



# Electron Transfer to/from Excited Electronic States

Molecular Photochemistry

CHEM 4801

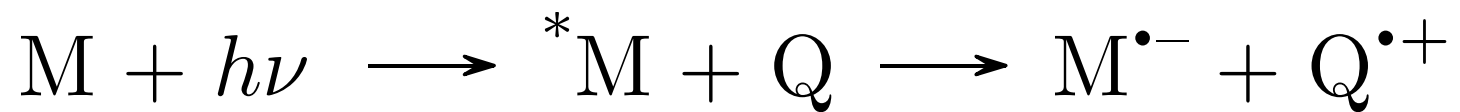
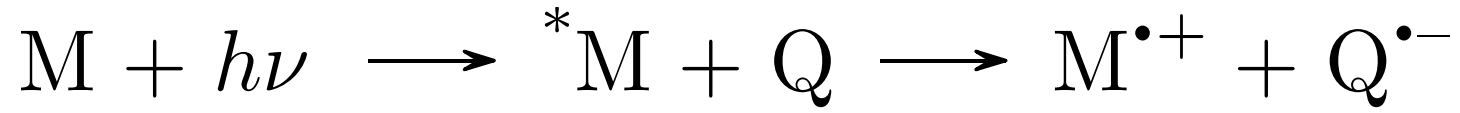


# Introduction to Electron Transfer

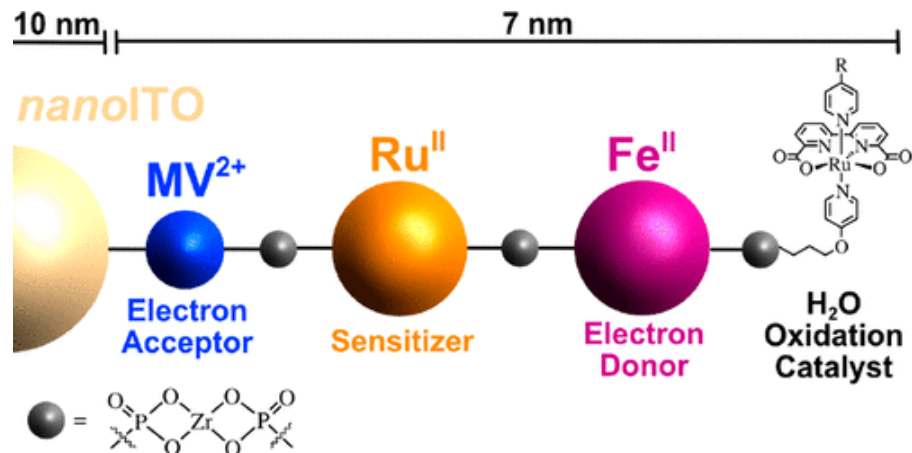
Electron Transfer to/from Excited Electronic States

# Photoinduced Electron Transfer (PET)

*Photoinduced electron transfer (PET)* refers to the transfer of an electron to or from an electronically excited state of a molecule.

