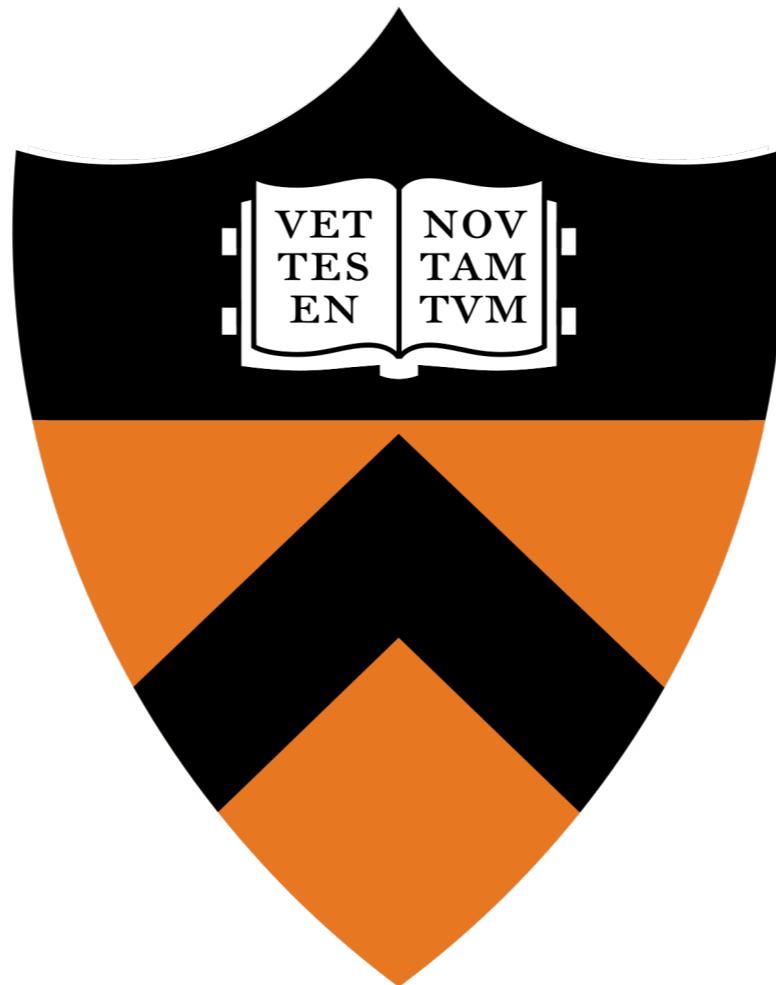
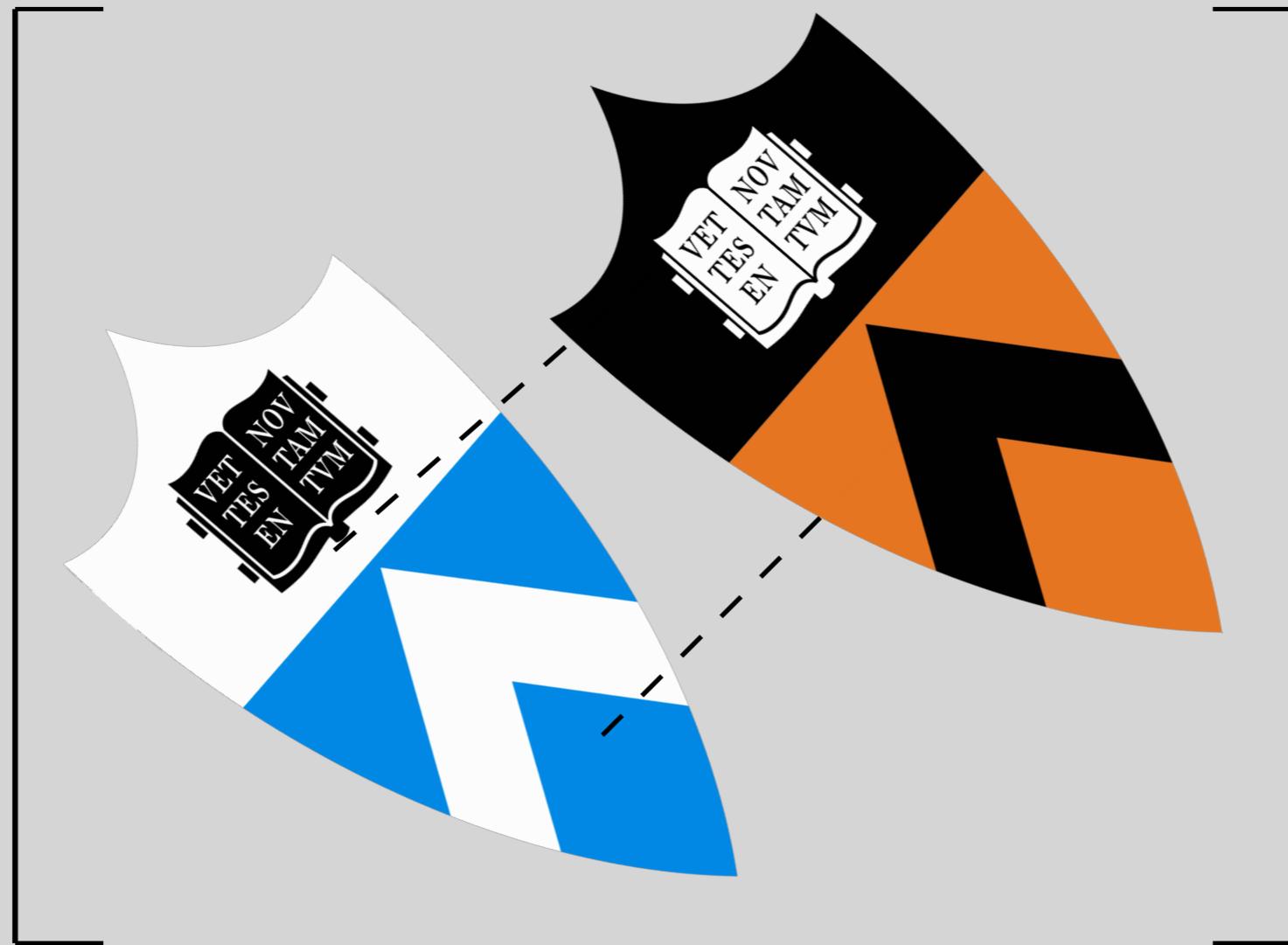


*Visible Light Induced Single Electron Transfer via  
EDA Complexes*



Noah B. Bissonnette  
MacMillan Group Meeting  
Literature Review  
Jan 31<sup>st</sup>, 2023

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# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

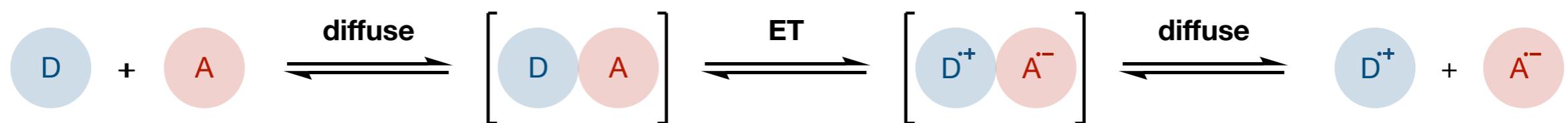
**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Electron Transfer Mechanisms*

## *Inner Sphere vs Outer Sphere ET*

### ■ Outer Sphere Electron Transfer



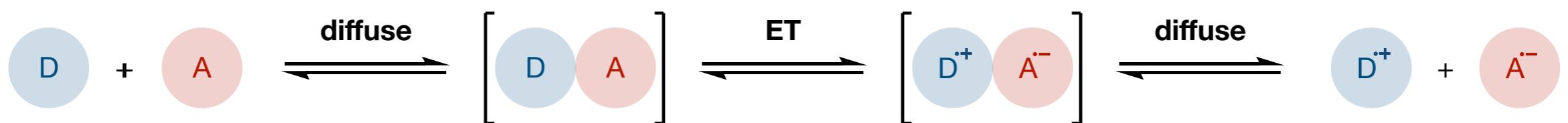
**“Donor” = Oxidant**

**“Acceptor” = Reductant**

# Electron Transfer Mechanisms

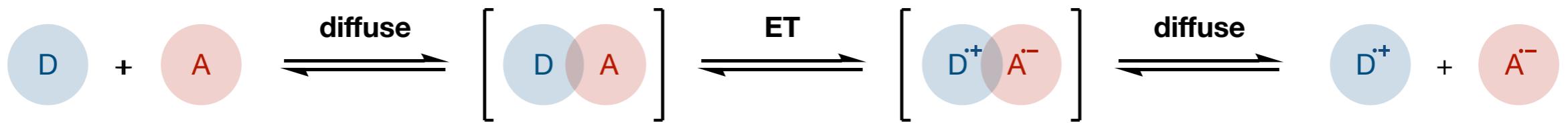
## Inner Sphere vs Outer Sphere ET

### Outer Sphere Electron Transfer



- Electron “hops” from D to A
- Entropically Favored
- Enthalpically Disfavored
- ET is typically rate determining

### Inner Sphere Electron Transfer

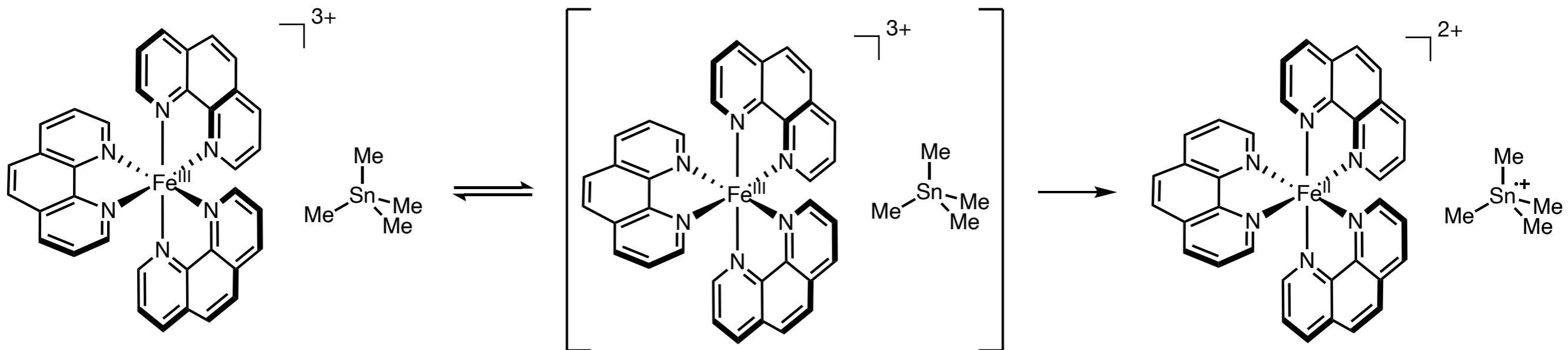


- Electron “passed” from D to A
- Entropically Disfavored
- Enthalpically Favored
- ET may not be rate determining

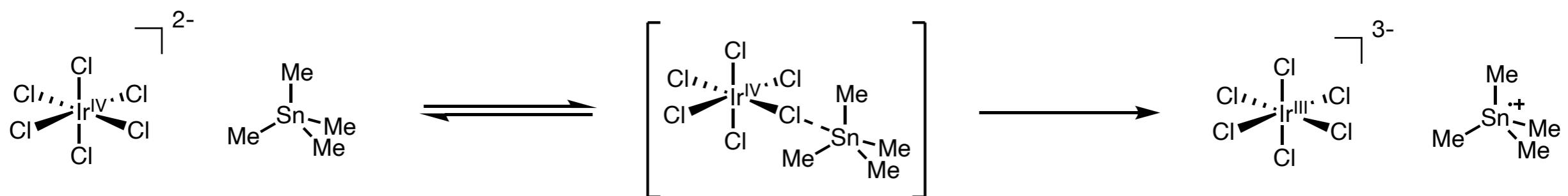
# Electron Transfer Mechanisms

## Inner Sphere vs Outer Sphere ET

### Outer Sphere Electron Transfer



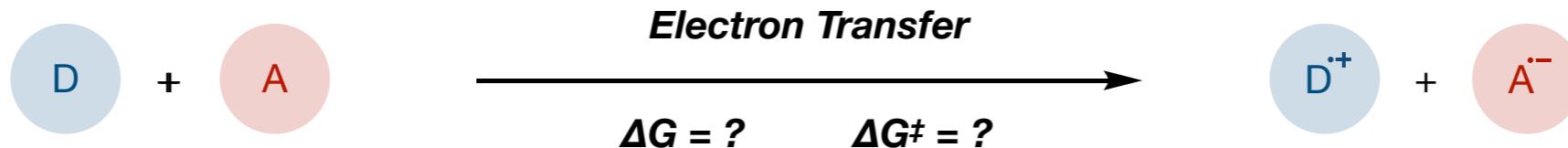
### Inner Sphere Electron Transfer



**Outer sphere ET only requires close association and orbital overlap,  
inner sphere ET typically occurs through a bridging ligand**

# *Electron Transfer Mechanisms*

*Thermodynamics and Kinetics of ET*



## **Thermodynamics**

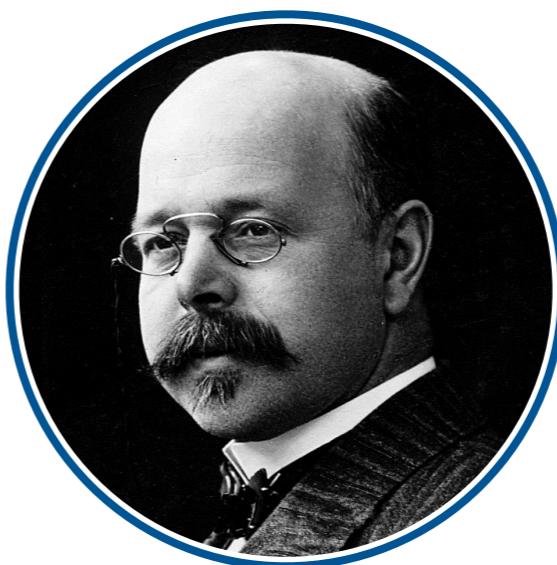
$$\Delta G = -nFE_{\text{cell}}$$

$n = \# \text{ electrons}$

$F = \text{Faraday's constant}$

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

### **Nernst Equation**

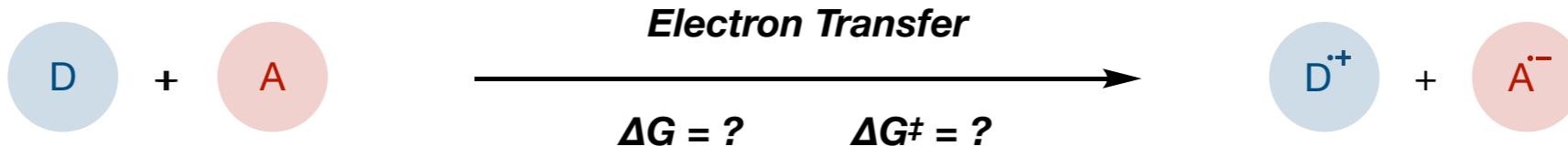


**Walther Nernst**  
1864-1941

**Successfully predicts  $\Delta G$  for inner or outer sphere ET**

# Electron Transfer Mechanisms

## Thermodynamics and Kinetics of ET



### Thermodynamics

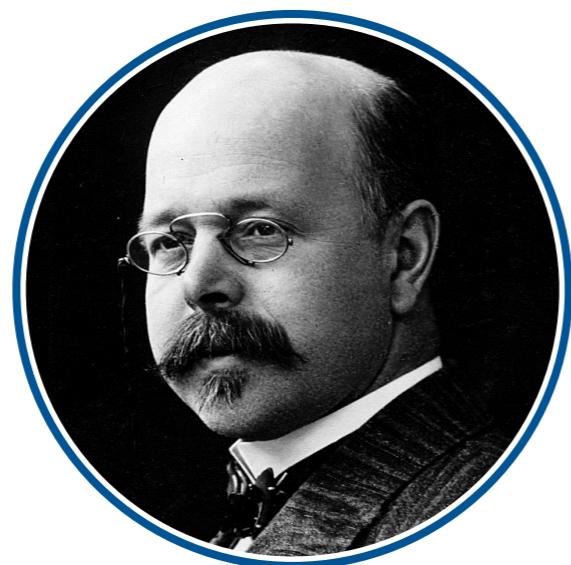
$$\Delta G = -nFE_{\text{cell}}$$

$n$  = # electrons

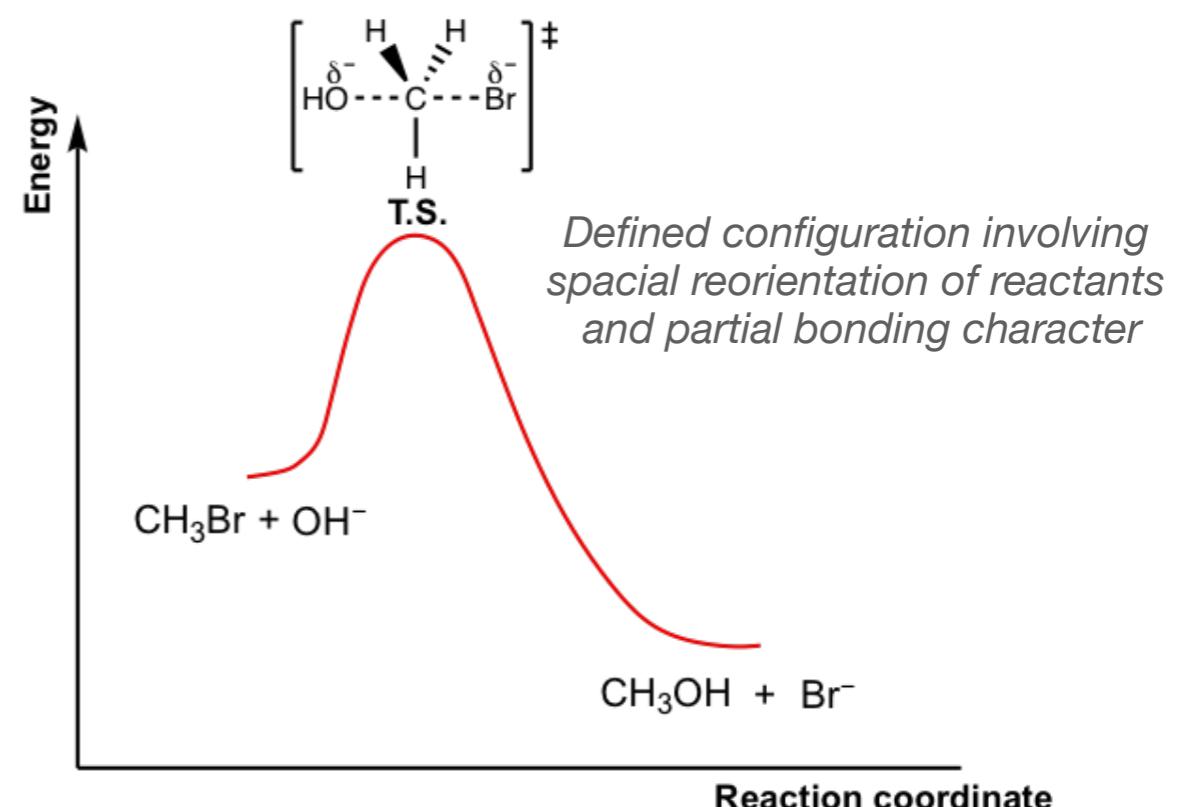
$F$  = Faraday's constant

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

### Nernst Equation



**Walther Nernst**  
1864-1941



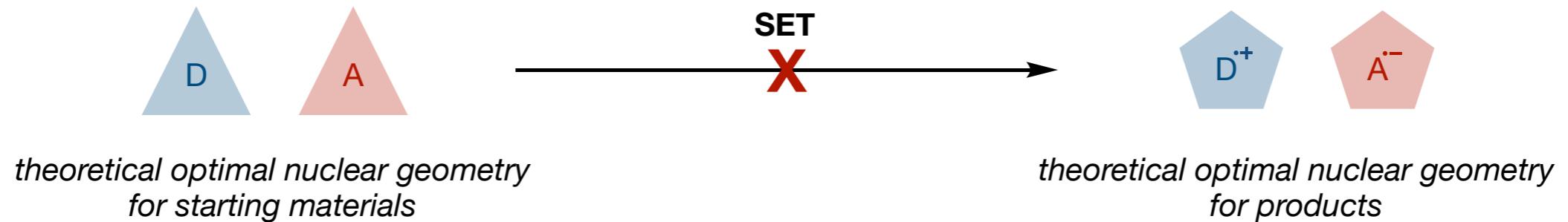
**Successfully predicts  $\Delta G$  for inner or outer sphere ET**

**Classical Eyring transition state theory can't be directly applied**

# *Electron Transfer Mechanisms*

## *Thermodynamics and Kinetics of ET*

### **Kinetics**



### **Franck-Condon principle**

*Electronic transitions ( $\sim 10^{-16}$  s) are much faster than nuclear vibrations ( $\sim 10^{-13}$  s)*

***ETs result in no immediate structural changes***

# Electron Transfer Mechanisms

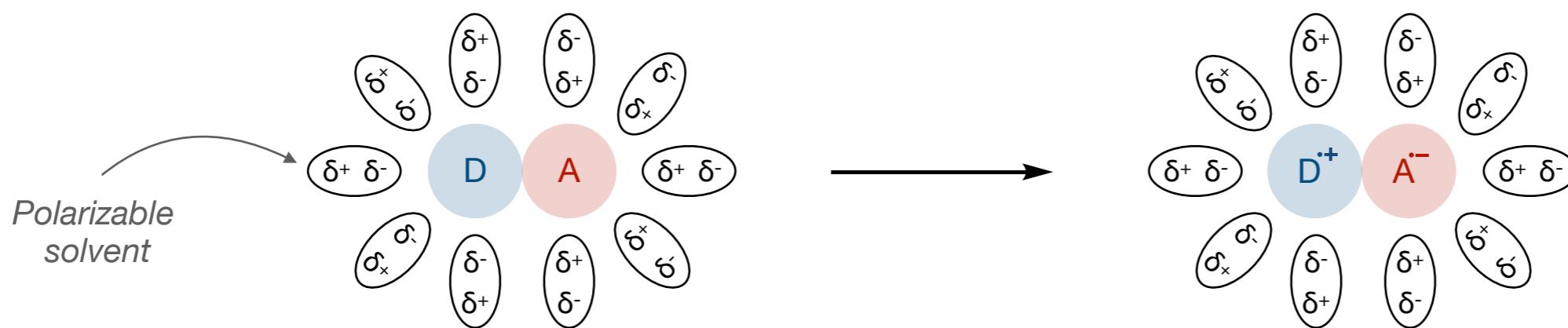
## Thermodynamics and Kinetics of ET

### Kinetics



### Franck-Condon principle

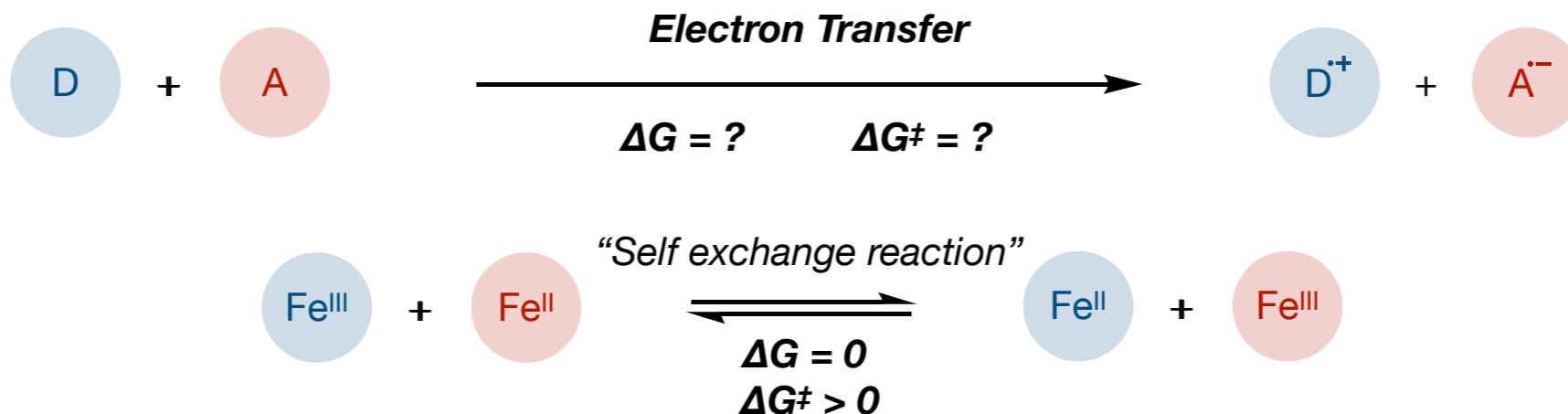
Electronic transitions ( $\sim 10^{-16}$  s) are much faster than nuclear vibrations ( $\sim 10^{-13}$  s)



