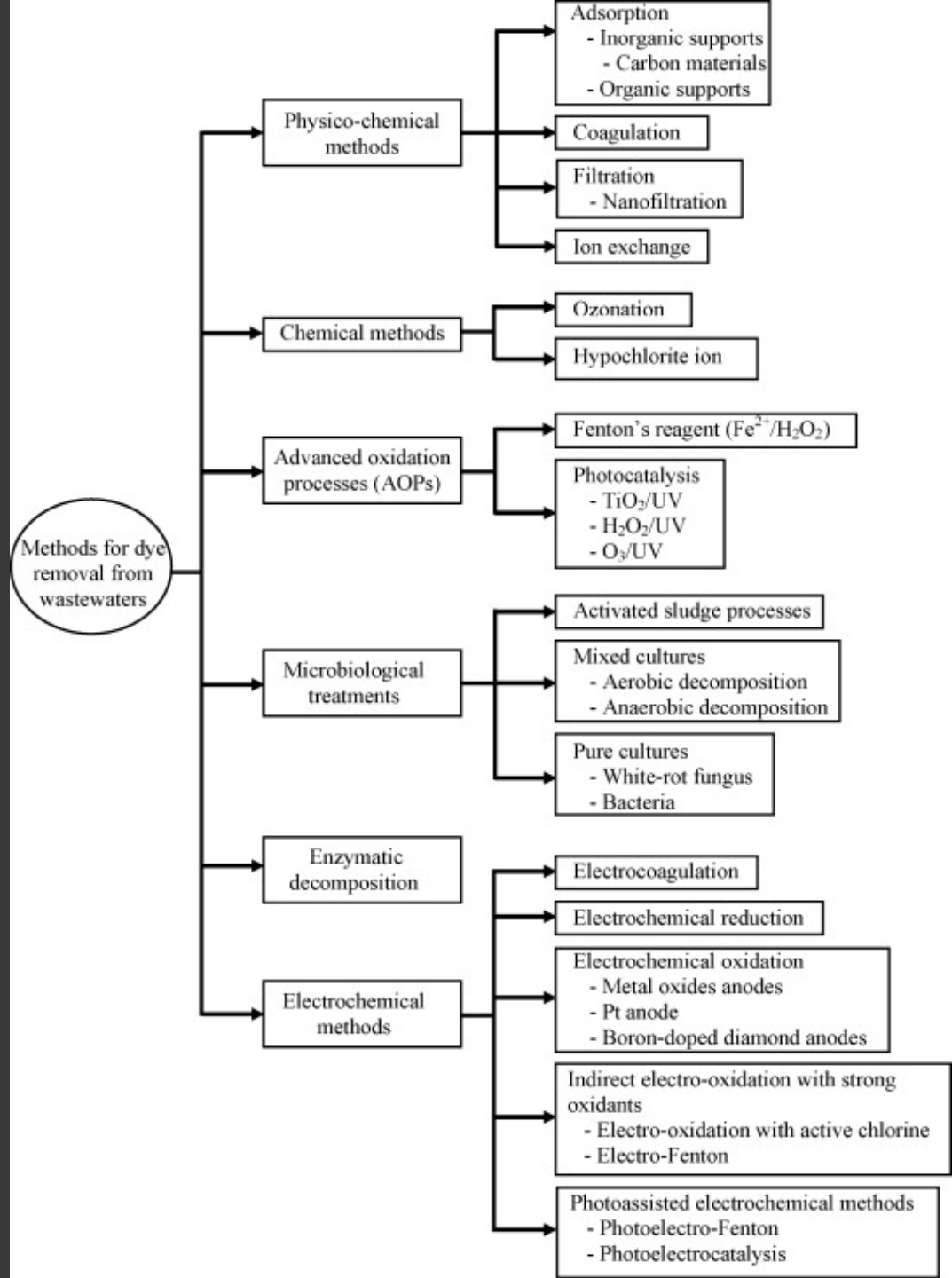
-high cost

Physical-chemical Methods:

eg. coagulation

-generation of secondary waste

Sometimes More Hazardous



Martínez-Huitle, C. A.; Brillas, E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. *Applied Catalysis B: Environmental* **2009**, *87*, 105-145.