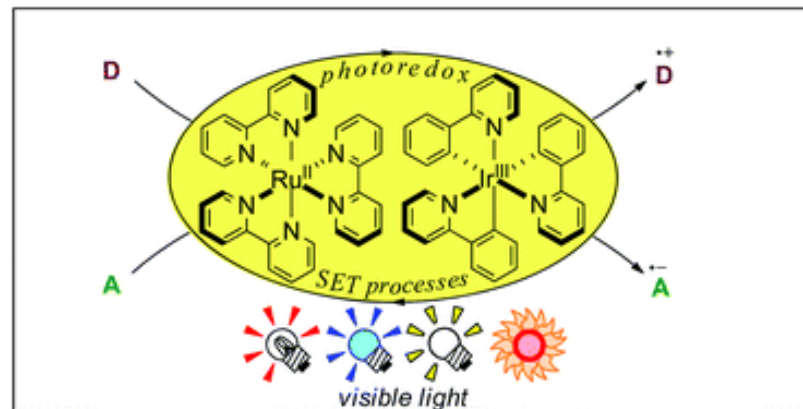


## Photosynthesis



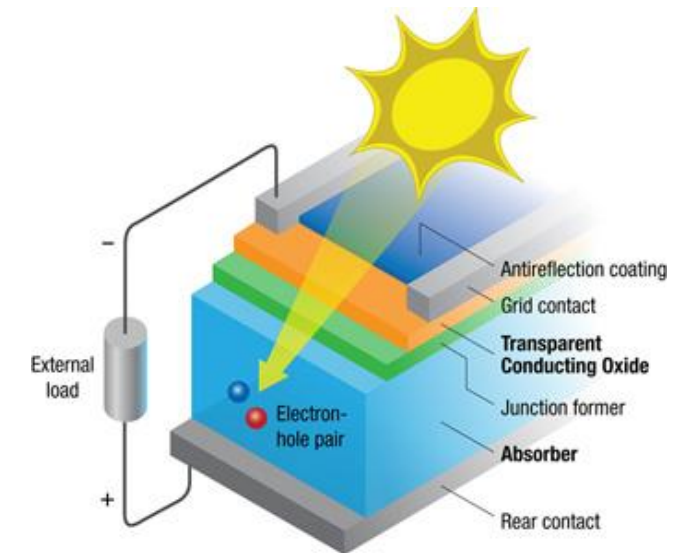
JACS 2019, 141, 7926.

## Photoredox catalysis



Inorg. Chem. Front. 2014, 1, 562.

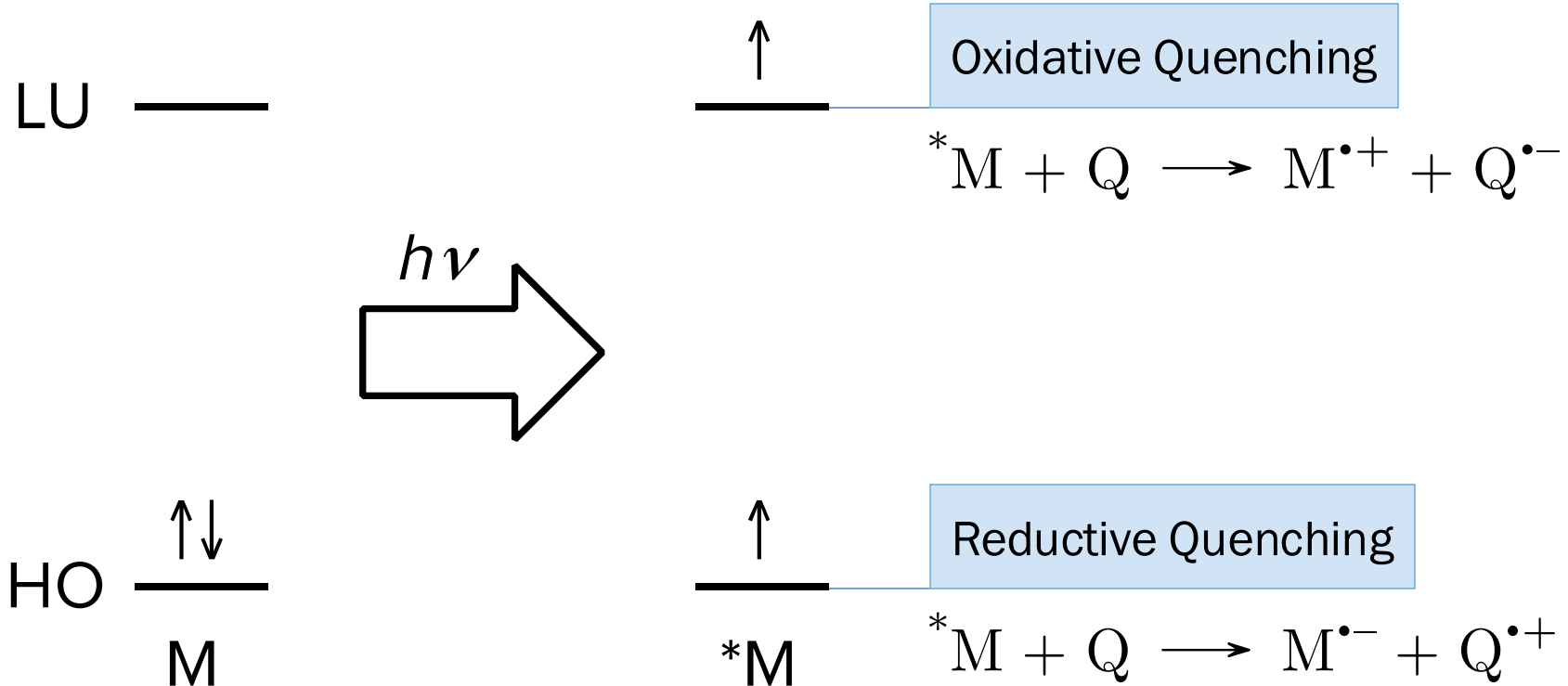
## Photovoltaic cells



<https://www.nrel.gov/pv/organic-photovoltaic-solar-cells.html>

# Excitation Enables Electron Transfer

Excited states are *both* stronger oxidizing agents *and* stronger reducing agents than their corresponding ground states.