**Solvent polarity can significantly impact rates of SET**

# Electron Transfer Mechanisms

## Thermodynamics and Kinetics of ET



$$G = \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \times \left( \frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_s} \right) \times (\Delta e)^2$$

$G$  = Gibbs free energy

$r_x$  = size of conducting spheres

$R$  = distance between spheres

$\epsilon_{opt}$  = optical dielectric constant (solvent)

$\epsilon_s$  = static dielectric constant (solvent)

$\Delta e$  = charge transferred between spheres



**Rudolph A. Marcus**  
1992 Nobel Prize in Chemistry  
1923-present

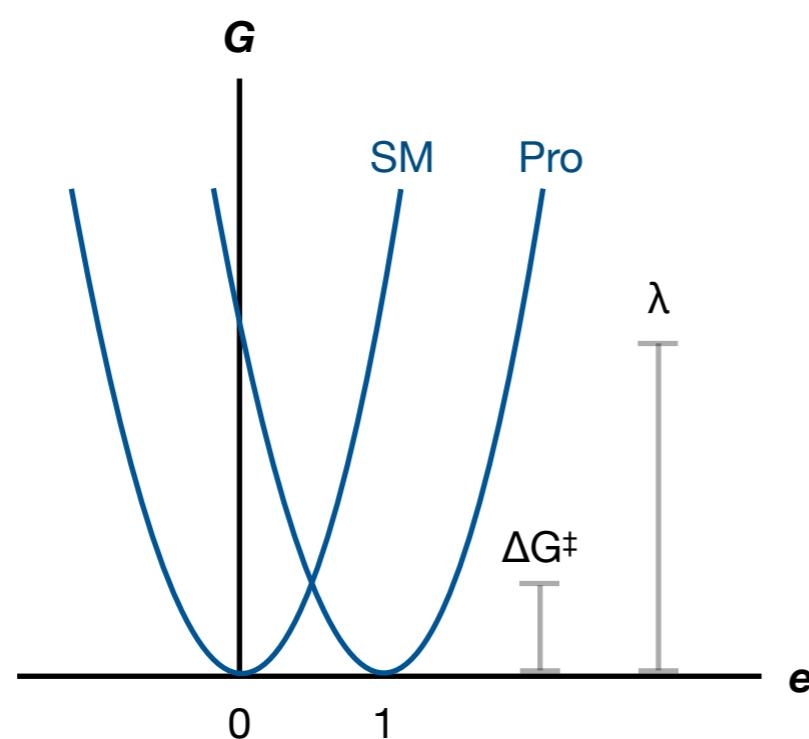
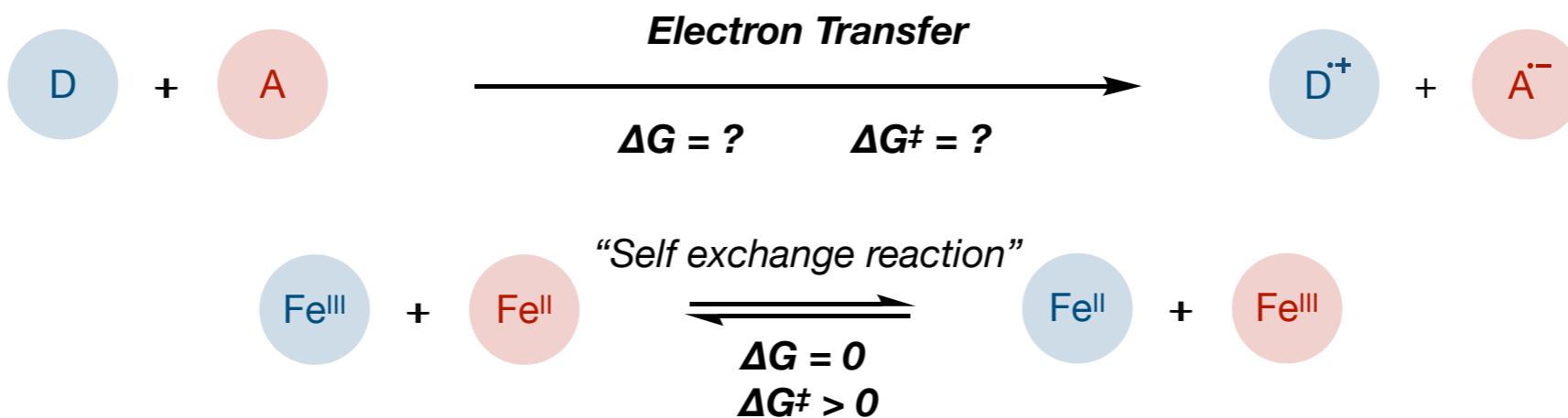
**Marcus modeled outer sphere ETs using classical electrostatics and correcting for quantized charge**

Marcus, R. A.; J. Chem. Phys. 1956, 24, 966-978.

Rosokha, S. V., Kochi, J. K.; Acc. Chem. Res. 2008, 41, 641-653

# Electron Transfer Mechanisms

## Thermodynamics and Kinetics of ET



**Rudolph A. Marcus**  
1992 Nobel Prize in Chemistry  
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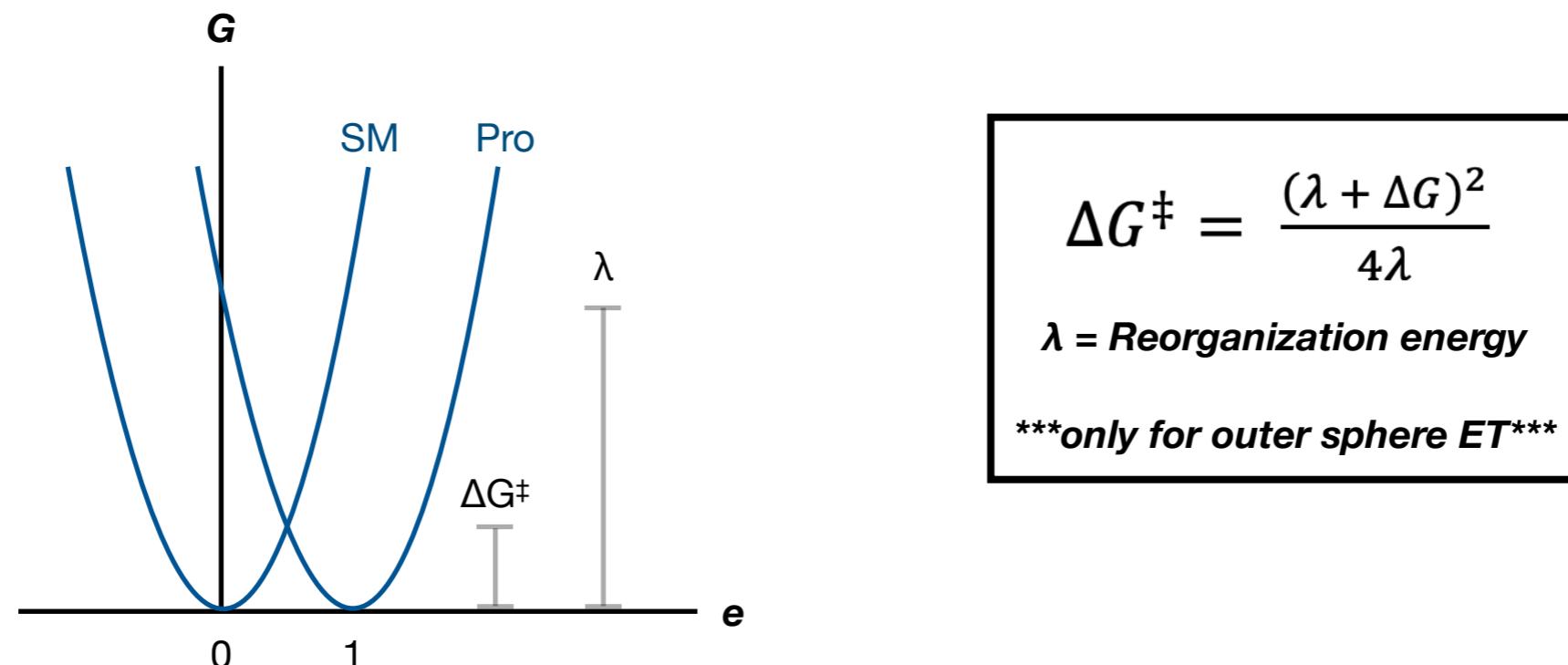
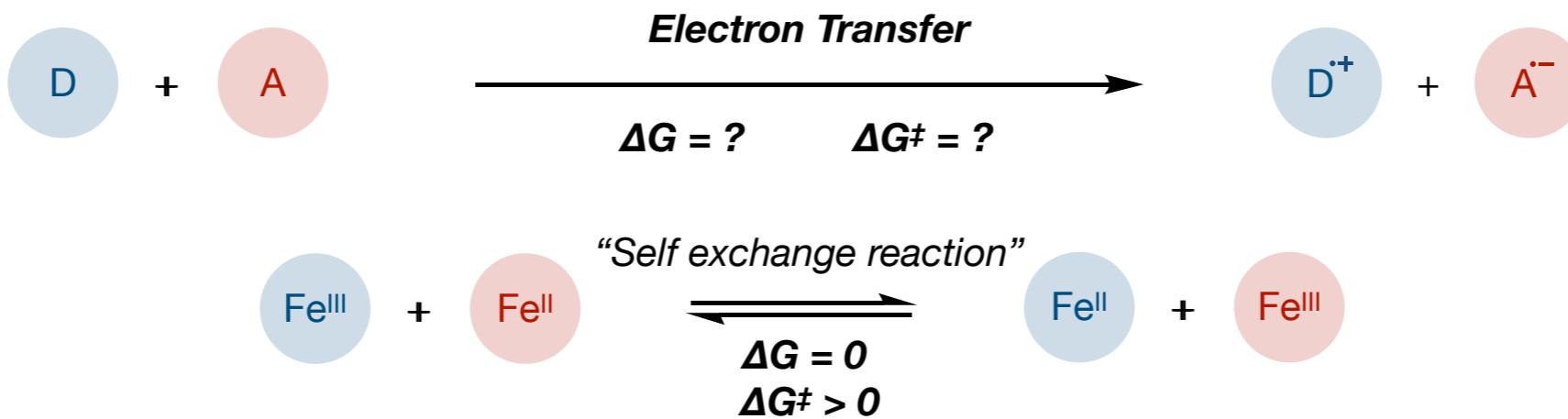
**Plotting a SET event for a self exchange reaction ( $\Delta G = 0$ ) results in 2 identical parabolas, intersection corresponds to the  $\Delta G^\ddagger$**

Marcus, R. A.; J. Chem. Phys. 1956, 24, 966-978.

Rosokha, S. V., Kochi, J. K.; Acc. Chem. Res. 2008, 41, 641-653

# Electron Transfer Mechanisms

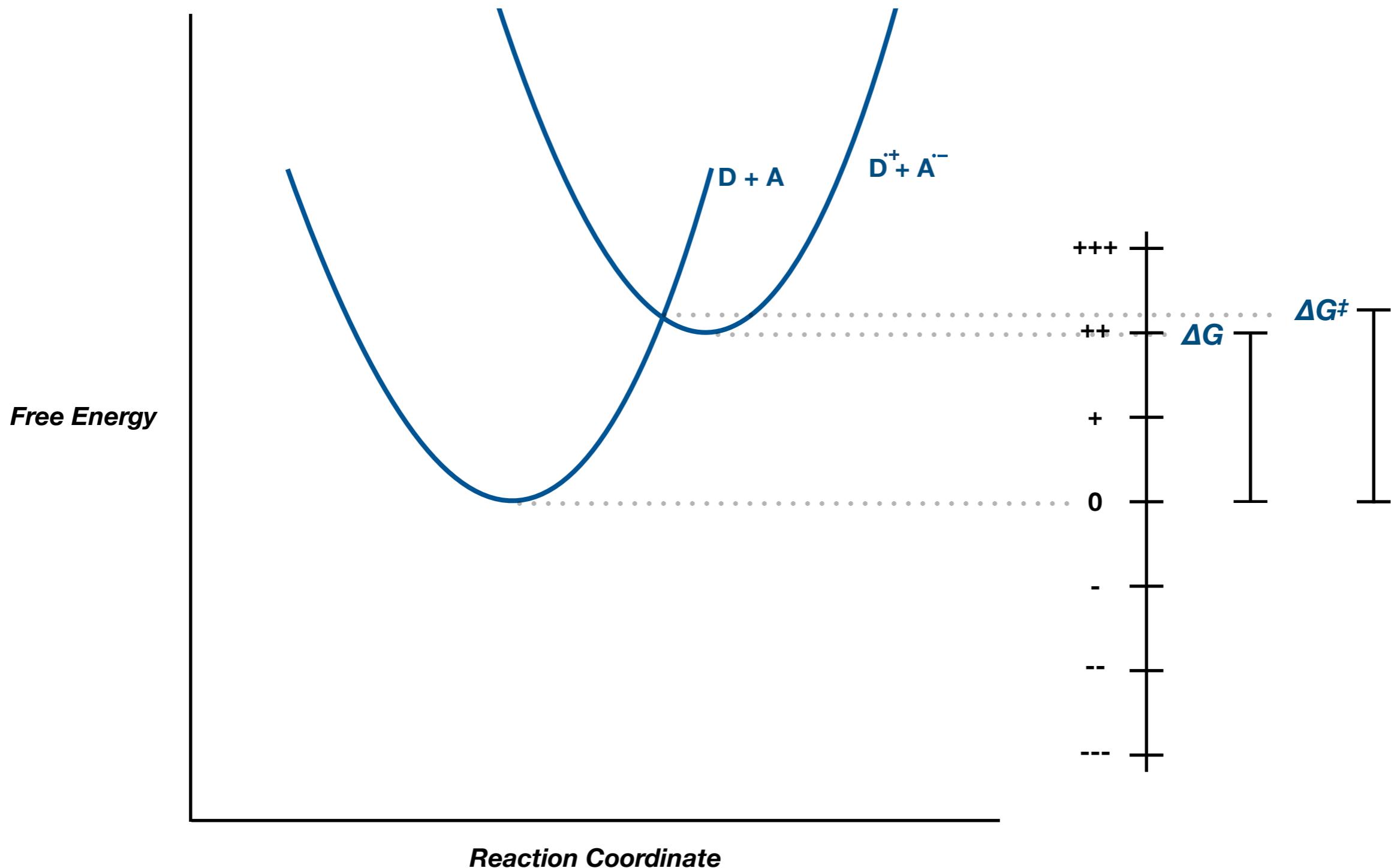
## Thermodynamics and Kinetics of ET



**Plotting a SET event for a self exchange reaction ( $\Delta G = 0$ ) results in 2 identical parabolas, intersection corresponds to the  $\Delta G^\ddagger$**

# *Electron Transfer Mechanisms*

## *Marcus Theory*



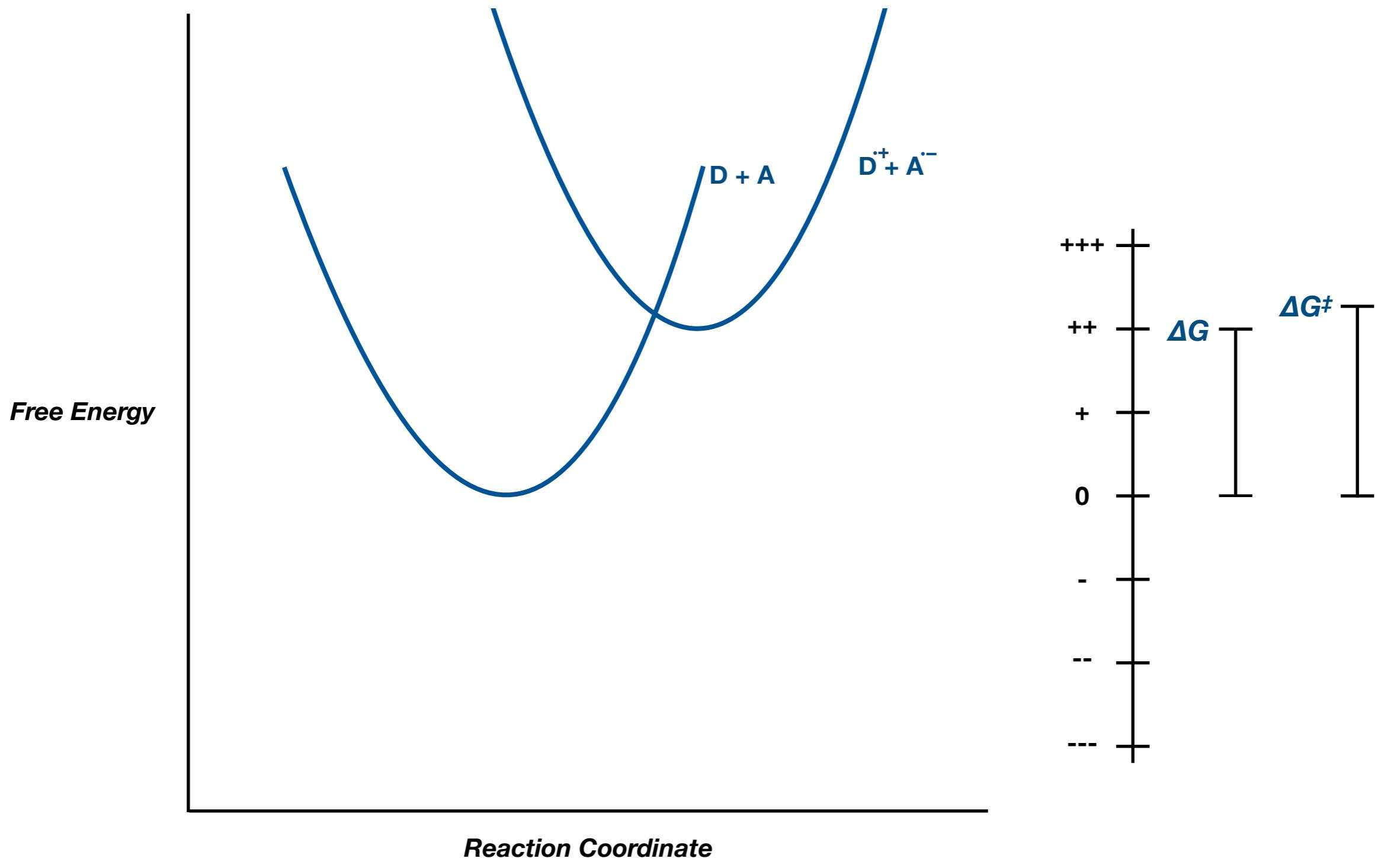
***This can be extended reactions where  $\Delta G \neq 0$  through vertical movement of the parabola***

Marcus, R. A.; *J. Chem. Phys.* 1956, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* 1993, 65, 599-610.

# *Electron Transfer Mechanisms*

## *Marcus Theory*

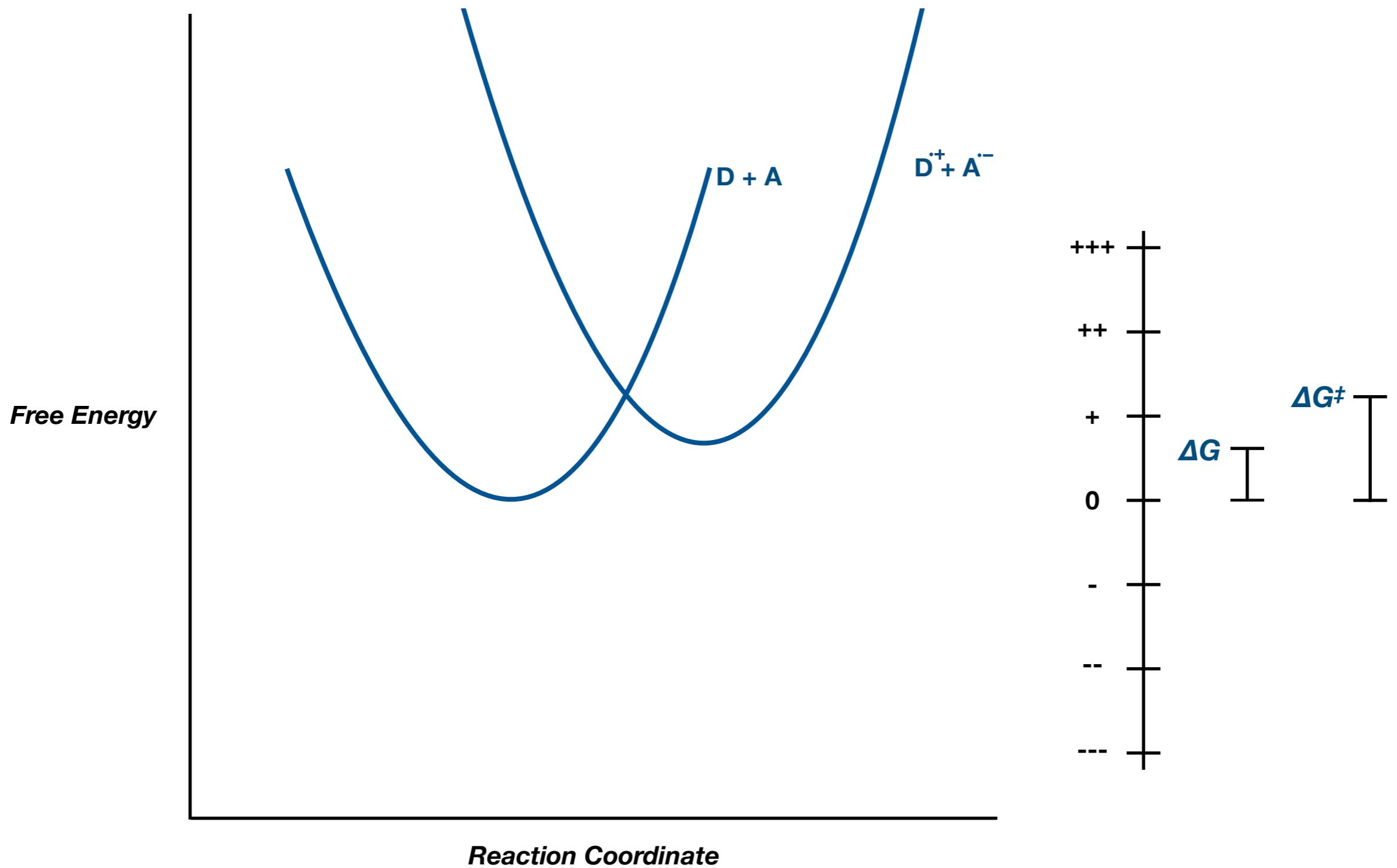


Marcus, R. A.; *J. Chem. Phys.* **1956**, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* **1993**, 65, 599-610.

# *Electron Transfer Mechanisms*

## *Marcus Theory*

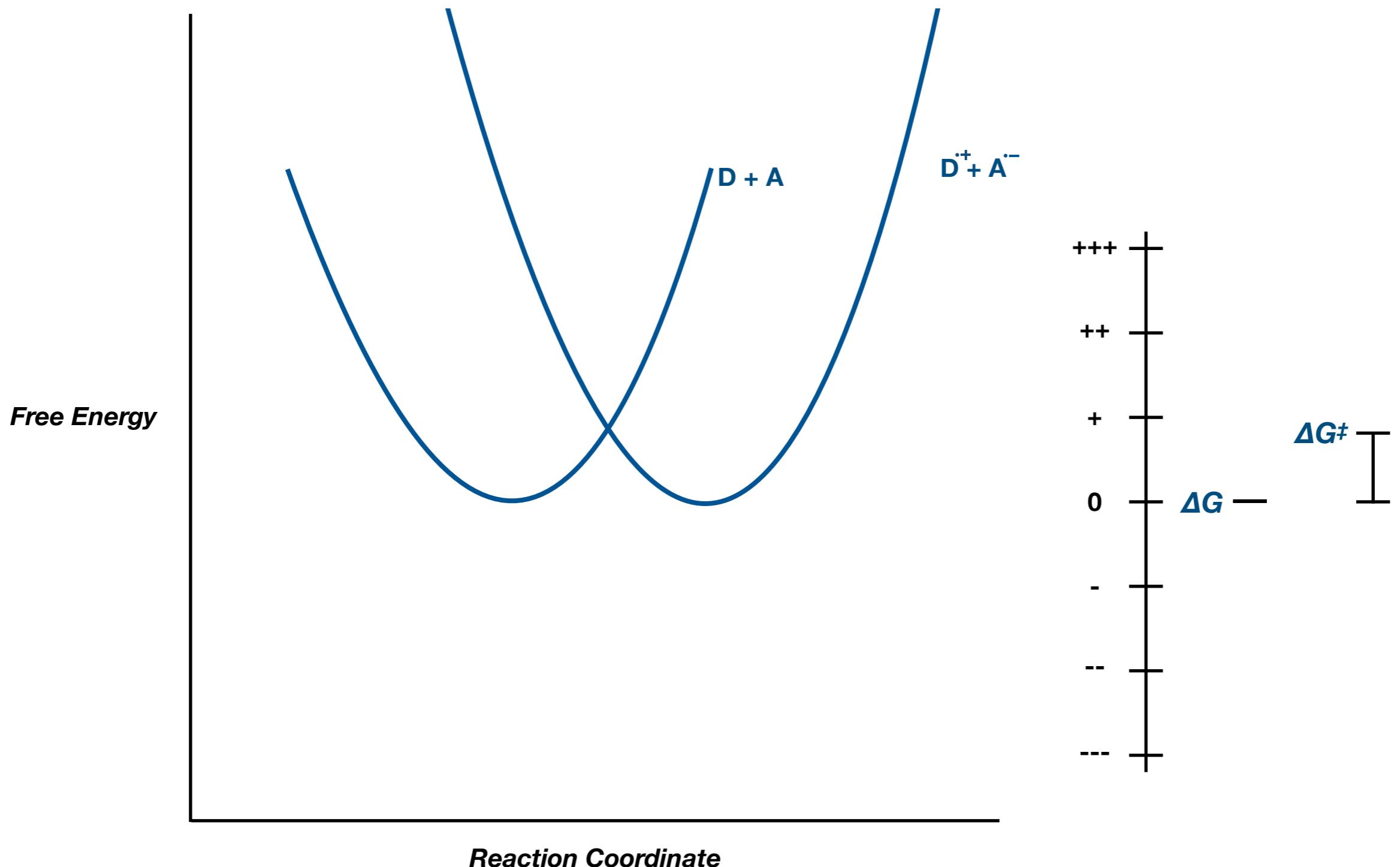


Marcus, R. A.; *J. Chem. Phys.* **1956**, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* **1993**, 65, 599-610.