Electrochemical methods

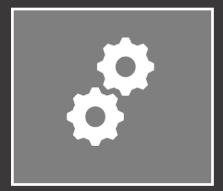
-Proton-Coupled Electron Transfer Studies

Bulk electrolysis:

- Controlled potential experiment
- Current over time

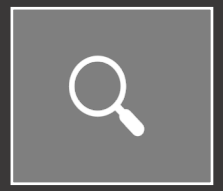
Linear sweep voltammetry (LSV):

- Potential between working & reference electrode is swept linearly in time



Cyclic voltammetry (CV):
-MAIN FOCUS

- Potential is swept in a way that the experiment ends where it started



Rotating disk voltammetry:

- The working electrode is rotated at a constant rat
- Current over Potential

Electrochemical impedance spectroscopy (EIS):

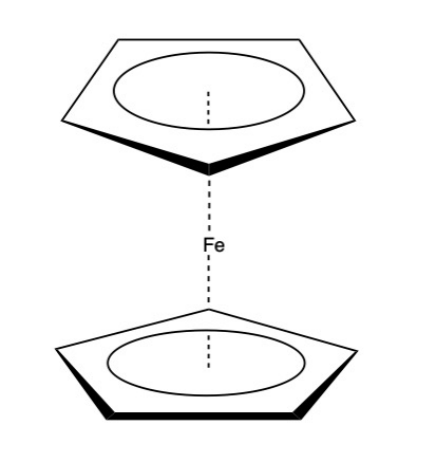
- Using AC potential instead of DC

Spectroelectrochemistry:

- Combination Electrochemical method & Spectroscopic technique

Studies of Cyclic Voltammetry - Ferrocene

Ferrocene: The Internal Standard

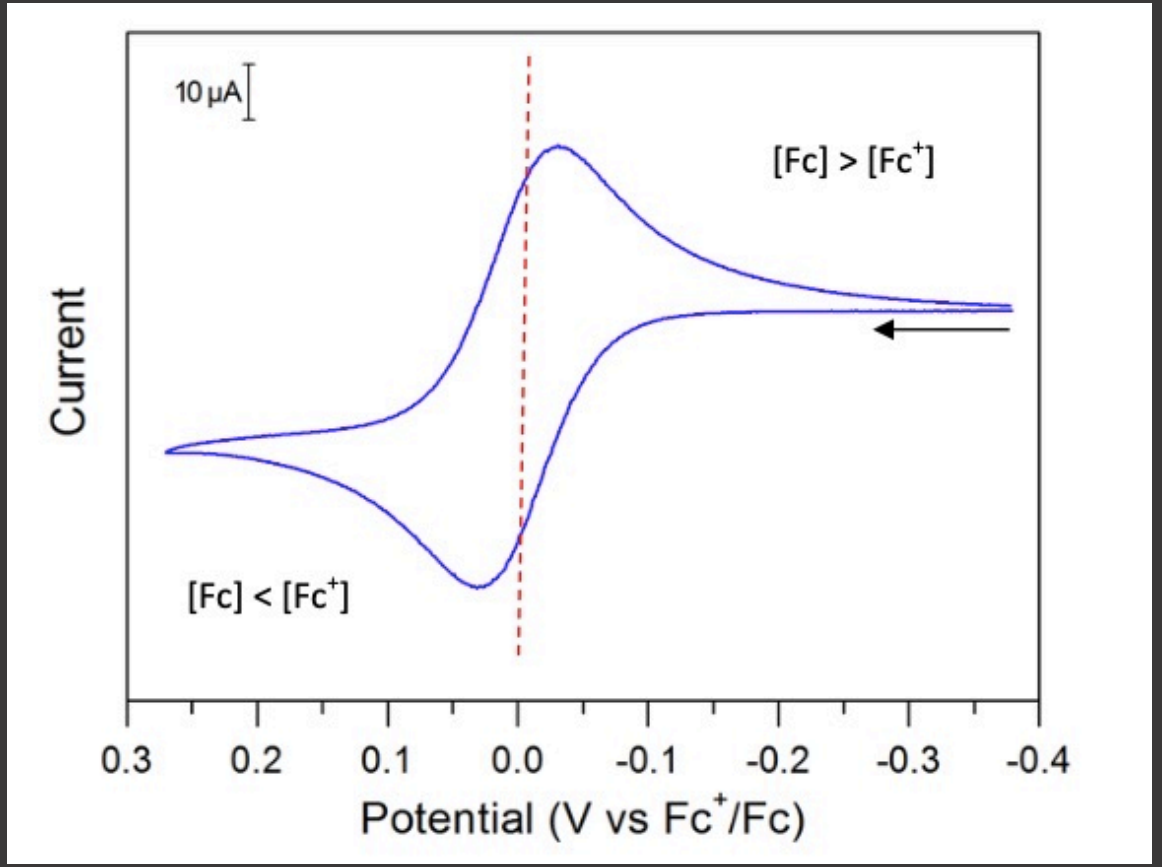


Special Properties:

Reversible redox properties
Two rotatory coplanar cyclopentadienyl (Cp) rings.