# *Electron Transfer Mechanisms*

## *Marcus Theory*



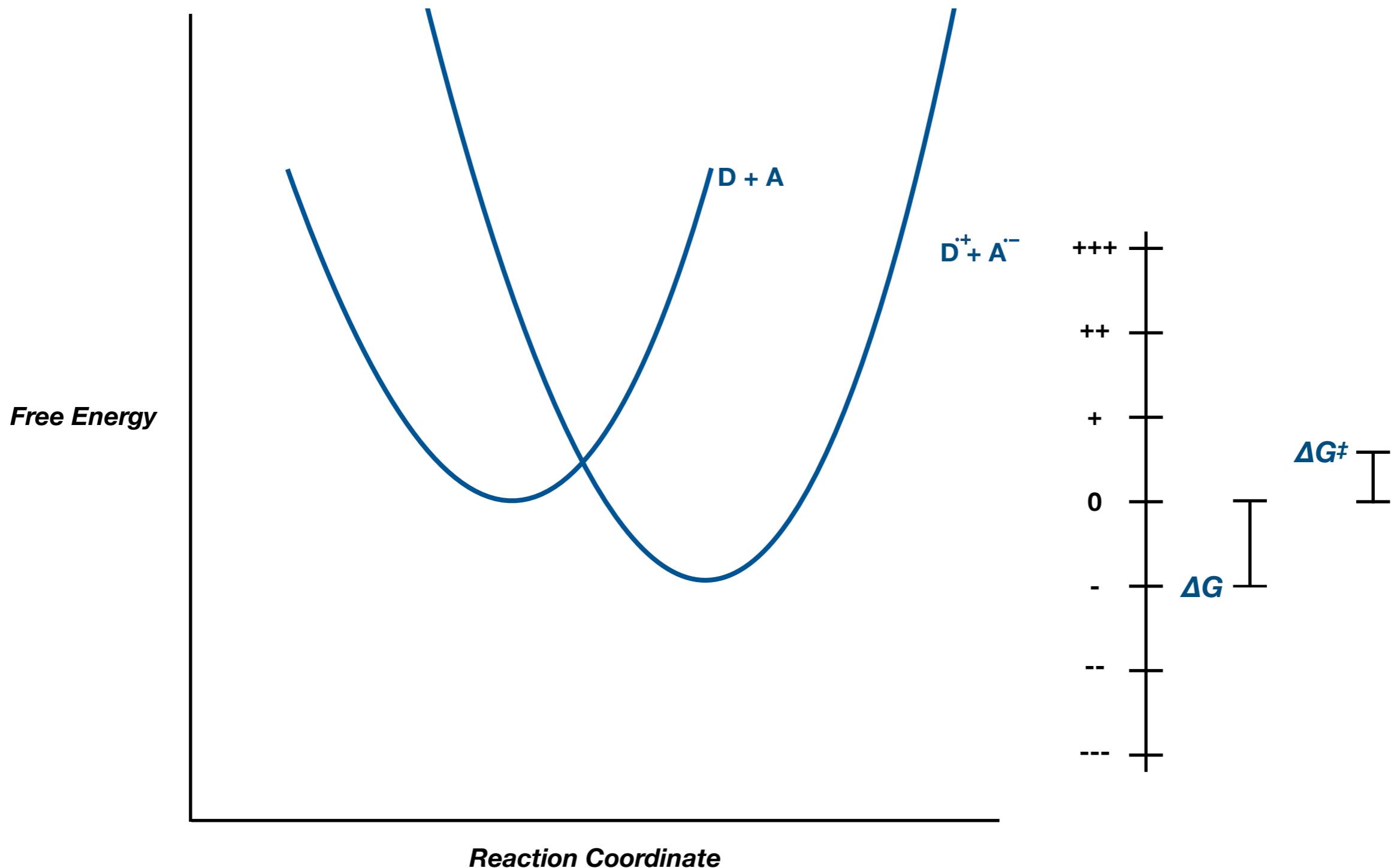
**Thermoneutral**

Marcus, R. A.; *J. Chem. Phys.* **1956**, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* **1993**, 65, 599-610.

# *Electron Transfer Mechanisms*

## *Marcus Theory*

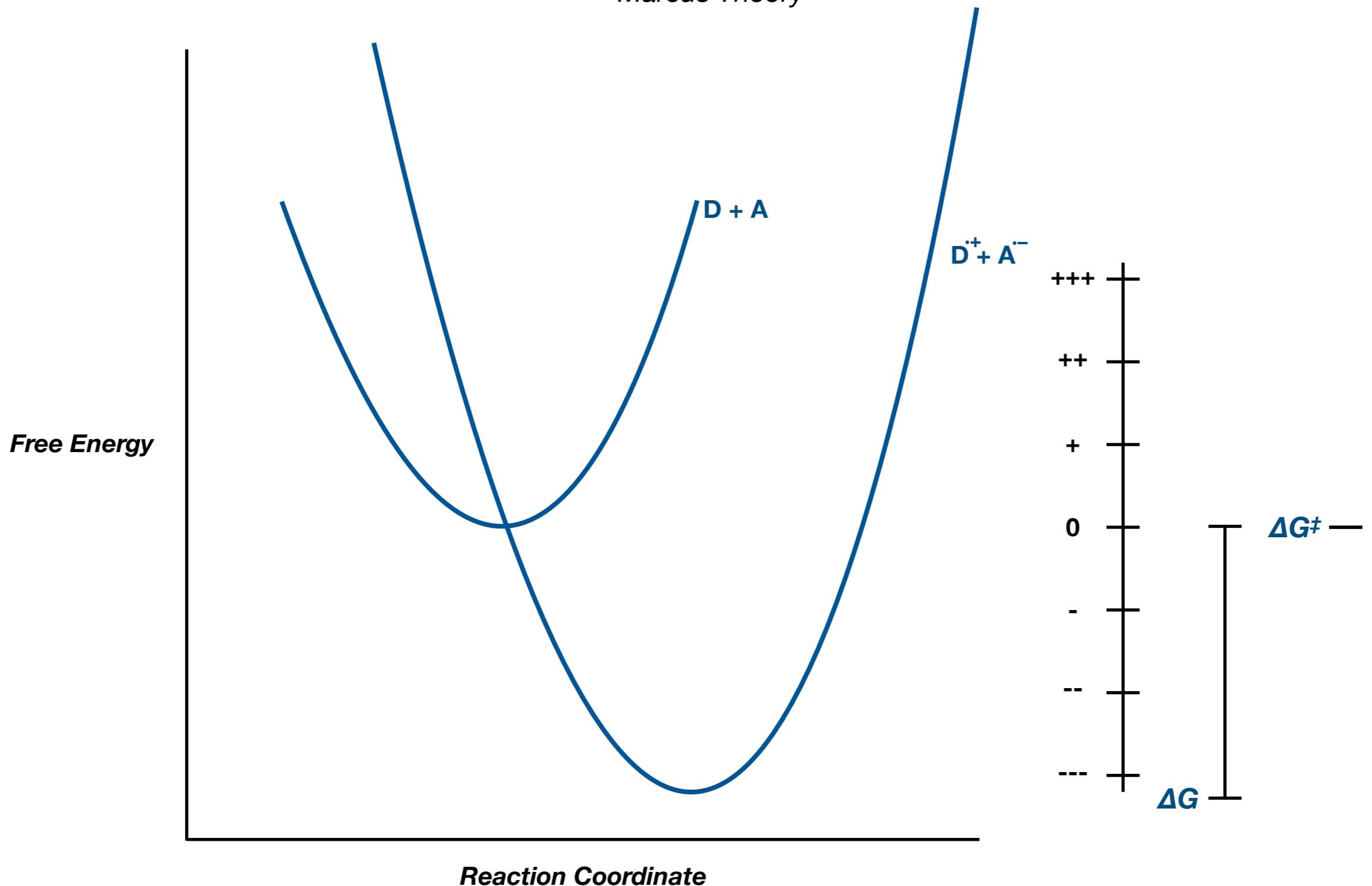


Marcus, R. A.; *J. Chem. Phys.* **1956**, 24, 966-978.

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# *Electron Transfer Mechanisms*

*Marcus Theory*

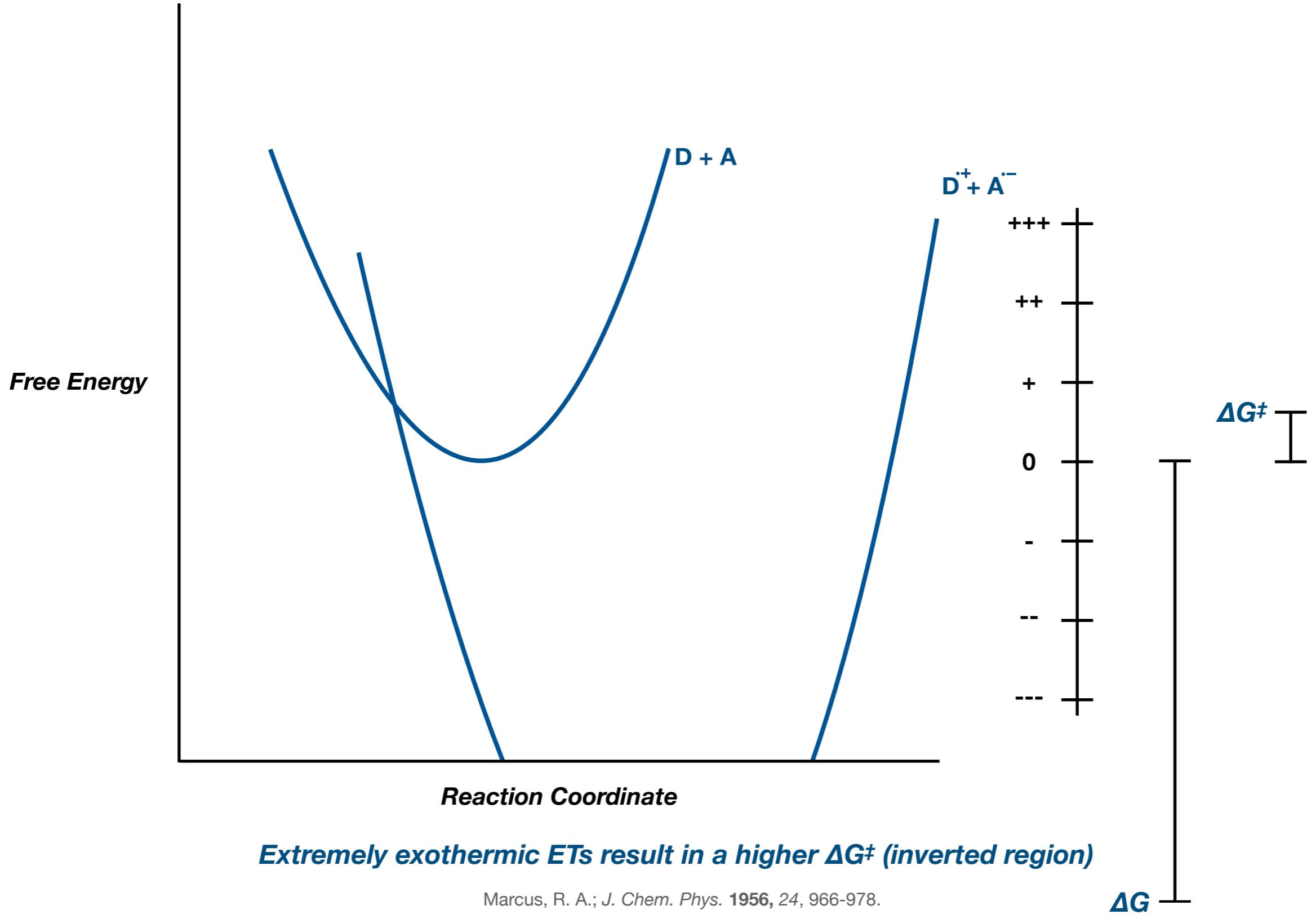


Marcus, R. A.; *J. Chem. Phys.* **1956**, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* **1993**, 65, 599-610.

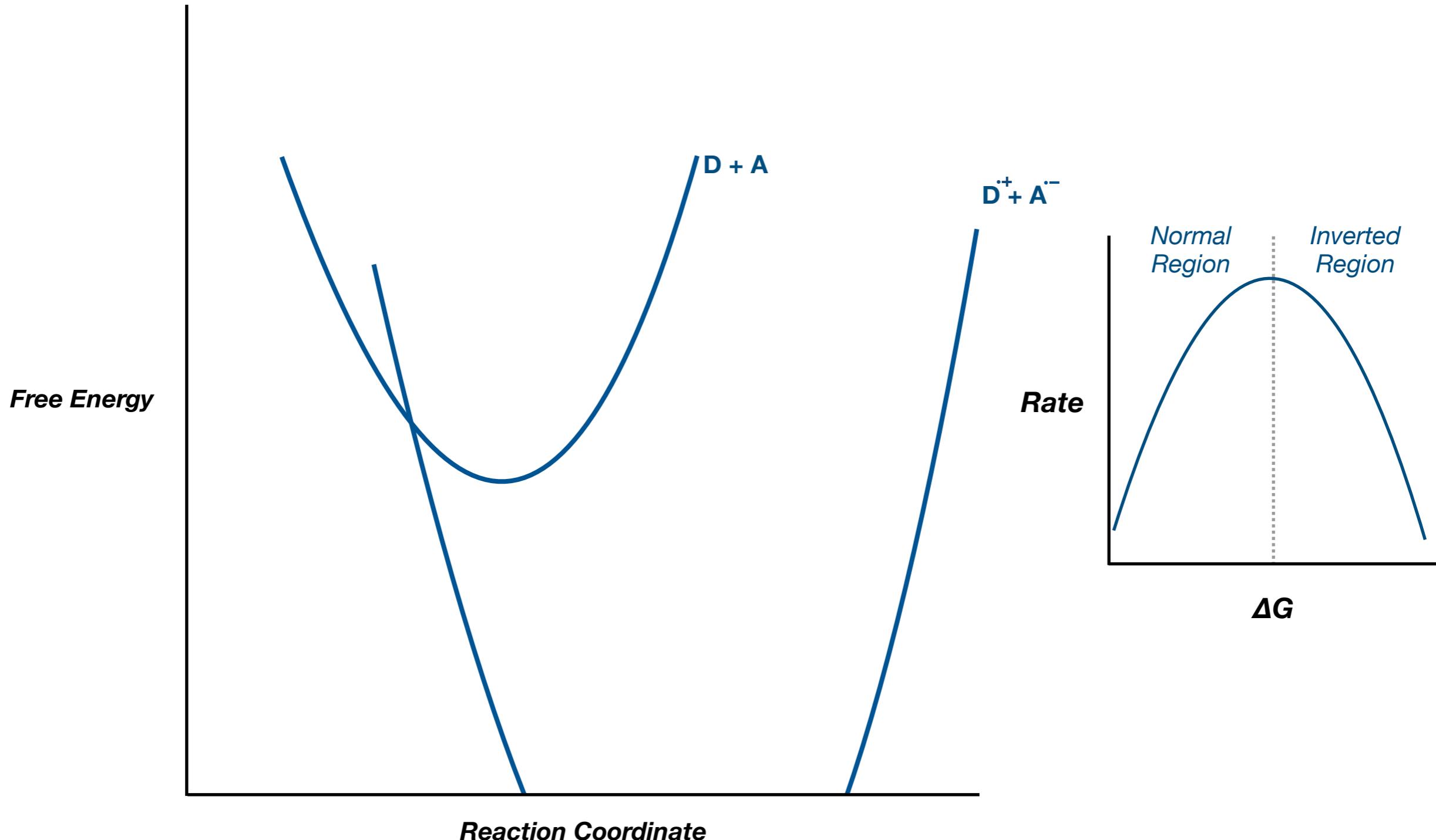
# *Electron Transfer Mechanisms*

## *Marcus Theory*



# *Electron Transfer Mechanisms*

## *Marcus Theory*



***Overall relationship between rate and free energy is parabolic***

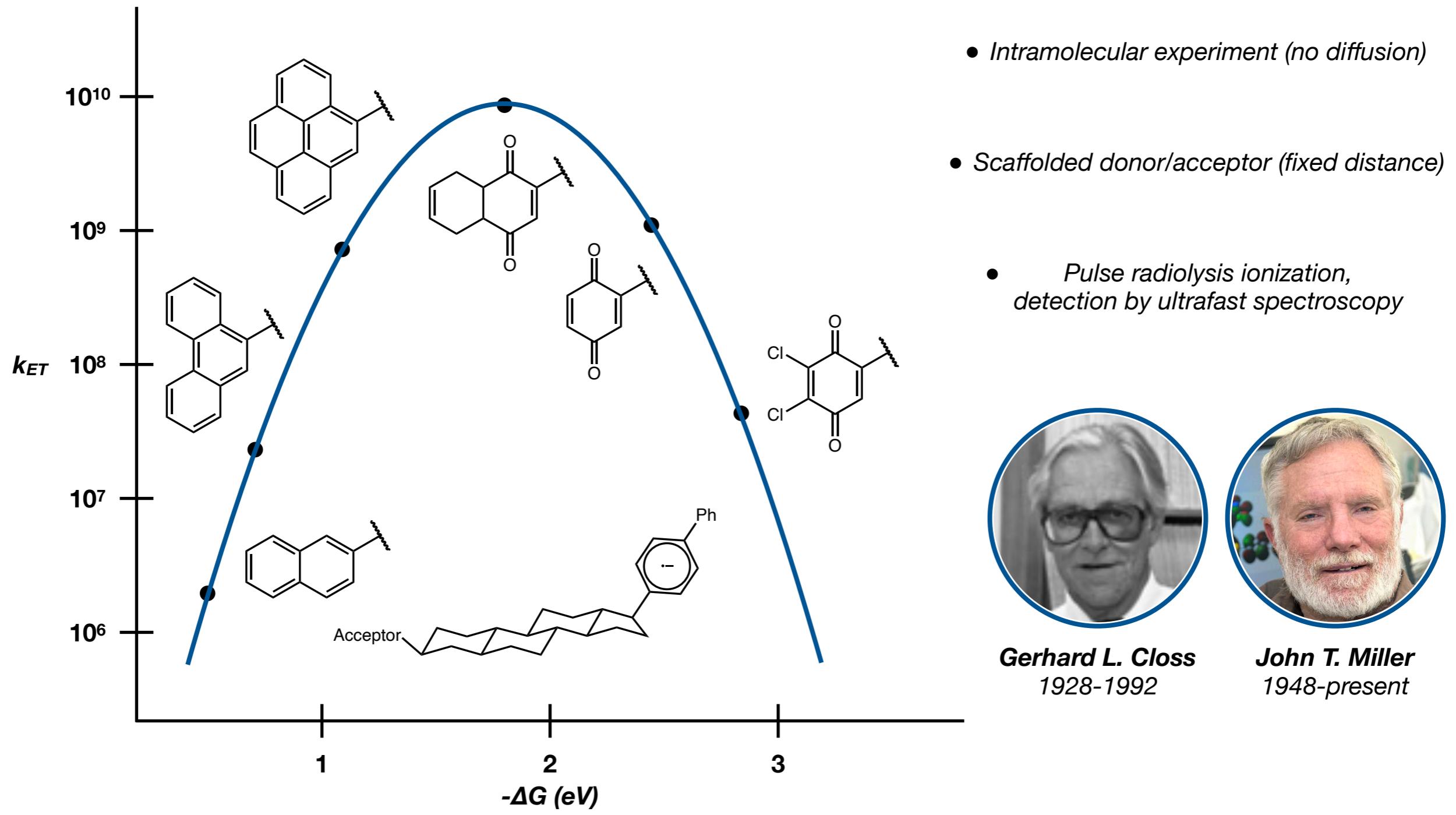
Marcus, R. A.; *J. Chem. Phys.* 1956, 24, 966-978.

Marcus, R. A.; *Rev. Mod. Phys.* 1993, 65, 599-610.

# Electron Transfer Mechanisms

## Marcus Theory

### Closs-Miller Experiment



**First experimental validation of the inverted Marcus region**

# Electron Transfer Mechanisms

## Non-Adiabatic vs Adiabatic ET

### Non-Adiabatic ET

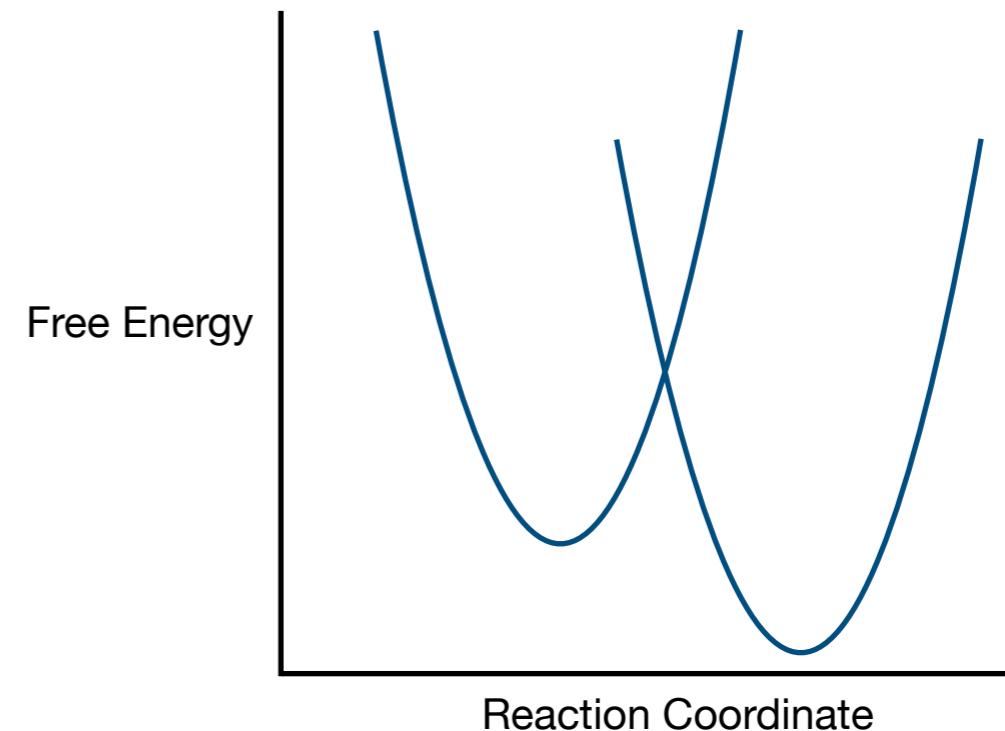
$$\Delta G^\ddagger = (\lambda - \Delta G)^2 / (4\lambda)$$

$$H_{DA} = 100 - 300 \text{ cm}^{-1}$$

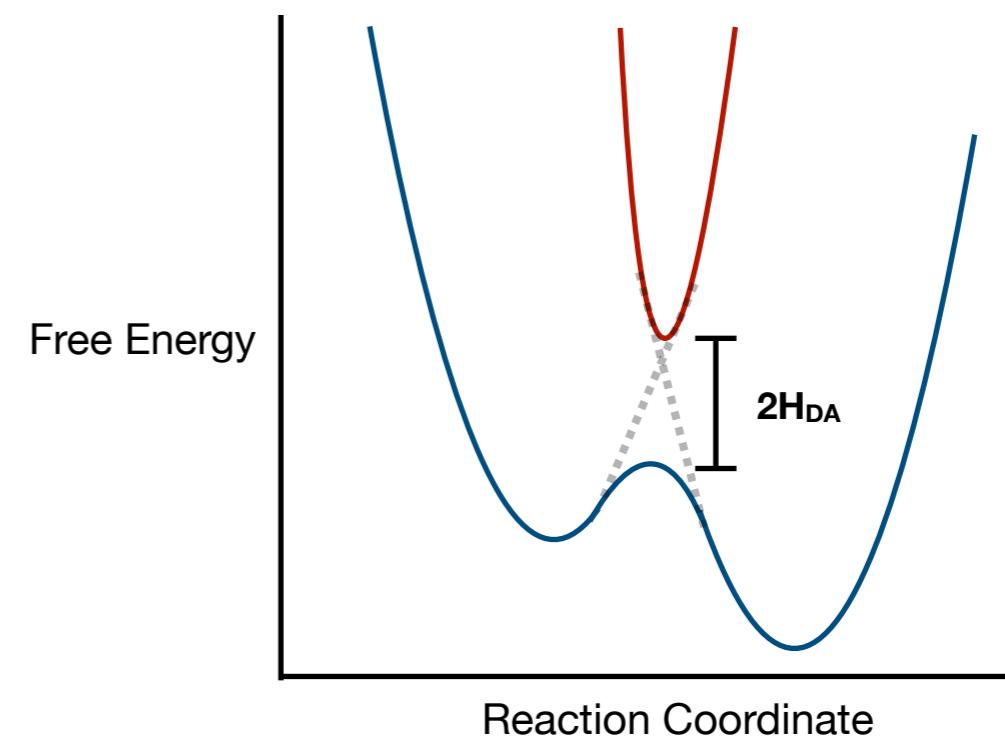
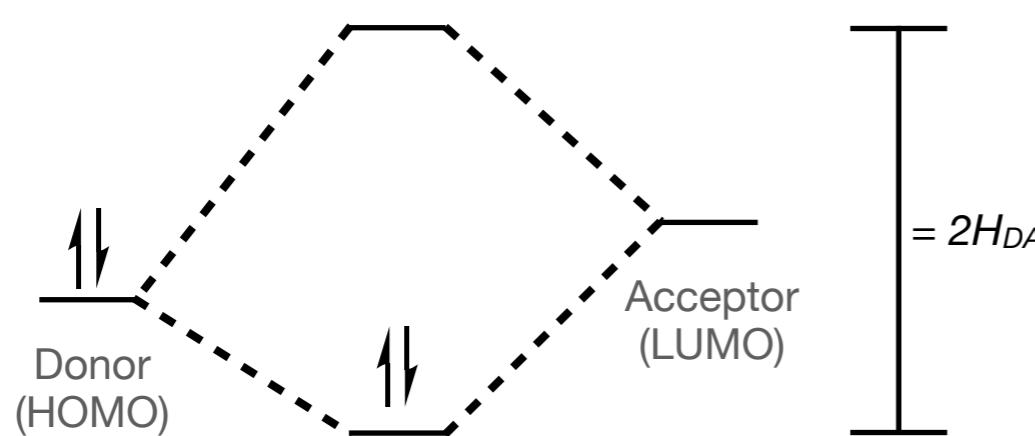
$$r_{DA} = 5.0 - 6.0 \text{ \AA}$$

Typical of outer sphere transfers

Well modeled by Marcus Theory



### Adiabatic ET



# Electron Transfer Mechanisms

## Non-Adiabatic vs Adiabatic ET

### ■ Non-Adiabatic ET

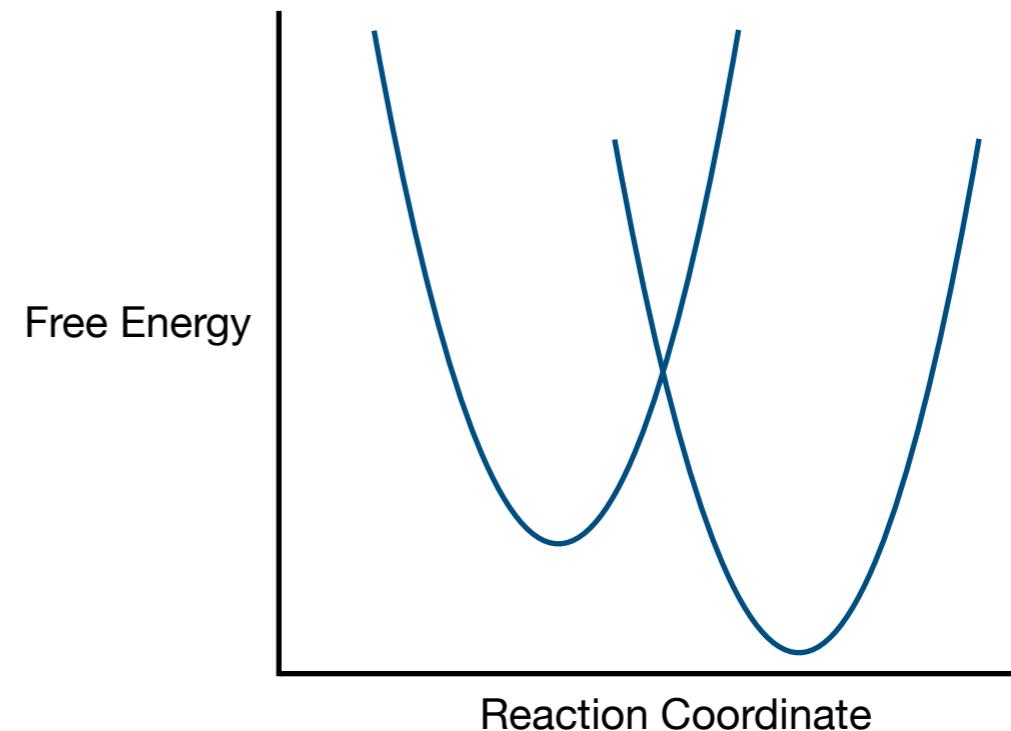
$$\Delta G^\ddagger = (\lambda - \Delta G)^2 / (4\lambda)$$

$$H_{DA} = 100 - 300 \text{ cm}^{-1}$$

$$r_{DA} = 5.0 - 6.0 \text{ \AA}$$

Typical of outer sphere transfers

Well modeled by Marcus Theory



### ■ Adiabatic ET

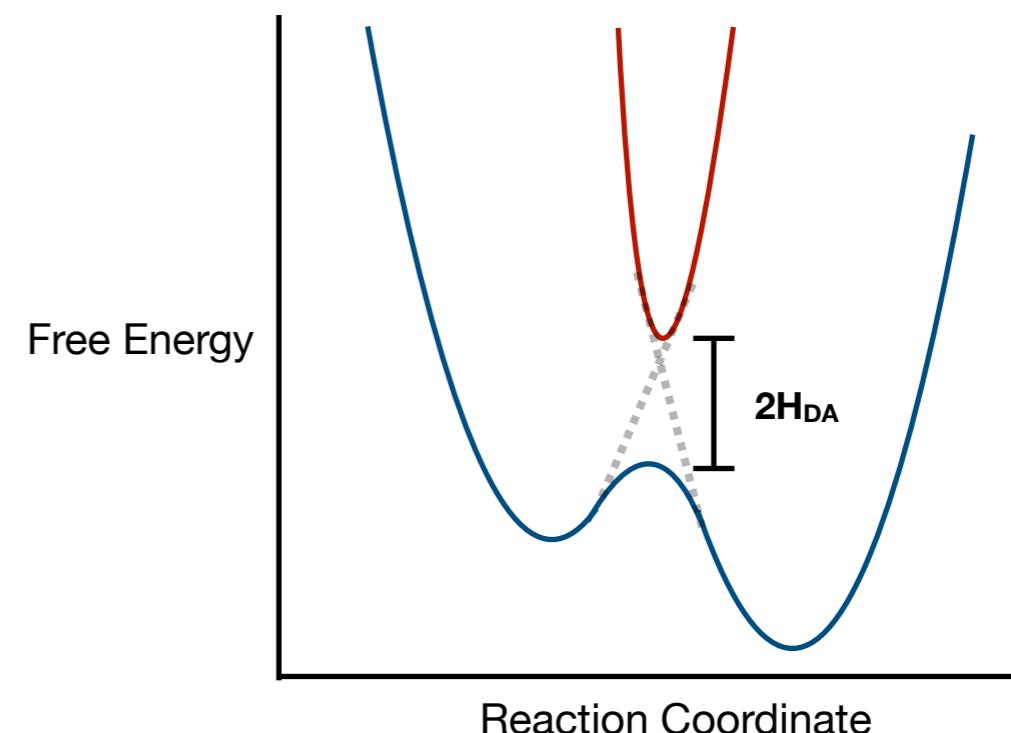
$$\Delta G^\ddagger = (\lambda - 2H_{DA})^2 / (4\lambda)$$

$$H_{DA} = 1000 - 3000 \text{ cm}^{-1}$$

$$r_{DA} = 3.0 - 3.3 \text{ \AA}$$

Typical of inner sphere transfers

Very hard to model *a priori*



# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Outline*

**Part I: Electron Transfer Mechanisms**

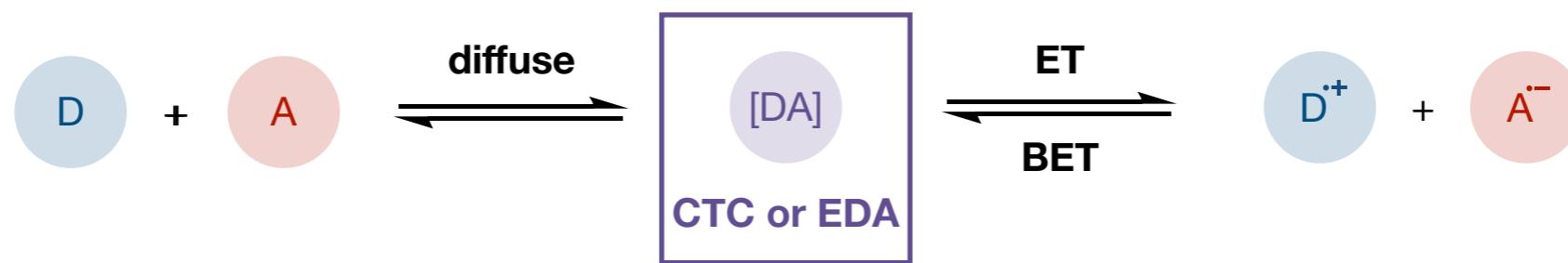
**Part II: Charge Transfer Complexes (CTCs)**

**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Charge Transfer Complexes*

## *Introduction*



- “Charge transfer complex” or “electron donor acceptor” complex
- No covalent bonding occurs during complex formation, only attraction through intermolecular forces and orbital overlap
  - Typically formed between organic oxidants and reductants

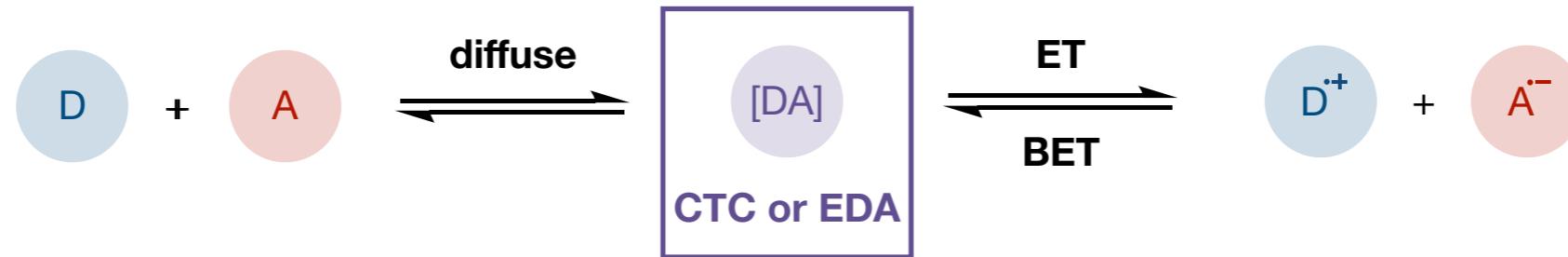
Mulliken, R. S.; *J. Am. Chem. Soc.*. **1952**, 74, 811-824.

Rosokha, S. V., Kochi, J. K.; *Acc. Chem. Res.* **2008**, 41, 641-653.

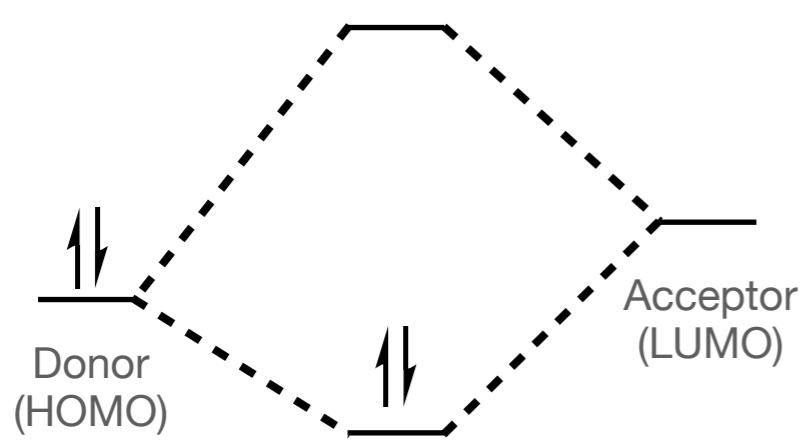
Lima, C. A., Lima, T. M., Duarte, M., Jurberg, I. D., Paixao, M. W.; *ACS. Catal.* **2016**, 6, 1389-1407.

# Charge Transfer Complexes

## Introduction



$$\psi_{ES} = b\psi_{D,A} - a\psi_{D^+,A^-}$$



$$\psi_{GS} = a\psi_{D,A} + b\psi_{D^+,A^-}$$

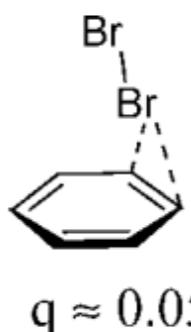
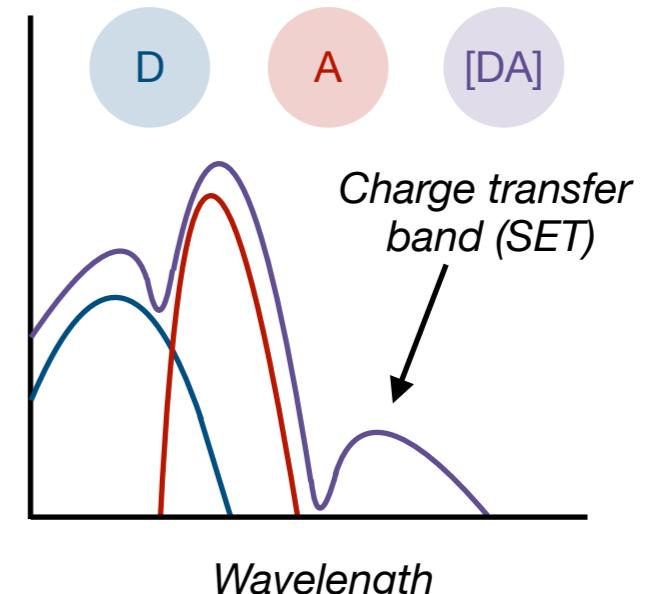
"degree of charge transfer" =  $q = b/a$

$$\lambda_{abs} = \frac{hc}{e} = \psi_{GS} \rightarrow \psi_{ES}$$

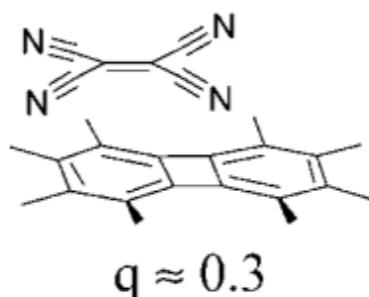
$h$  = Planck's Constant

$c$  = speed of light

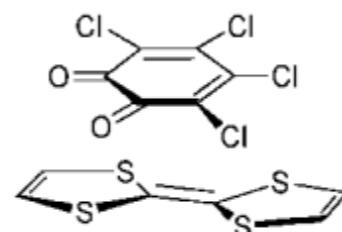
$e$  = energy gap



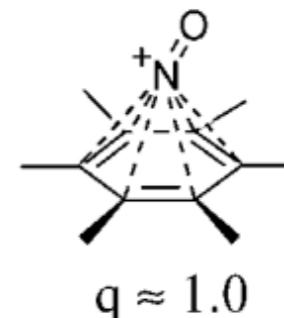
$q \approx 0.05$



$q \approx 0.3$



$q \approx 0.6$



$q \approx 1.0$

**SET can be induced thermally or by irradiation at the  $\lambda_{abs}$  of the charge transfer band**

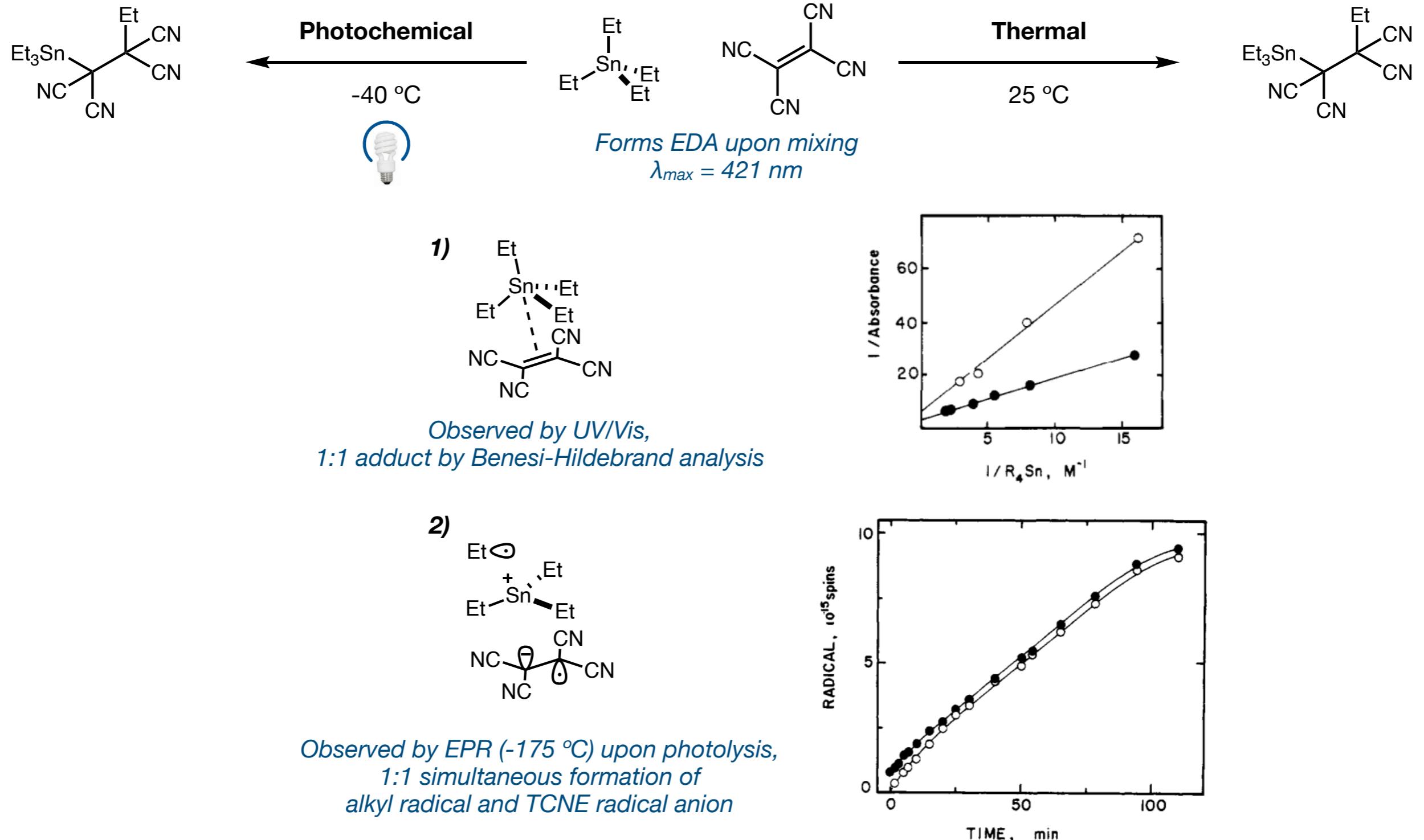
Mulliken, R. S.; J. Am. Chem. Soc.. 1952, 74, 811-824.

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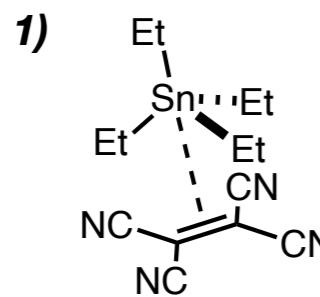
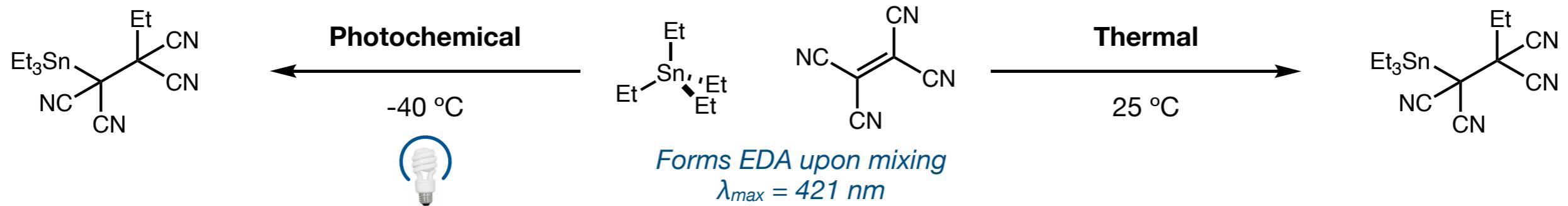
# Charge Transfer Complexes

## Thermal vs Photochemical Activation

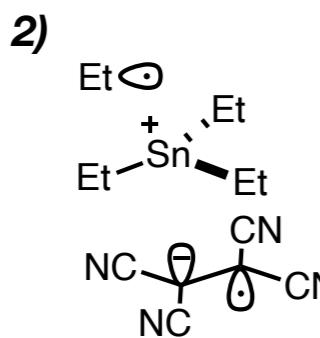


# Charge Transfer Complexes

## Thermal vs Photochemical Activation

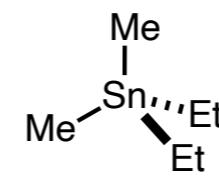


Observed by UV/Vis,  
1:1 adduct by Benesi-Hildebrand analysis



Observed by EPR (-175 °C) upon photolysis,  
1:1 simultaneous formation of  
alkyl radical and TCNE radical anion

3)      **Organotin**



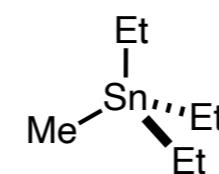
**Method**

Thermal

7:1

Photo.

7:1



Thermal

11:1

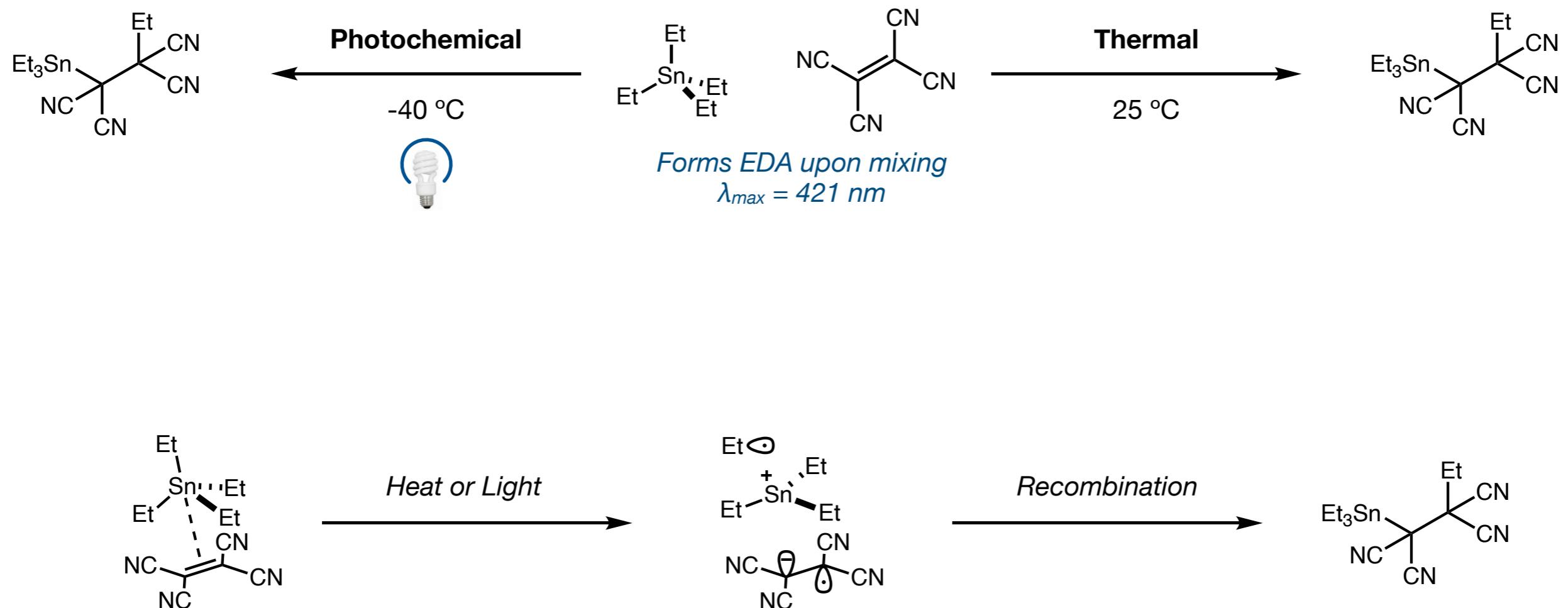
Photo.