Work as Scaffold
Work as catalysts (its synthesized ligand)

The Cyclic Voltammogram of Ferrocene



Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A practical beginner's guide to cyclic voltammetry. *J. Chem. Educ.* **2018**, *95*, 197-206.

Mechanism Studies - PCET Reactions

Two Different mechanisms

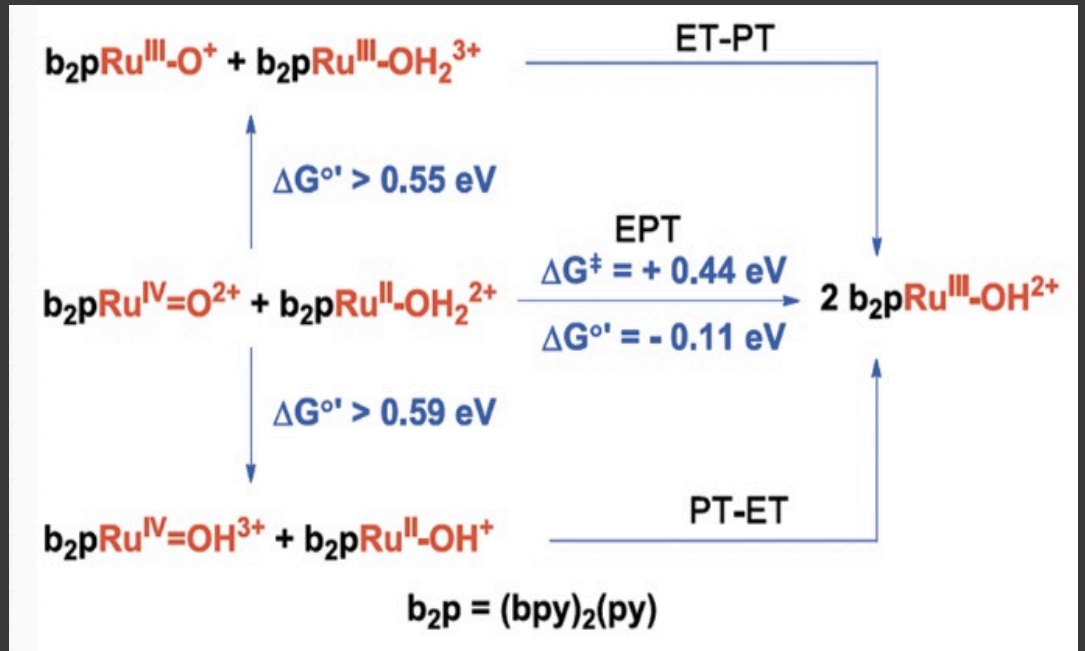
Concerted PCET

Avoid high energy intermediate
More complex

Stepwise PCET

high reaction barriers and low rates

Comparison: Concerted VS. Stepwise



Concerted PCET

-Two mechanisms

Electron-Proton Transfer (EPT)