11:1

When heteroleptic Sn is used, thermal and photochemical methods result in the same product distribution

# Charge Transfer Complexes

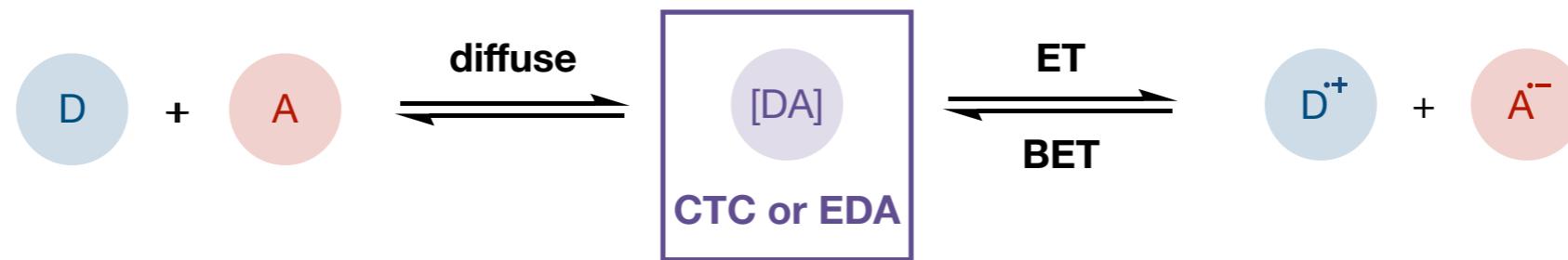
## Thermal vs Photochemical Activation



**Initiation method does not matter, SET via EDAs proceeds through the same mechanism**

# Charge Transfer Complexes

## Thermodynamics and Kinetics



### Extension of the Nernst Eq to EDAs

$$\Delta_{et}G^\circ = N_A [e(E^\circ(D^+/D) - E^\circ(A/A^-)) + w(D^+, A^-) - w(D, A)] - \Delta E_{0,0}$$

$N_A$  = Avogadro's Number

$e$  = # of electron's transferred

$w(D, A)$  = electrostatic work to form EDA pre ET

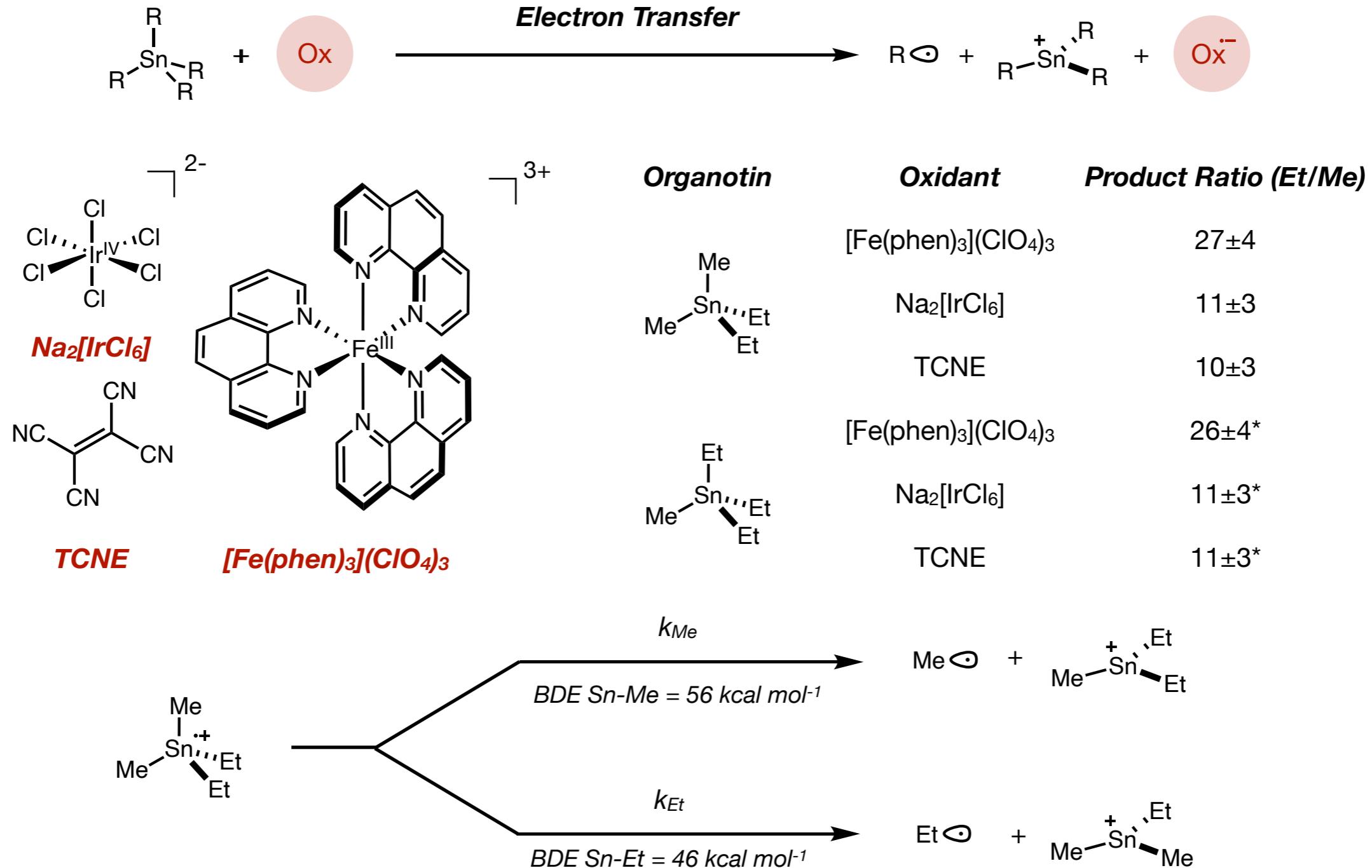
$w(D^+, A^-)$  = electrostatic work to separate EDA post ET

$\Delta E_{0,0}$  = EDA HOMO/LUMO gap

### What about calculating $\Delta G^\ddagger$ ?

# Charge Transfer Complexes

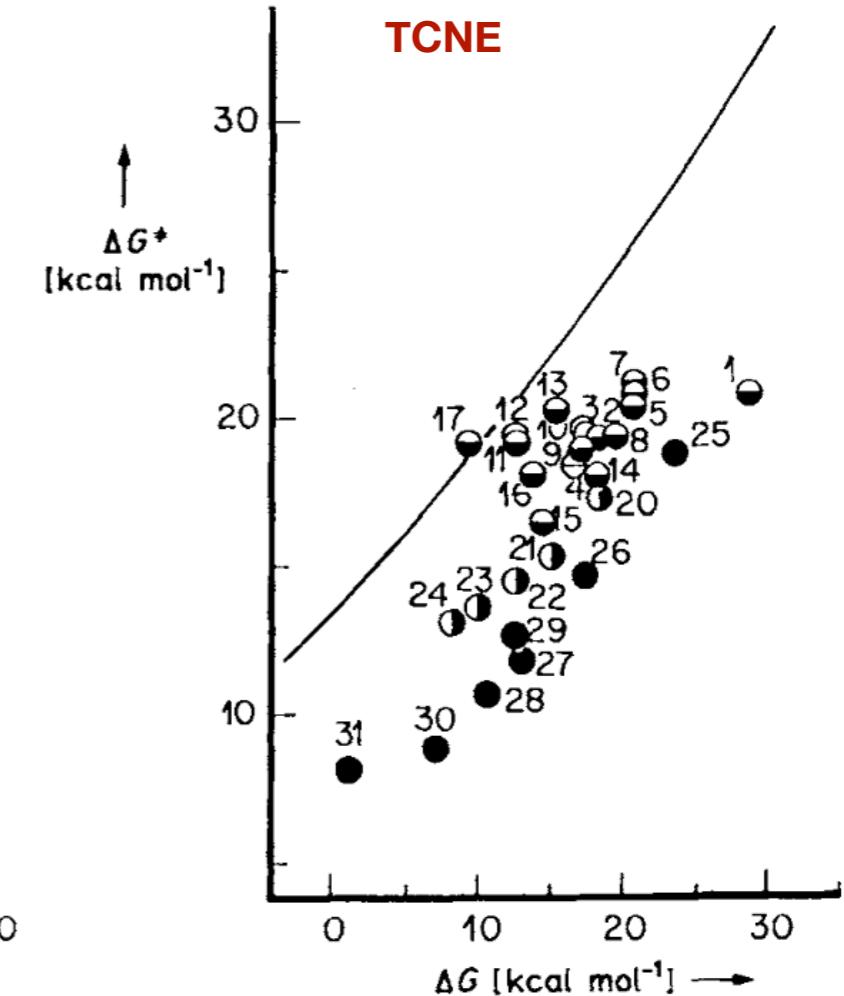
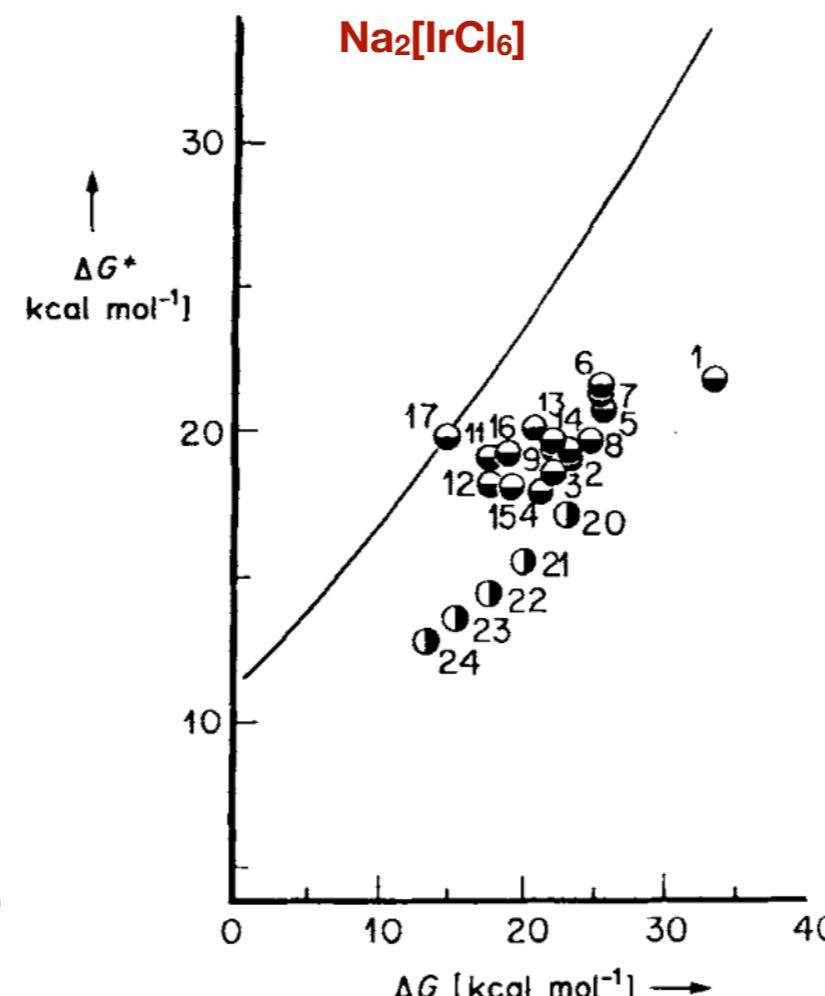
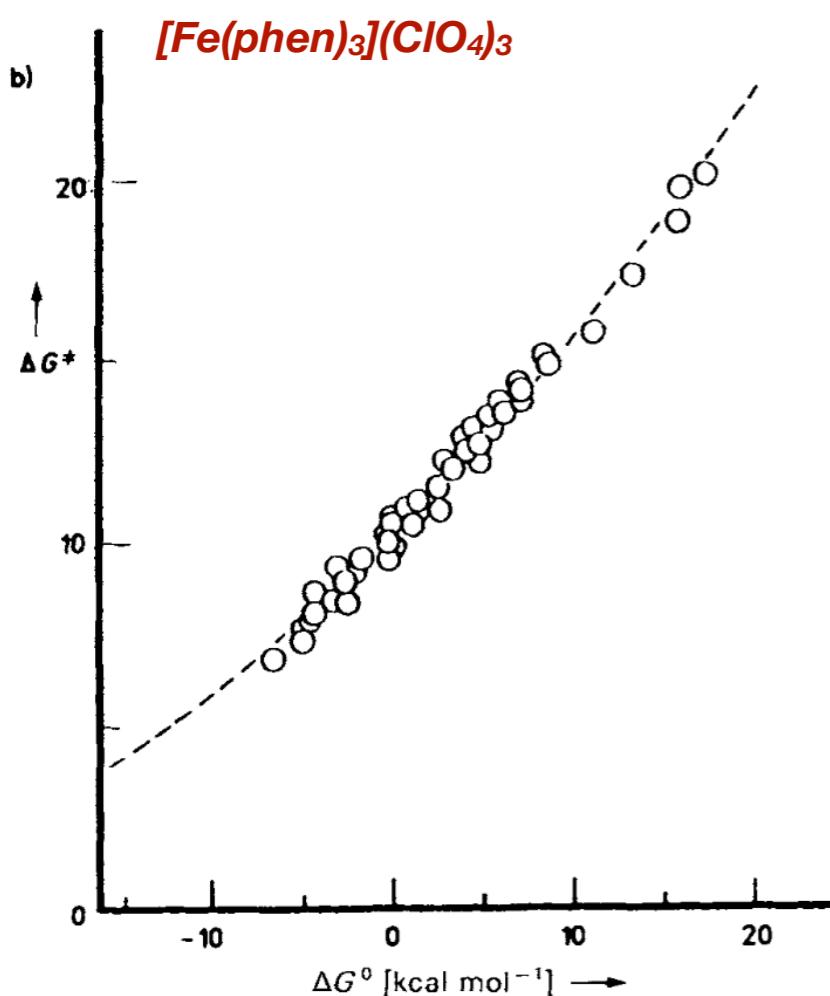
*Inner or Outer Sphere ET?*



**Product distribution suggests EDAs proceed through an inner sphere ET (Sn radical cation in similar environments)**

# Charge Transfer Complexes

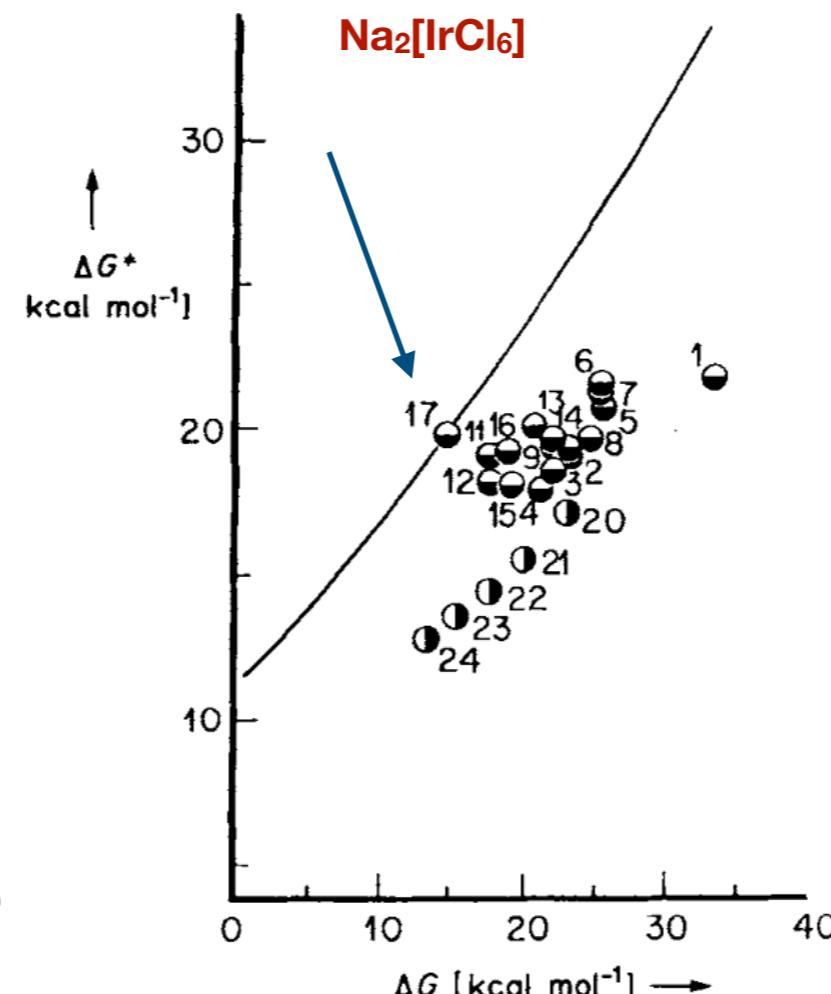
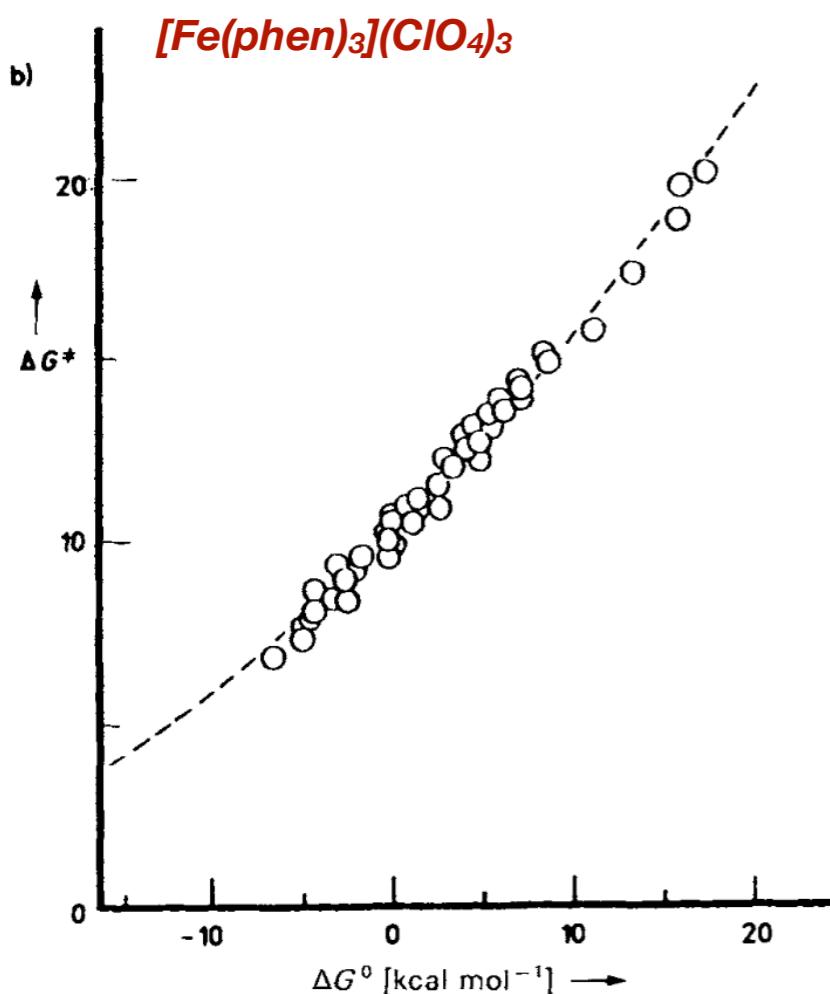
*Inner or Outer Sphere ET?*



**SET from alkyl tins to Fe correlates with rates predicted by Marcus Theory, SET to Ir and TCNE occurs at rates faster than predicted rates by Marcus Theory**

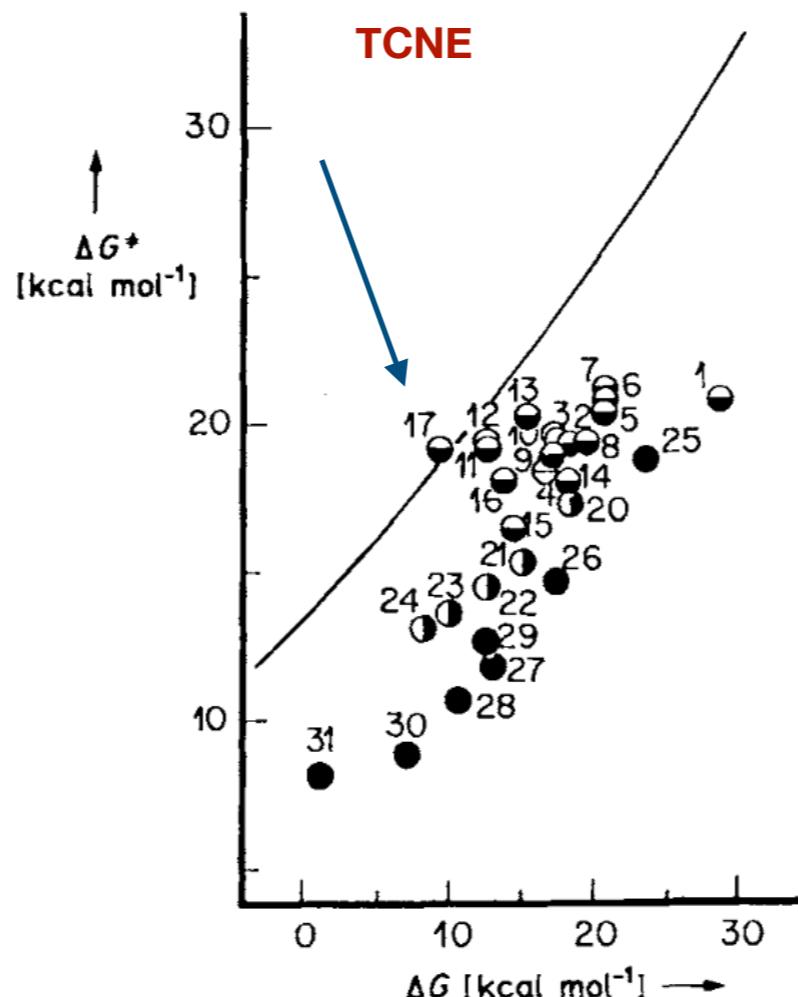
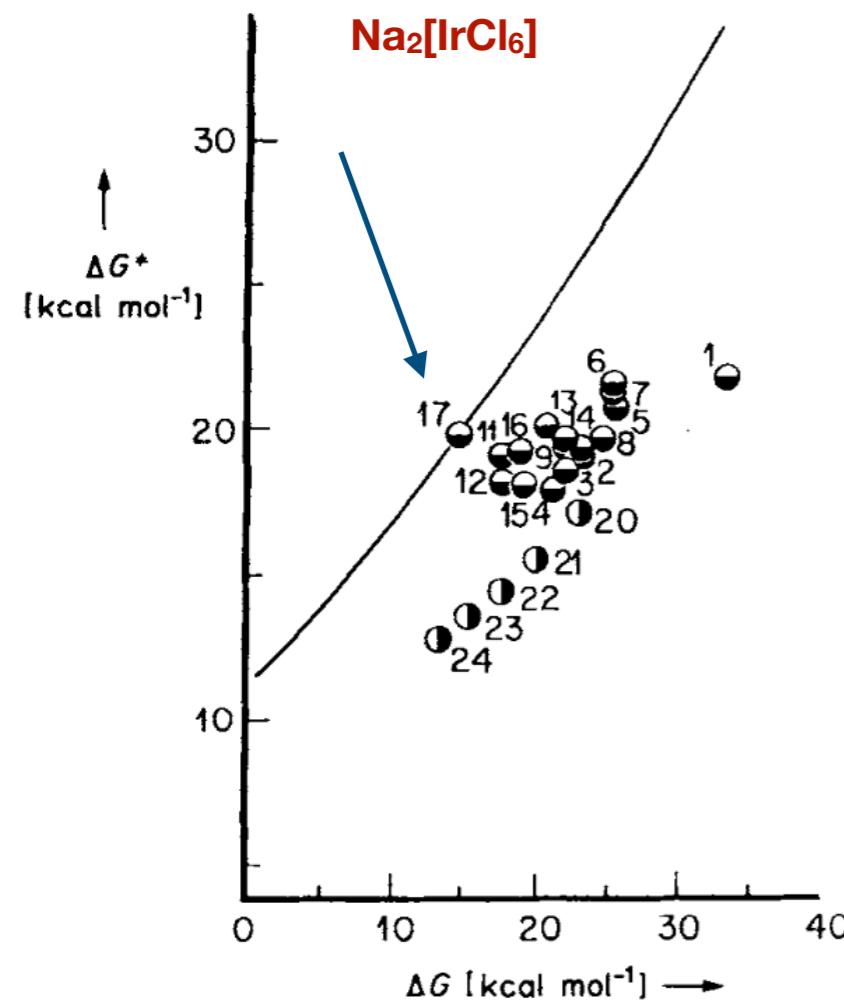
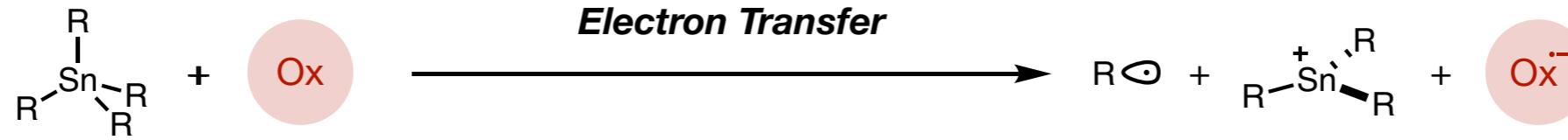
# Charge Transfer Complexes

*Inner or Outer Sphere ET?*

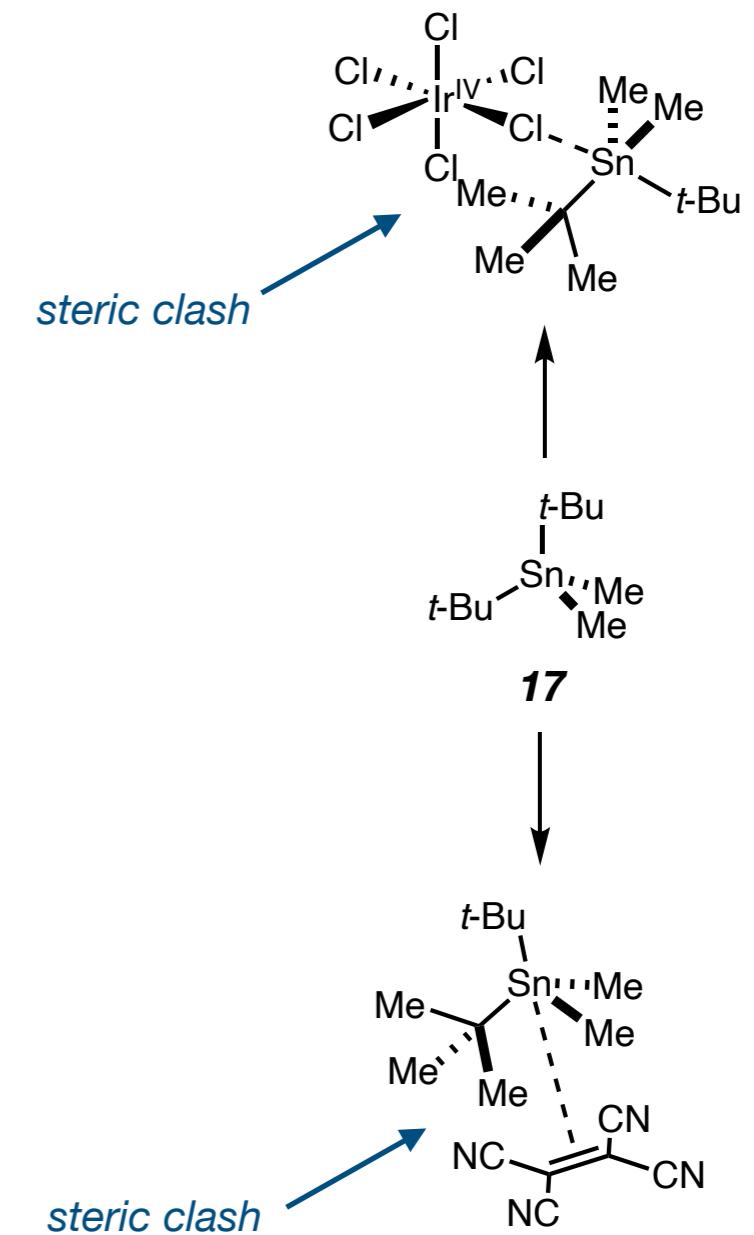


# Charge Transfer Complexes

*Inner or Outer Sphere ET?*

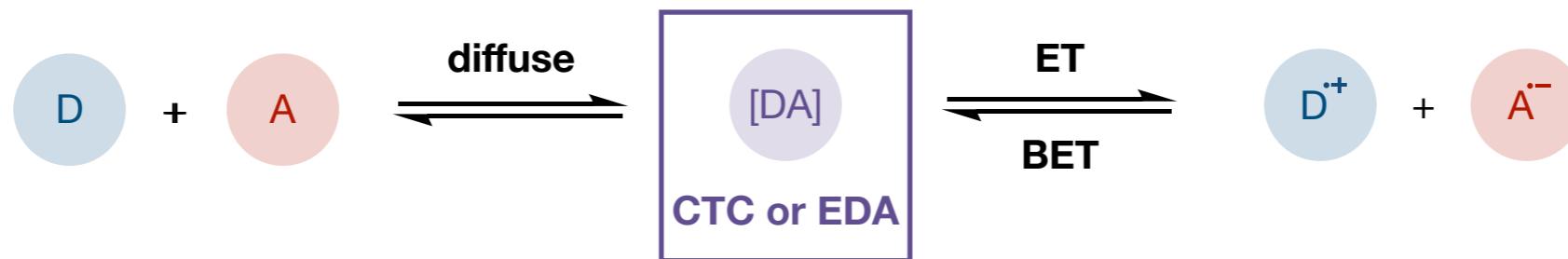


**Steric clash limits overlap  
(outer sphere ET)**



# Charge Transfer Complexes

## Thermodynamics and Kinetics



### Extension of the Nernst Eq to EDAs

$$\Delta_{et}G^\circ = N_A [e(E^\circ(D^+/D) - E^\circ(A/A^-)) + w(D^+, A^-) - w(D, A)] - \Delta E_{0,0}$$

$N_A$  = Avogadro's Number

$e$  = # of electron's transferred

$w(D, A)$  = electrostatic work to form EDA pre ET

$w(D^+, A^-)$  = electrostatic work to separate EDA post ET

$\Delta E_{0,0}$  = EDA HOMO/LUMO gap

### Adiabatic ET Eq for EDAs

$$\Delta G^\ddagger = (\lambda_0 - 2H_{DA})^2 / (4\lambda_0)$$

$H_{DA}$  = resonance integral

$\lambda_0$  = reorganizational energy

# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

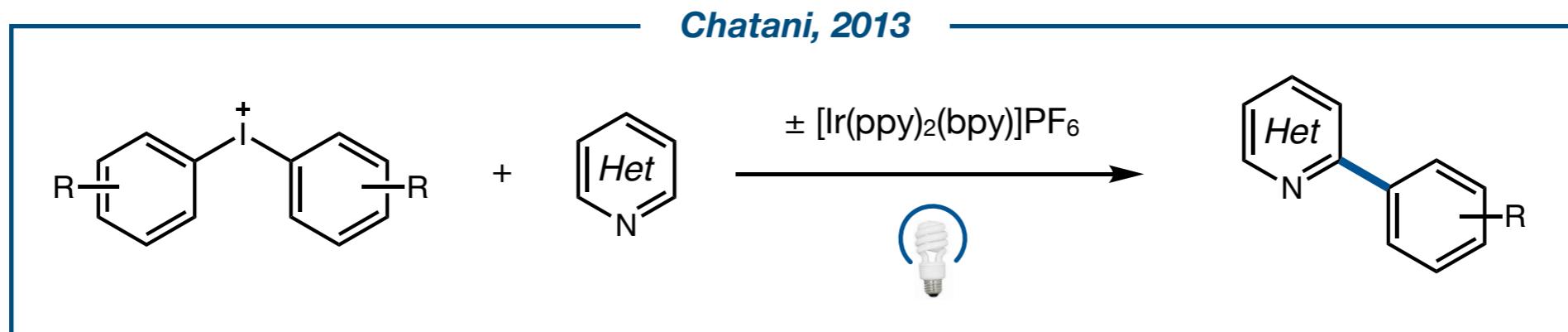
**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

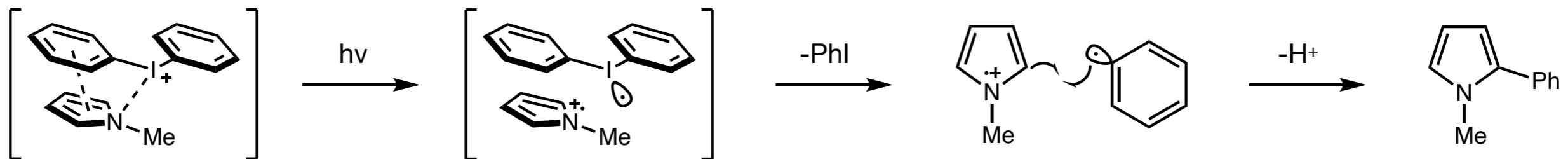
# Synthetic Applications

## Visible Light EDAs

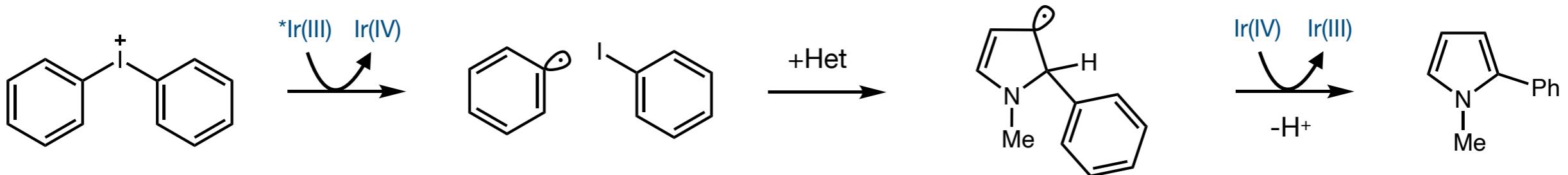
### ■ Stoichiometric Visible Light EDAs



### EDA Mechanism



### Photocatalytic Mechanism



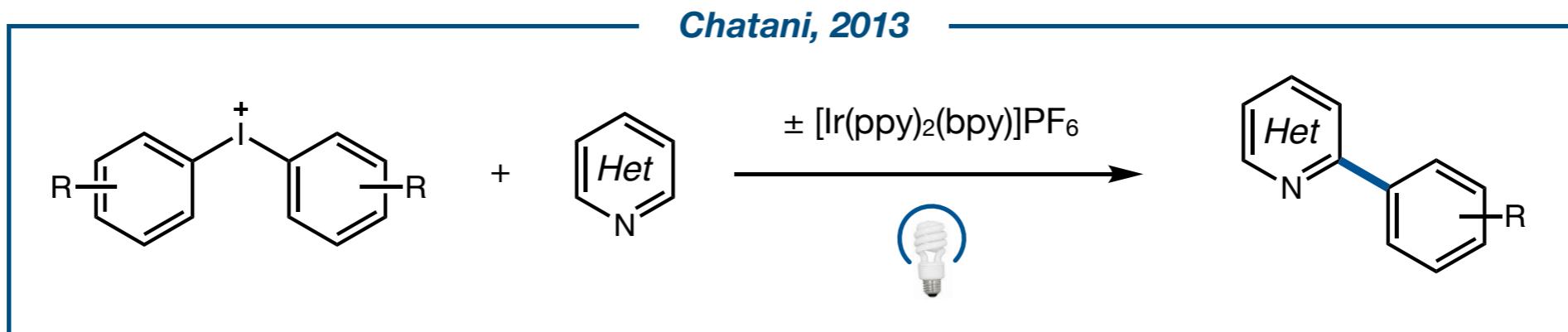
Tobisu, M., Furukawa, T., Chatani, N.; *Chem. Lett.* **2013**, 42, 1203-1205.

Crisenza, G. E. M., Mazzarella, D., Melchiorre, P.; *J. Am. Chem. Soc.* **2020**, 142, 5461-5476.

# Synthetic Applications

## Visible Light EDAs

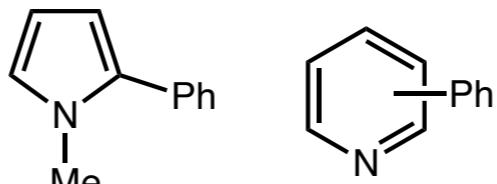
### ■ Stoichiometric Visible Light EDAs



### Conditions

+  $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$       88%      57%  
(54 : 30 : 16)

-  $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$       54%      9%  
(56 : 44 : 0)

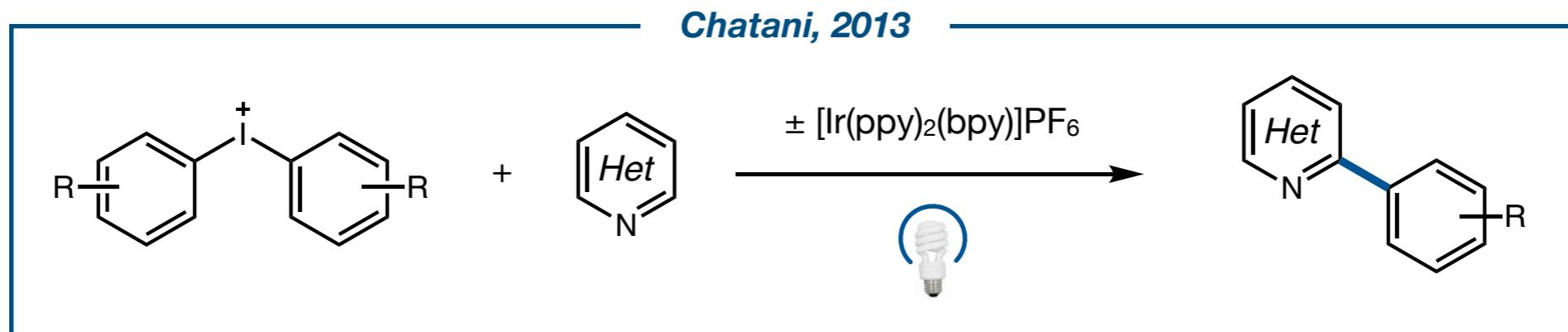


**Photocatalytic conditions outperformed EDA conditions**

# Synthetic Applications

## Visible Light EDAs

### ■ Stoichiometric Visible Light EDAs



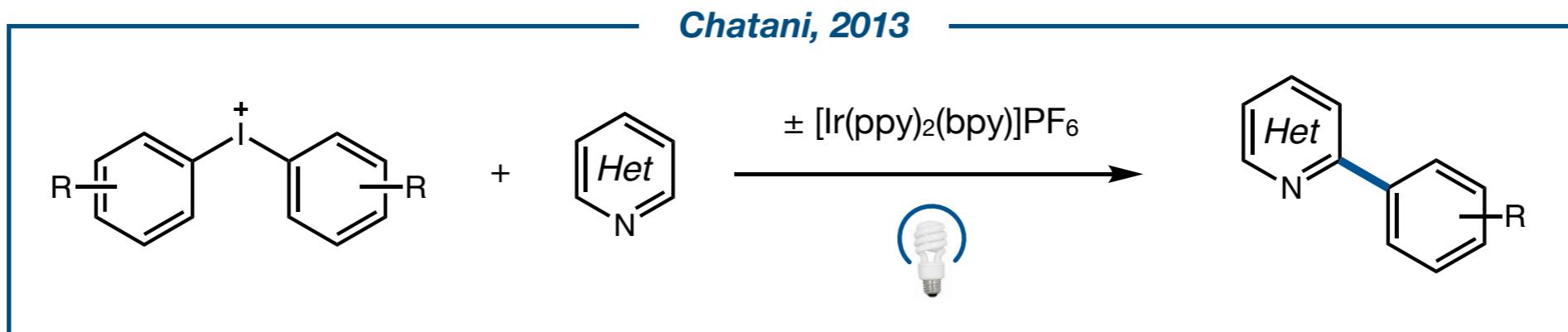
<b>Conditions</b>				$E_{1/2}^{\text{red}} = -0.36 \text{ to } -0.26 \text{ V}$
+ [Ir(ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	88%	57% (54 : 30 : 16)		
- [Ir(ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	54%	9% (56 : 44 : 0)		$E_{1/2}^{\text{ox}} = 1.2 \text{ V}$

***The lower yield with pyridine for EDA conditions is most likely due to weaker charge transfer interactions***

# Synthetic Applications

## Visible Light EDAs

### ■ Stoichiometric Visible Light EDAs



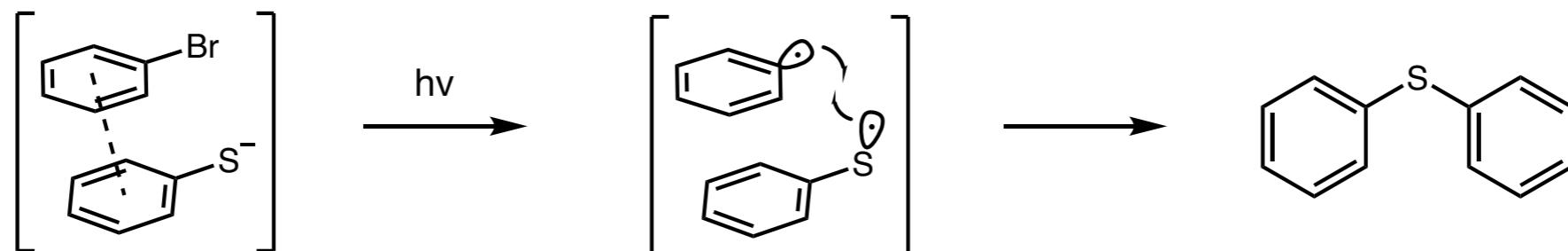
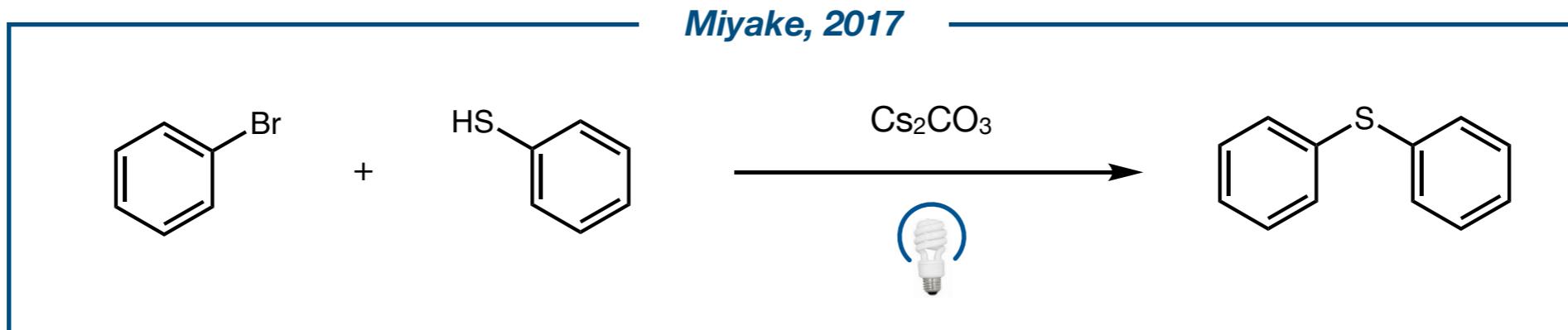
<b>Conditions</b>				$E_{1/2}^{\text{red}} = -0.36 \text{ to } -0.26 \text{ V}$
+ [Ir(ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	88%	57% (54 : 30 : 16)		
- [Ir(ppy) <sub>2</sub> (bpy)]PF <sub>6</sub>	54%	9% (56 : 44 : 0)		$E_{1/2}^{\text{ox}} = 1.2 \text{ V}$

**Stoichiometric EDAs typically suffer from limited scope, photocatalysts can bring generality**

# Synthetic Applications

## Visible Light EDAs

### ■ Stoichiometric Visible Light EDAs

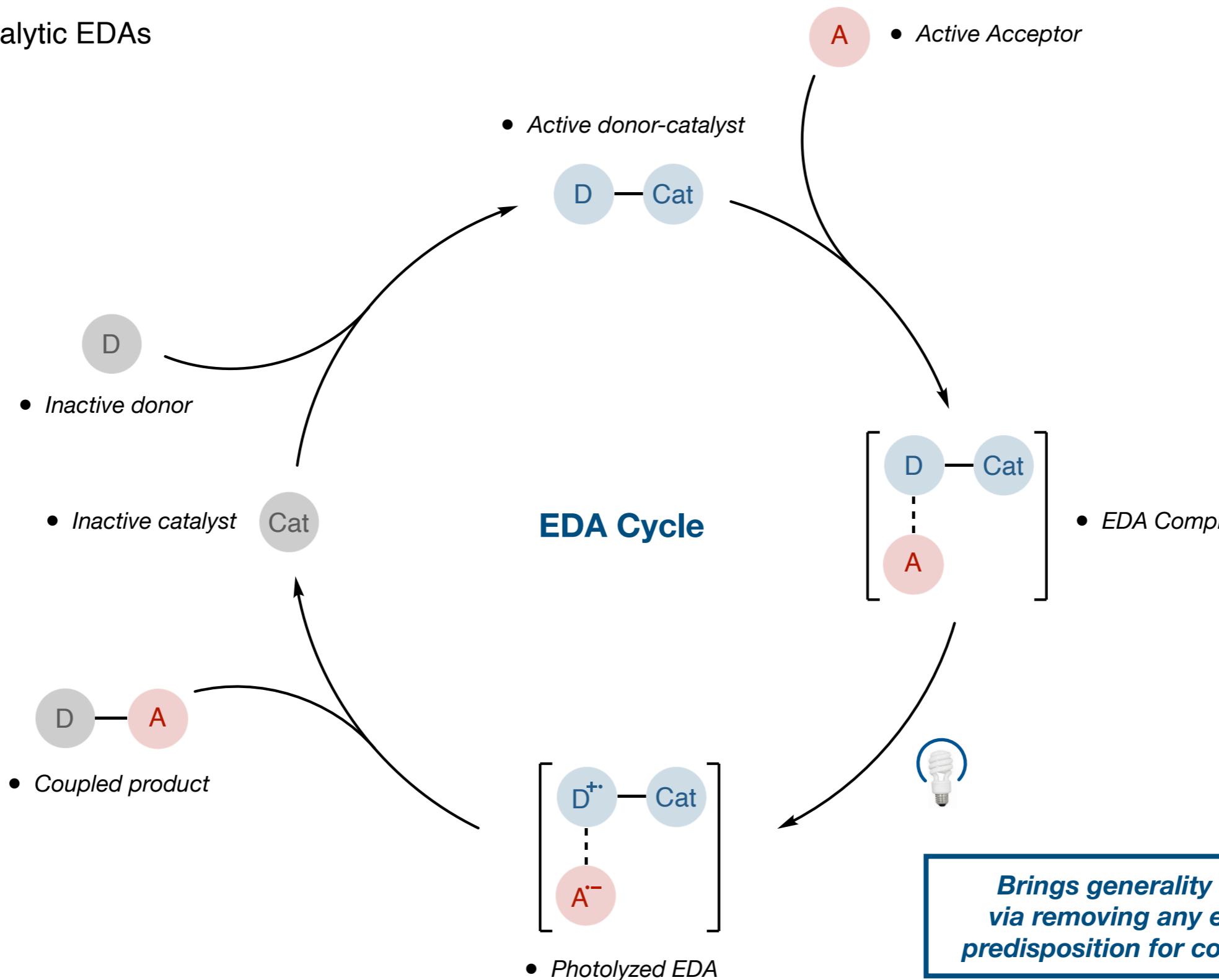


**However stoichiometric EDAs can undergo in cage radical recombination**

# Synthetic Applications

## Visible Light EDAs

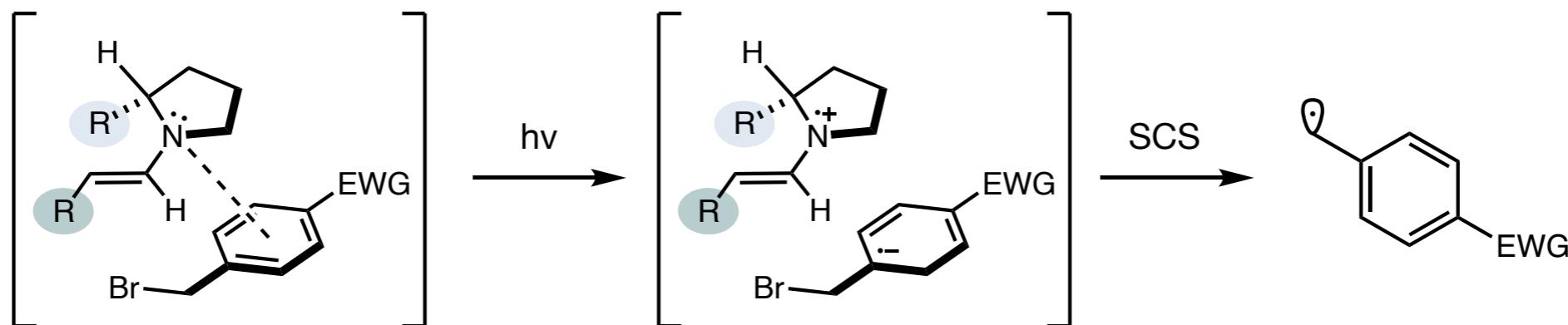
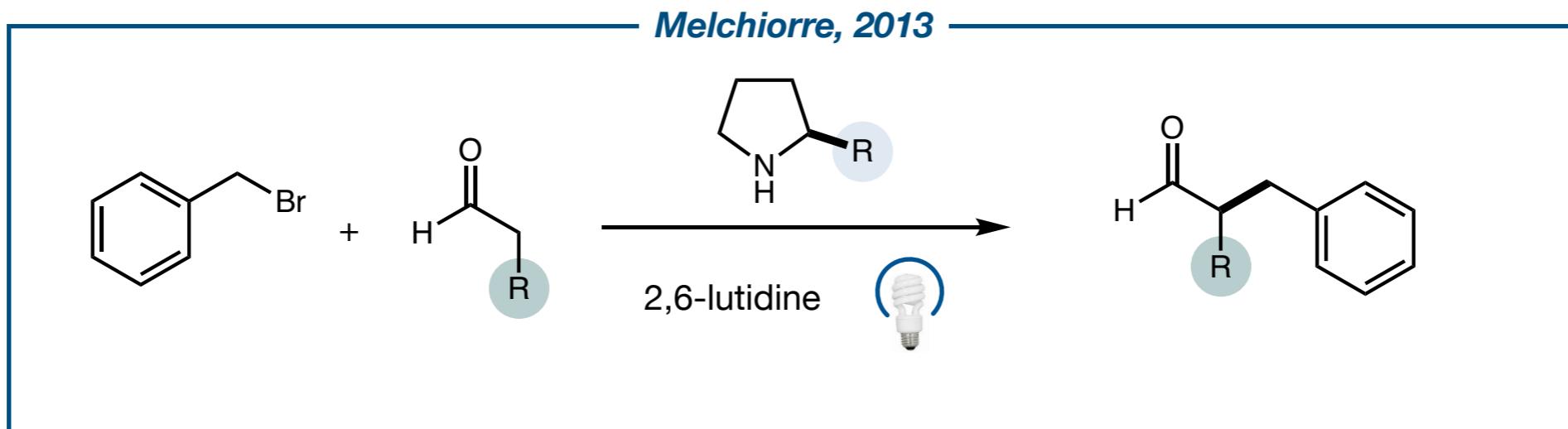
### Catalytic EDAs