Transfer of an electron and proton between different donors and acceptors

-significant charge redistribution

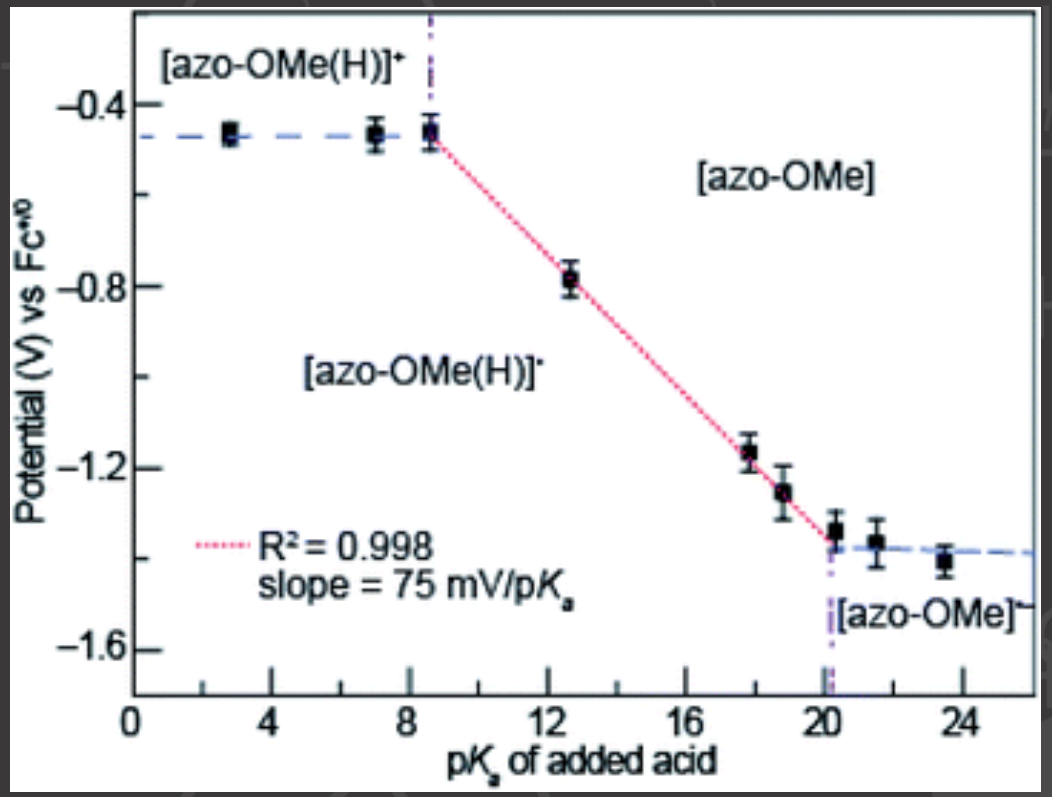
H-atom Transfer (HAT)

Transfer of an electron and proton between the same donors and acceptors

-negligible charge redistribution

Thermodynamic Studies- PCET Reaction

Potential-pK_a Diagram: To understand PCET reactions in non-aqueous solutions



Useful Information Obtained

The number of discrete species

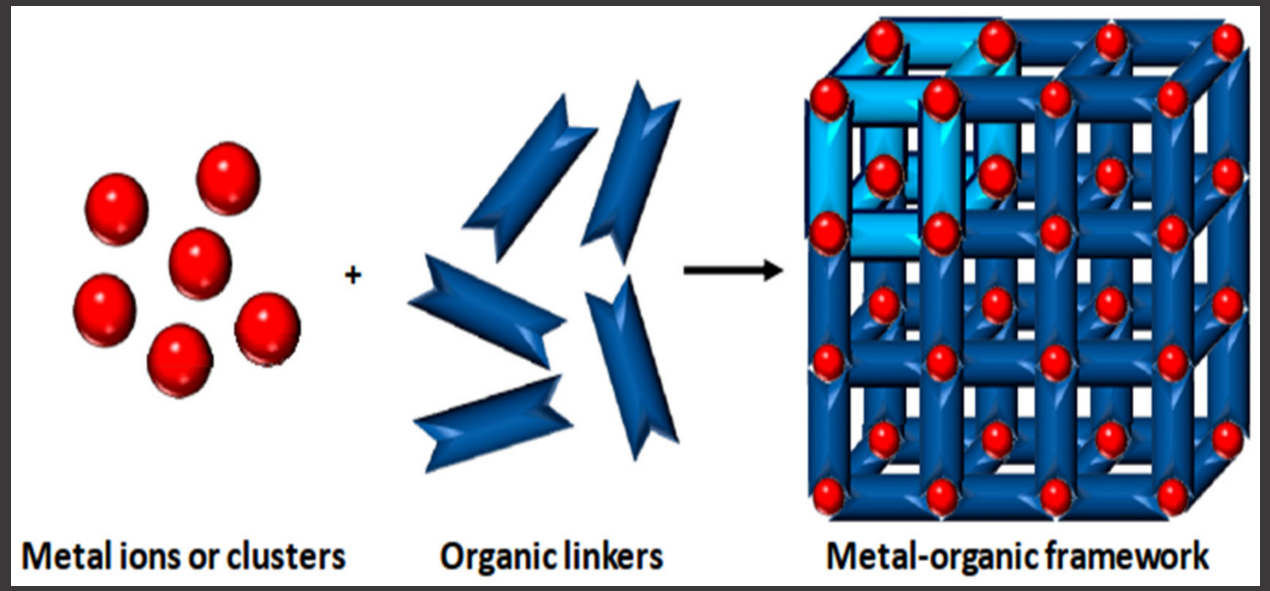
pKa values

Thermodynamically stable species

Stoichiometry in protons and electrons for each PCET event.