# Synthetic Applications

## Visible Light EDAs

### Catalytic EDAs



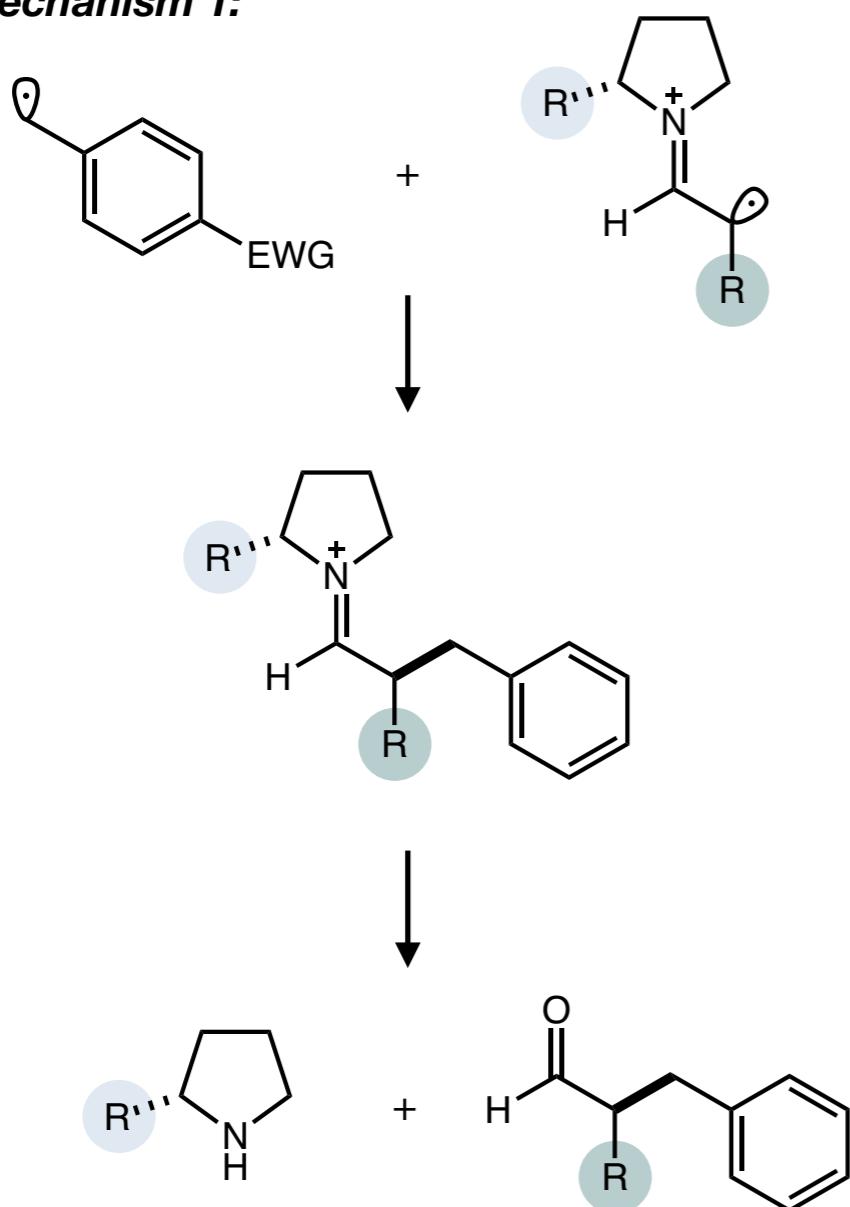
**Organocatalyst enables catalytic donor formation (enamine) and controls stereochemistry of addition**

# Synthetic Applications

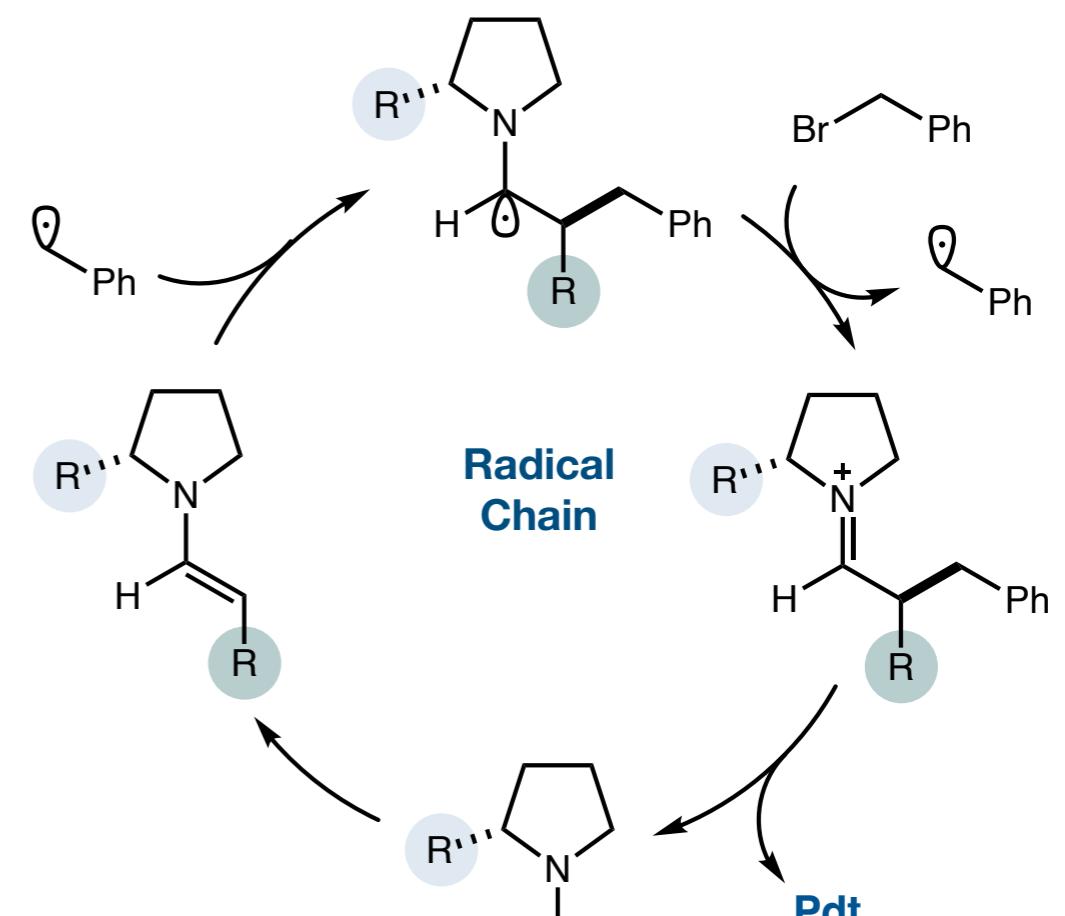
## Visible Light EDAs

### Catalytic EDAs

#### Mechanism 1:



#### Mechanism 2:



Radical Chain

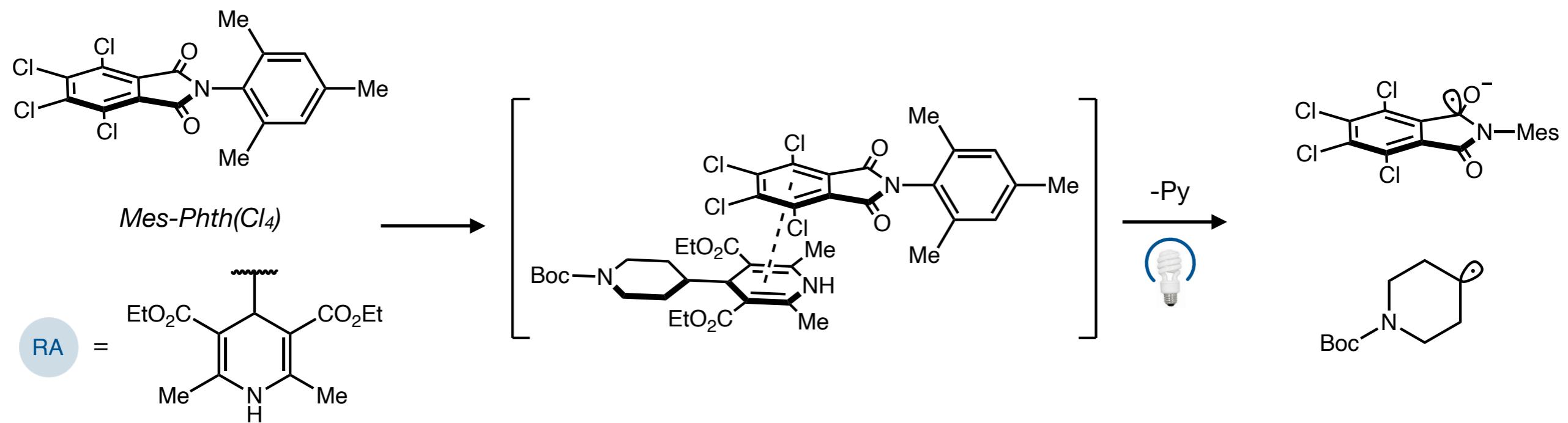
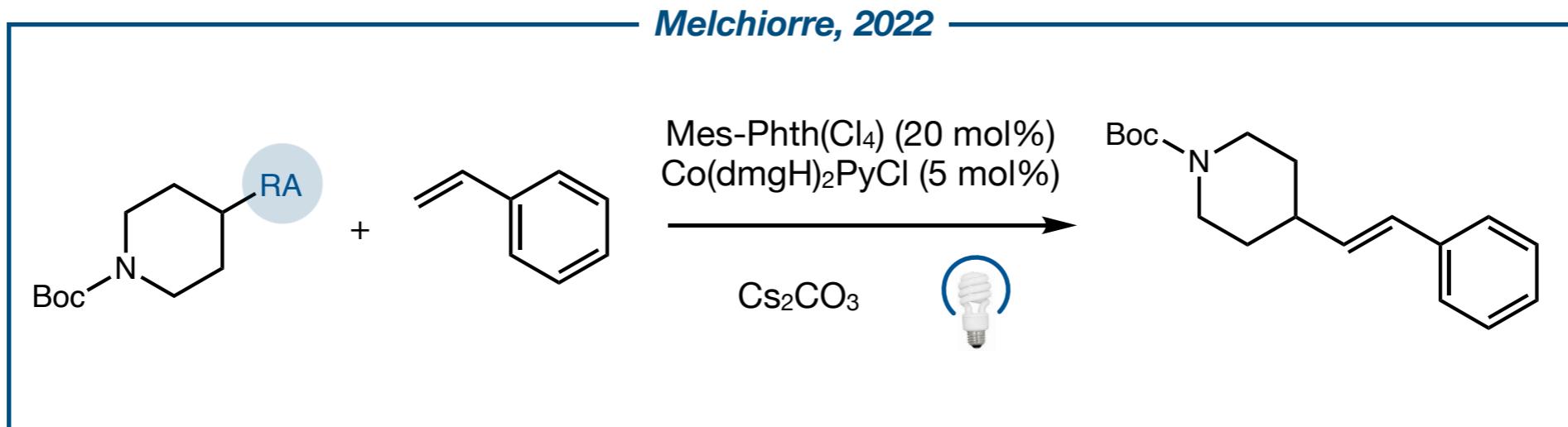
Pdt

Quantum yield calculations implicate mechanism 2 ( $\phi = 20$ )

# Synthetic Applications

## Visible Light EDAs

### Catalytic EDAs

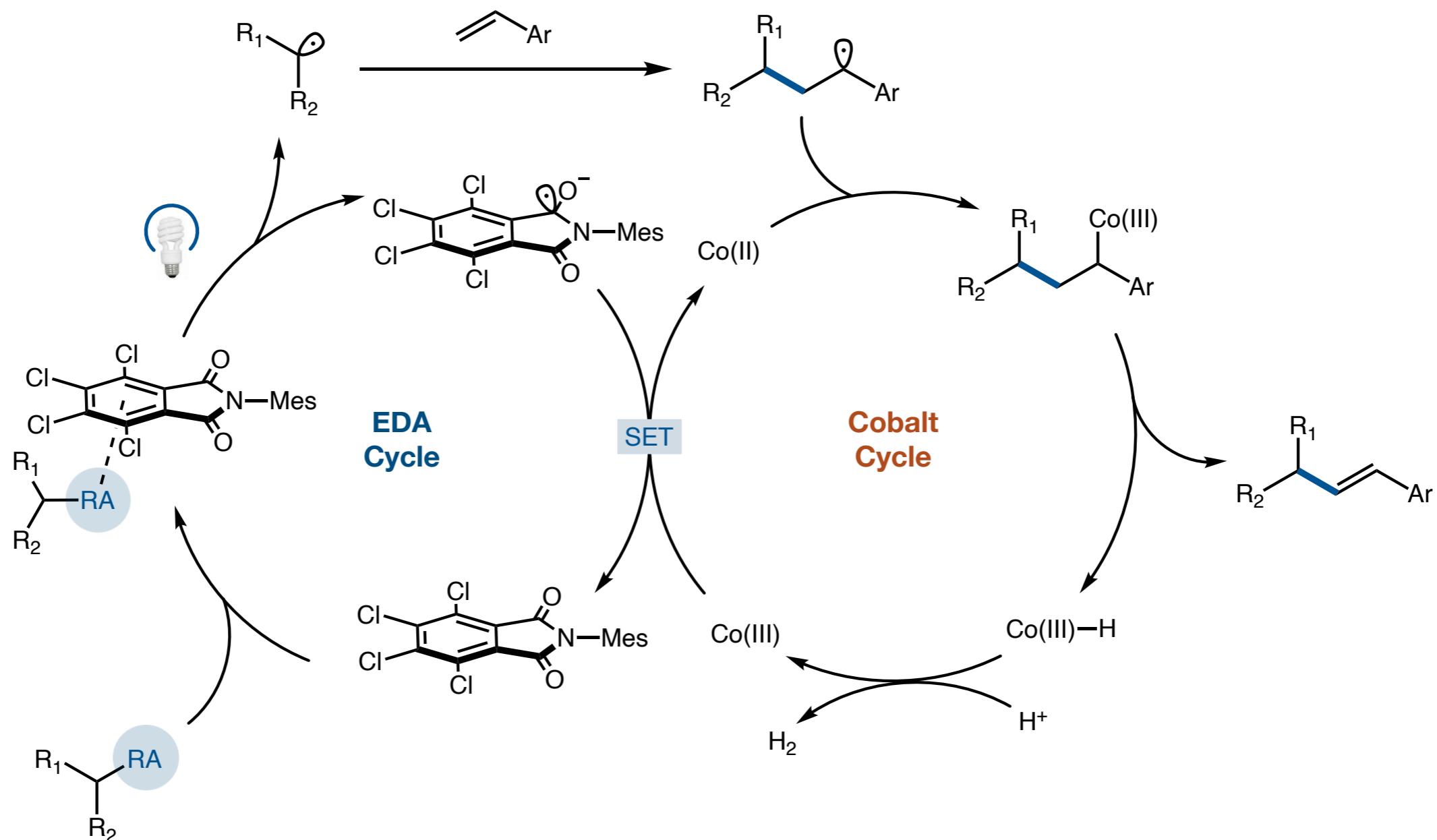


**Mes-Phth(Cl<sub>4</sub>) serves as a catalytic acceptor for EDA**

# Synthetic Applications

## Visible Light EDAs

### Catalytic EDAs

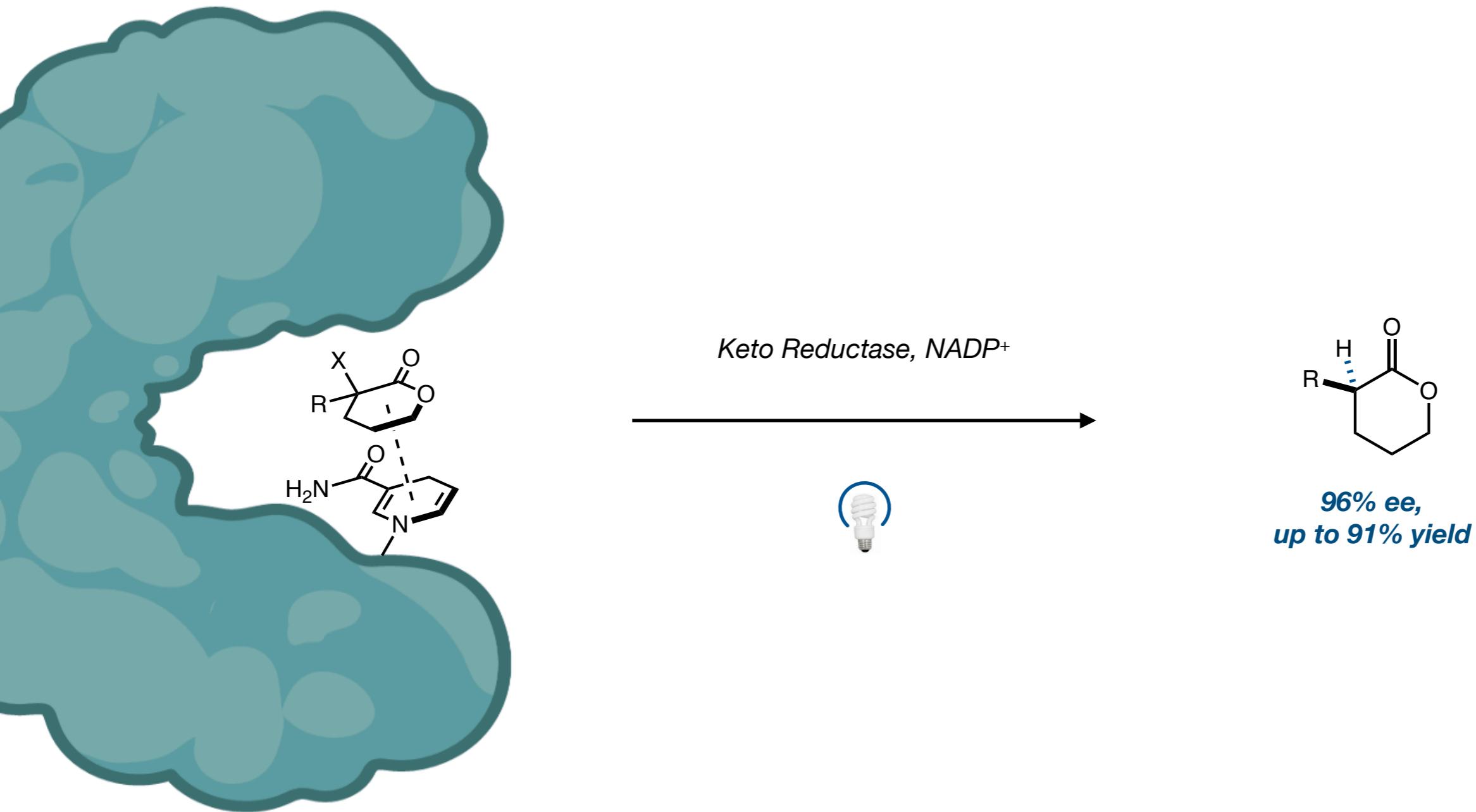


**Mes-Pth( $\text{Cl}_4$ ) is turned over by reducing  $\text{Co(III)}$  closing both catalytic cycles**

# Synthetic Applications

## Visible Light EDAs

### Enzymatic CTCs



**CTCs can enable photochemistry where otherwise difficult (ie enzyme pocket)**

# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

# *Outline*

**Part I: Electron Transfer Mechanisms**

**Part II: Charge Transfer Complexes (CTCs)**

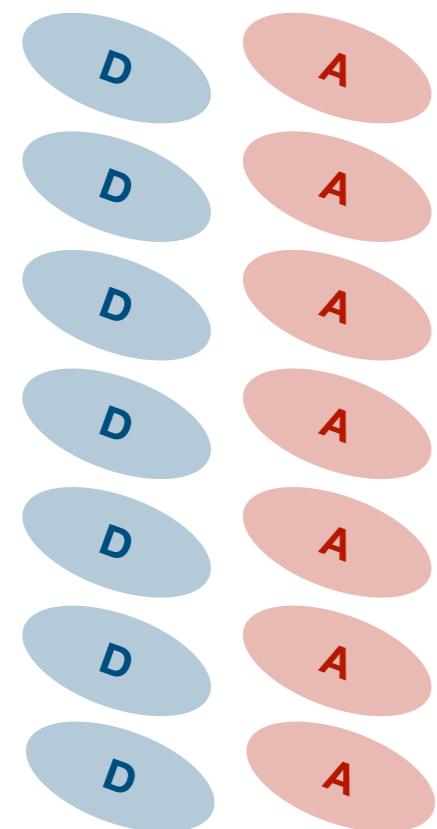
**Part III: Synthetic Applications**

**Part IV: Materials Applications and Outlook**

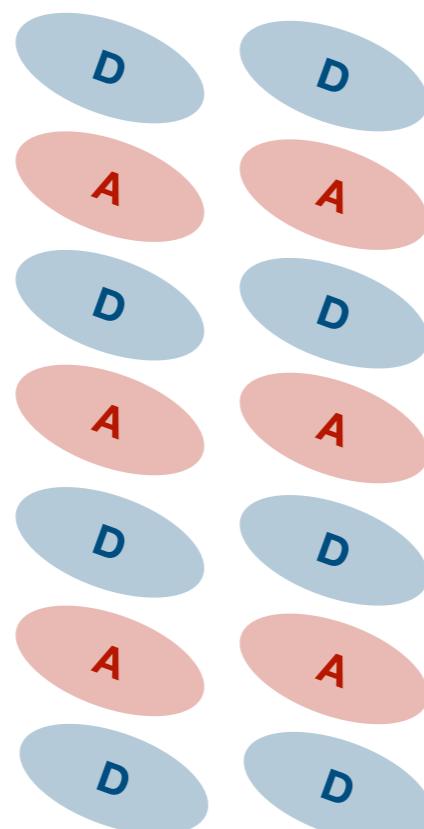
# Materials Applications

## Organic Materials

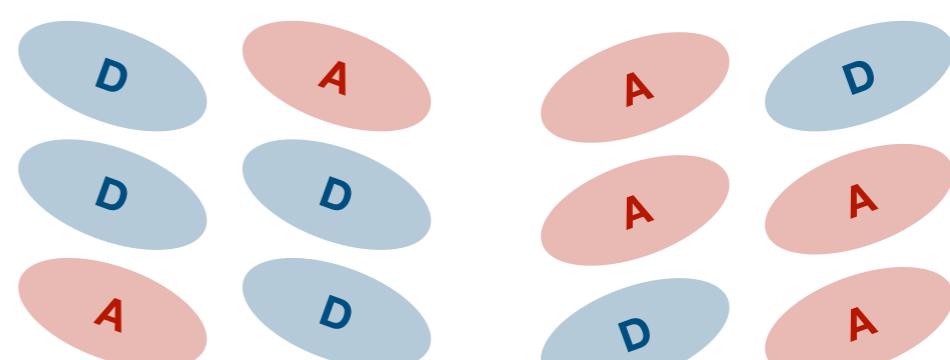
### ■ Supramolecular EDAs



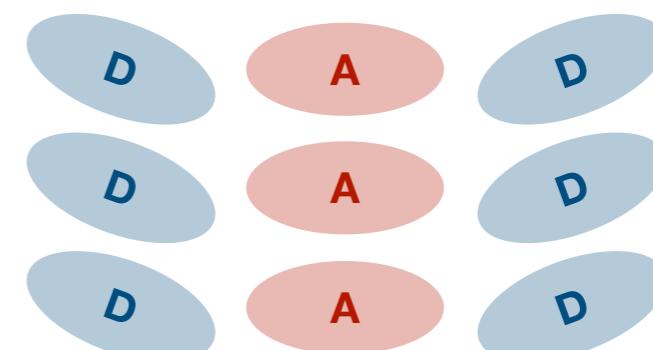
Segregated 1:1 Stacking  
(Strong end on interactions)



Mixed 1:1 Stacking  
(Strong  $\pi$ - $\pi$  interactions)



Mixed 2:1 (or 1:2) Stacking



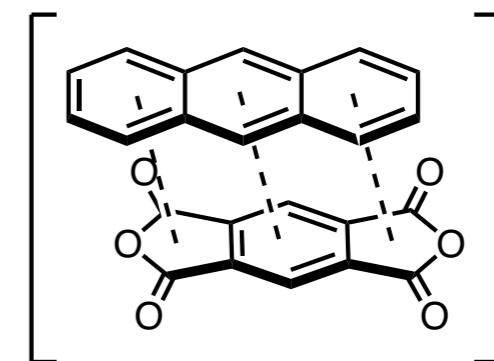
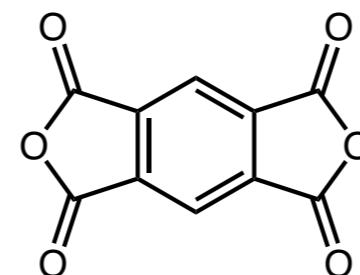
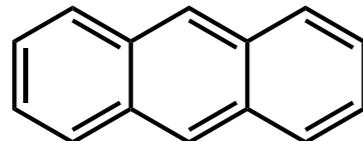
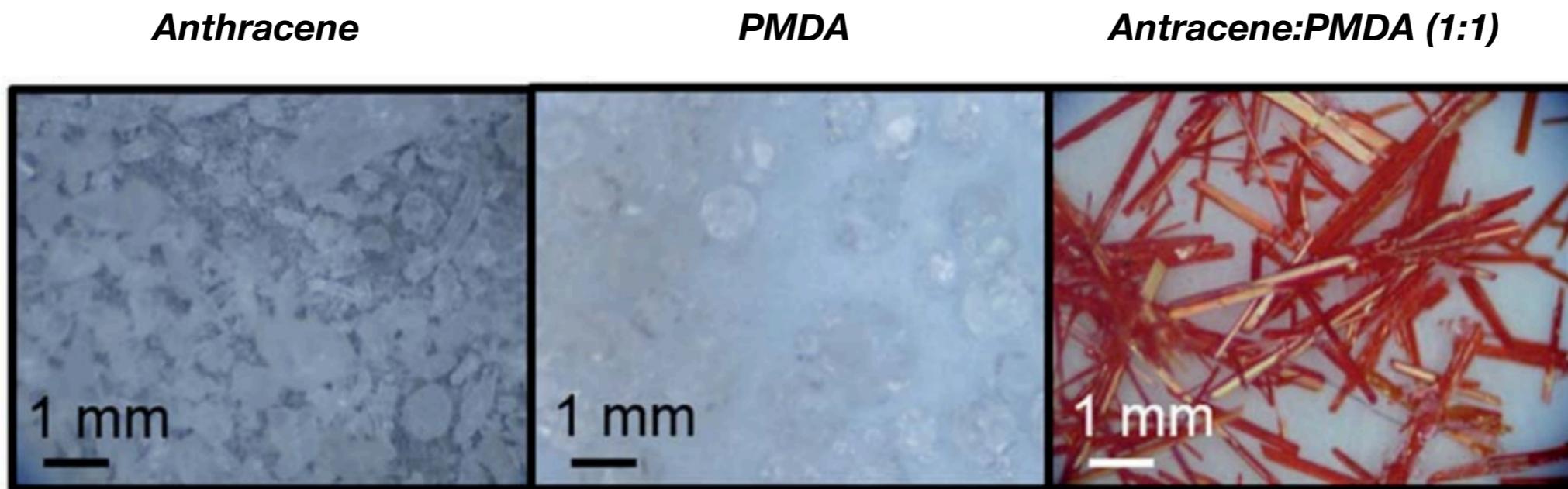
Segregated 2:1 Stacking

**Many types of supramolecular assemblies are possible for EDAs, 1:1 is most common (>90%)**

# Materials Applications

## Organic Materials

### ■ Supramolecular EDAs



**Co-crystallization of anthracene and PMDA results in a colored, conductive material**

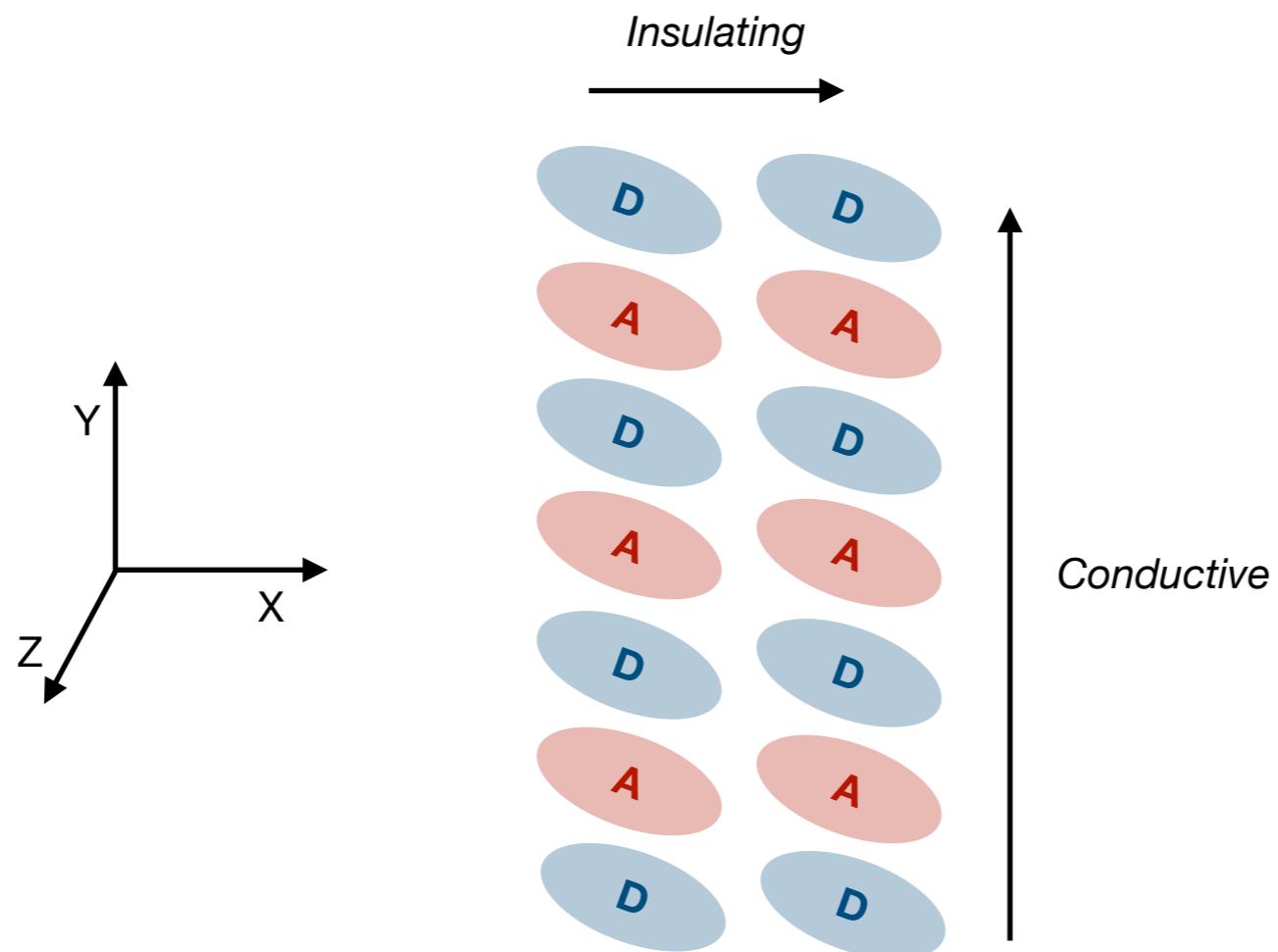
Brillante, A., Haarer, P. D.; *Chem. Phys. Lett.* **1978**, 2, 218-220.

Goetz, K. P., Vermeulen, D., Payne, M. E., Kloc, C., McNeil, L. E., Jurchescu, O. D.; *J. Mater. Chem. C* **2014**, 2, 3065-3076.

# *Materials Applications*

## *Organic Materials*

### Conductivity



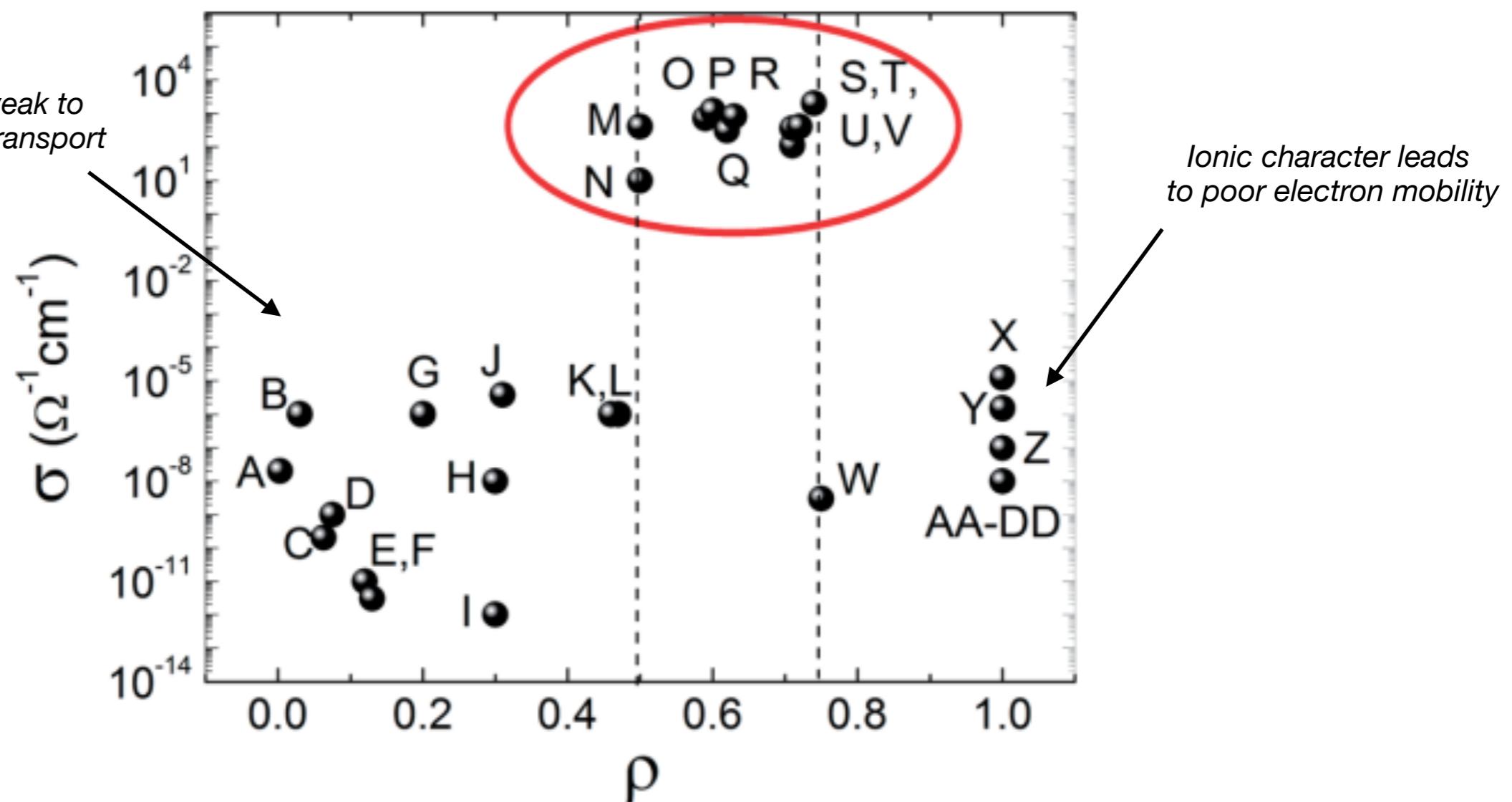
**Supramolecular EDAs often display 1 dimensional conductivity**

# Materials Applications

## Organic Materials

### Conductivity

*EDA interactions are too weak to allow for efficient electron transport*

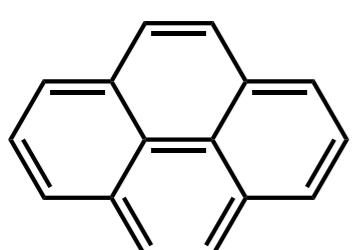


**Conductivity can be correlated to degree of charge transfer ( $\rho$ )**

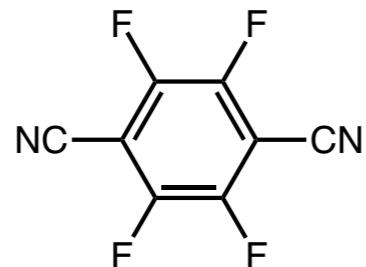
## Materials Applications

### Organic Materials

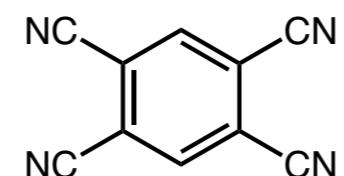
#### ■ Organic Light Harvesting Devices



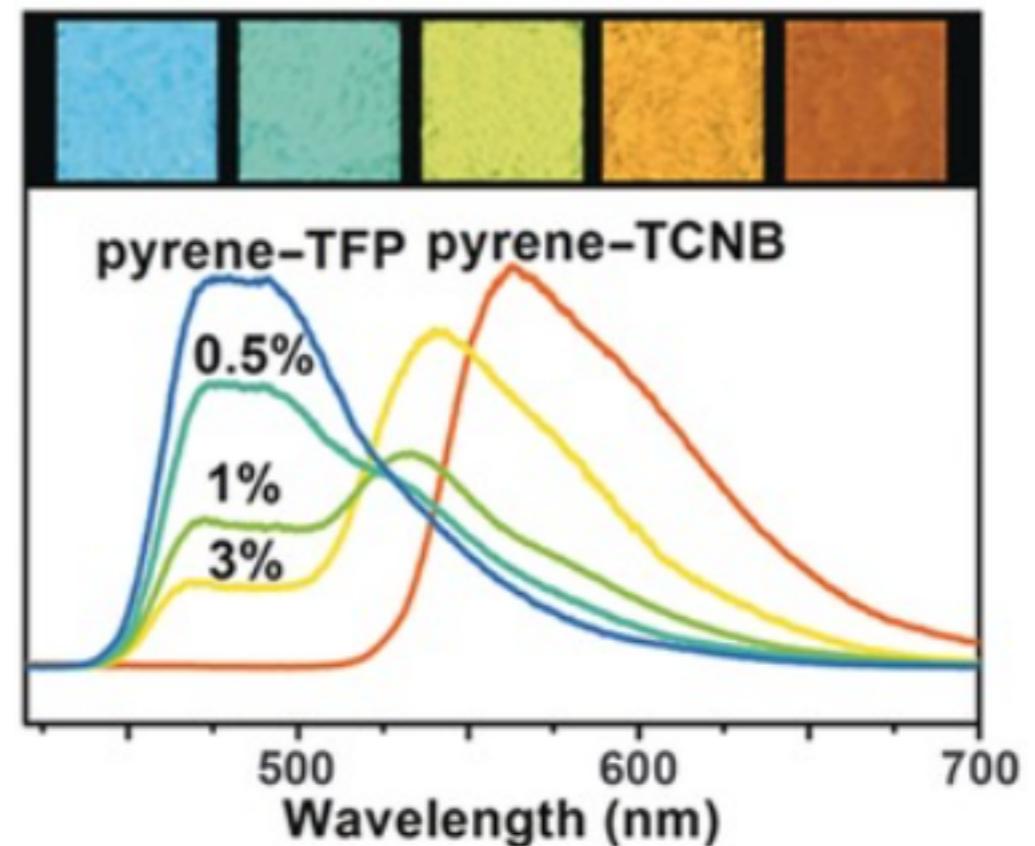
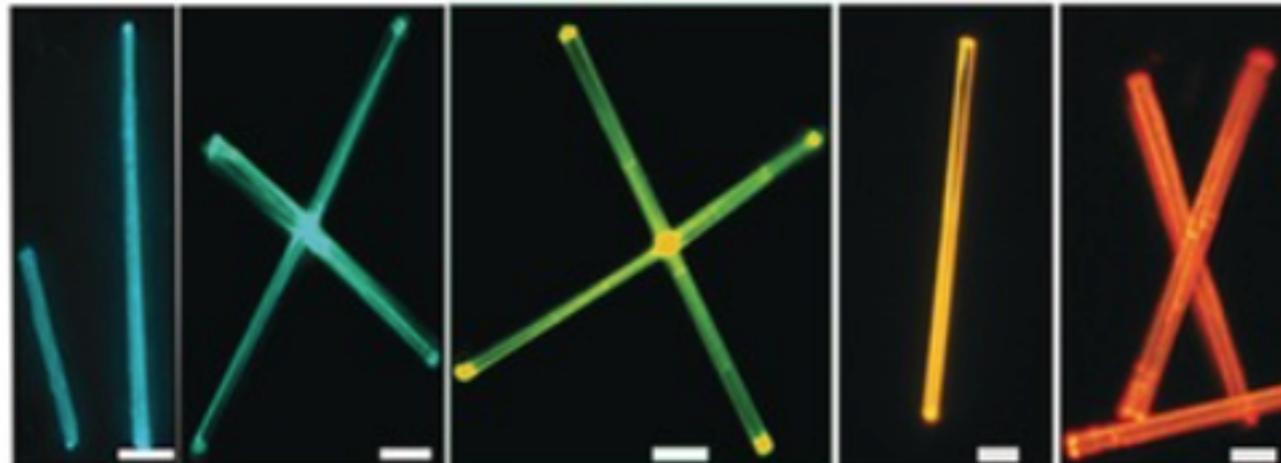
**Pyrene**



**TFP**

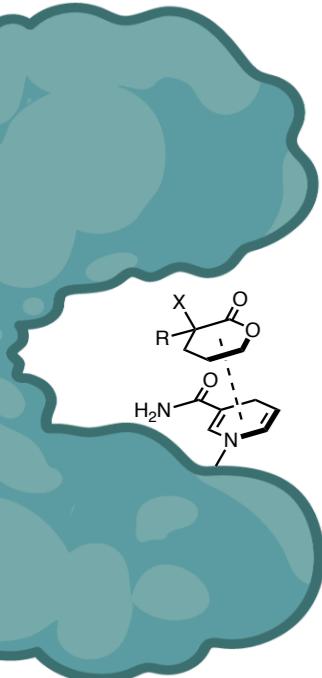


**TCNB**

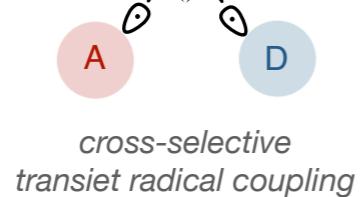


**Broad spectrum UV/blue light harvesting molecular wires can be constructed via cocrystallization, emission dependent upon TCNB doping percentage**

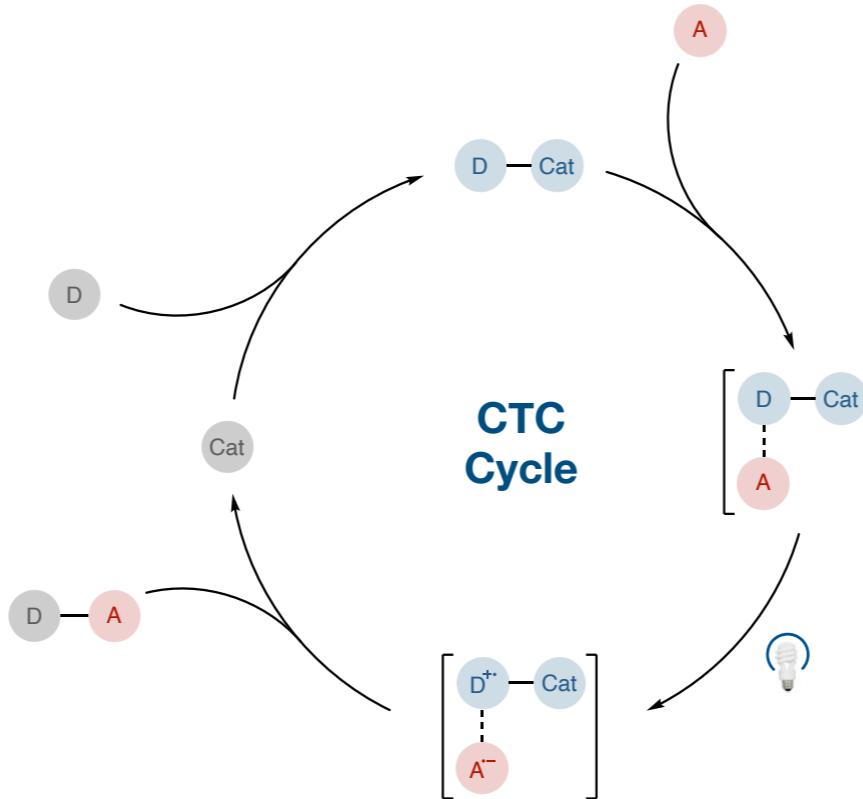
## *Outlook* *Conclusion*



or



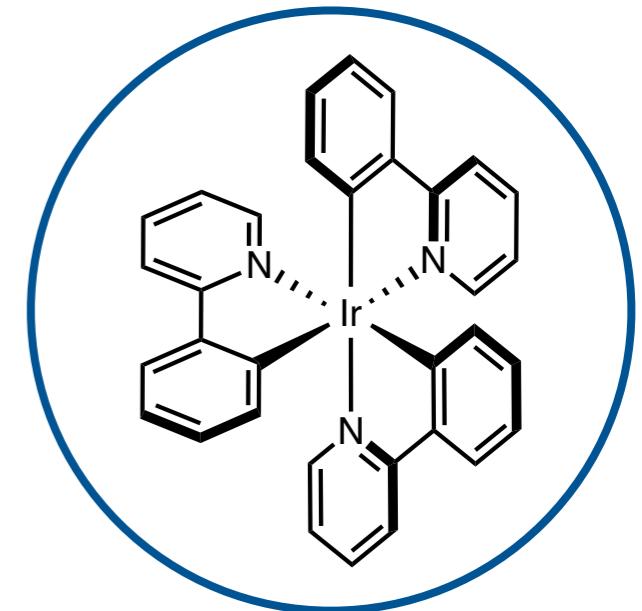
*cross-selective  
transient radical coupling*



**CTCs can enable reactivity difficult to otherwise obtain via photoredox**

**Methods with catalytic CTC components significantly improve scope**

**Always run a no photocatalyst control**



## Acknowledgments



**Prof. David MacMillan**

*The MacMillan group*

### — Advisory Committee —

Prof. Erik Sorensen

Prof. Mohammad Seyedsayamdst