Oldacre, A. N.; Young, E. R. Electrochemical proton-coupled electron transfer of an anthracene-based azo dye. *RSC Advances* **2020**, *10*, 14804-14811.

Supramolecular Metal-Organic Frameworks - As Electrocatalysts



Common Applications:

- Molecular separation
- Gas storage
- Drug delivery
- Catalysts

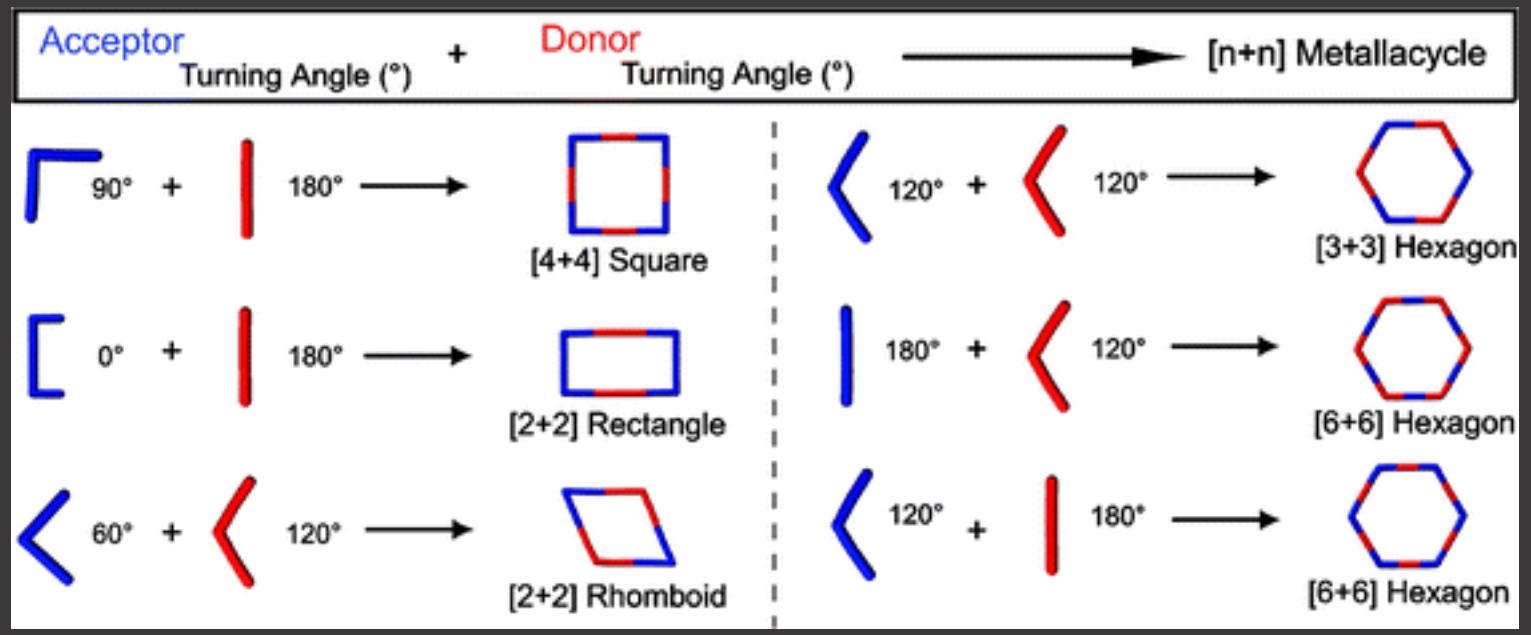
Synthesis Methods:

- Electrochemical synthesis
- Solvothermal methods
- Microwave synthesis

Rasheed, T.; Rizwan, K.; Bilal, M.; Iqbal, H. Metal-organic framework-based engineered materials—Fundamentals and applications. *Molecules* **2020**, *25*, 1598.

Synthesis of MOFs:

- Coordination-driven Self-assembly Techniques



Northrop, B. H.; Yang, H.; Stang, P. J. Coordination-driven self-assembly of functionalized supramolecular metallacycles. *Chemical communications* **2008**, 5896-5908.

Thank You!