# Kinetics and Thermodynamics of Photoinduced Electron Transfer

Electron Transfer to/from Excited Electronic States

# Kinetics of Electron Transfer (and More!)



Two kinetic “regimes” are important in electron-transfer processes. These are also important for *any* photochemical reaction!

Reaction	Description	Rate
$^*M \longrightarrow M + h\nu$	Radiative decay	$k_{em}[^*M]$
$^*M \longrightarrow M$	Nonradiative decay	$\sum k_i[^*M]$
$^*M + Q \longrightarrow ^*[MQ]$	Diffusional encounter	$k_d[^*M][Q]$
$^*[MQ] \longrightarrow ^*M + Q$	Reactant separation	$k_{-d}[^*[MQ]]$
$^*[MQ] \longrightarrow [M^{\bullet+}, Q^{\bullet-}]$	Reaction	$k_r[^*[MQ]]$
$[M^{\bullet+}, Q^{\bullet-}] \longrightarrow ^*[MQ]$	Reverse reaction	$k_{-r}[[M^{\bullet+}, Q^{\bullet-}]]$
$[M^{\bullet+}, Q^{\bullet-}] \longrightarrow M^{\bullet+} + Q^{\bullet-}$	Product separation	$k_s[[M^{\bullet+}, Q^{\bullet-}]]$

Note that what we formerly just called “quenching” now amounts to five distinct processes.

# Kinetics of Electron Transfer (and More!)



Two kinetic “regimes” are important in electron-transfer processes. These are also important for *any* photochemical reaction!

General result for rate constant of quenching  $k_q$

$$k_q = \frac{k_d k_r k_s}{k_{-d} k_{-r} + k_{-d} k_s + k_r k_s}$$

**Case 1.** Activation control. *Reaction much slower than diffusion*

$$k_q \approx \left( \frac{k_d}{k_{-d}} \right) k_r = K_d k_r$$

**Case 2.** Diffusion control. *Reaction faster than diffusion*

$$k_q \approx k_d$$

# Redox Analysis of PET

Photoinduced electron transfer, like all redox reactions, can be envisioned as two half-reactions. The ensuing analysis reveals the energy of a PET process in terms of redox potentials.



Coulombic attraction of radical ions

$$\Delta G_{OQ}^{\circ} = F[E^{\circ}(A/A^{\bullet-}) - E^{\circ}(D^{\bullet+}/D)] - E_{*D}$$



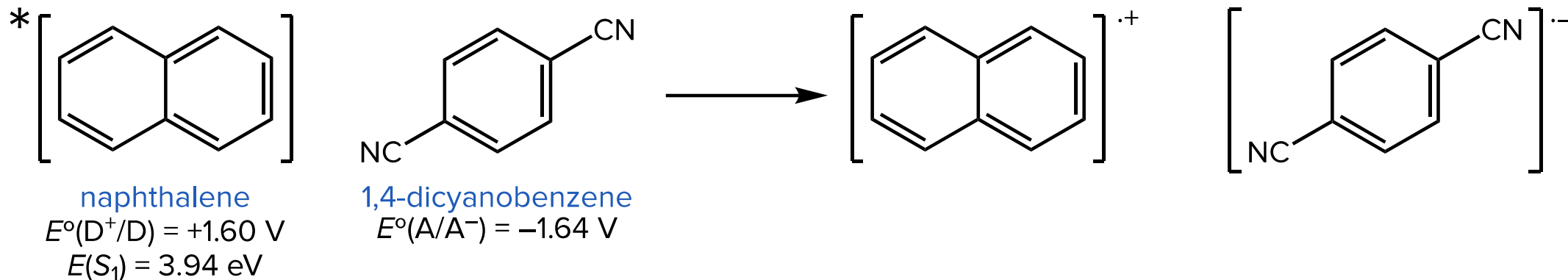
$$\Delta G_{RQ}^{\circ} = F[E^{\circ}(A/A^{\bullet-}) - E^{\circ}(D^{\bullet+}/D)] - E_{*A}$$



# Redox Analysis of PET

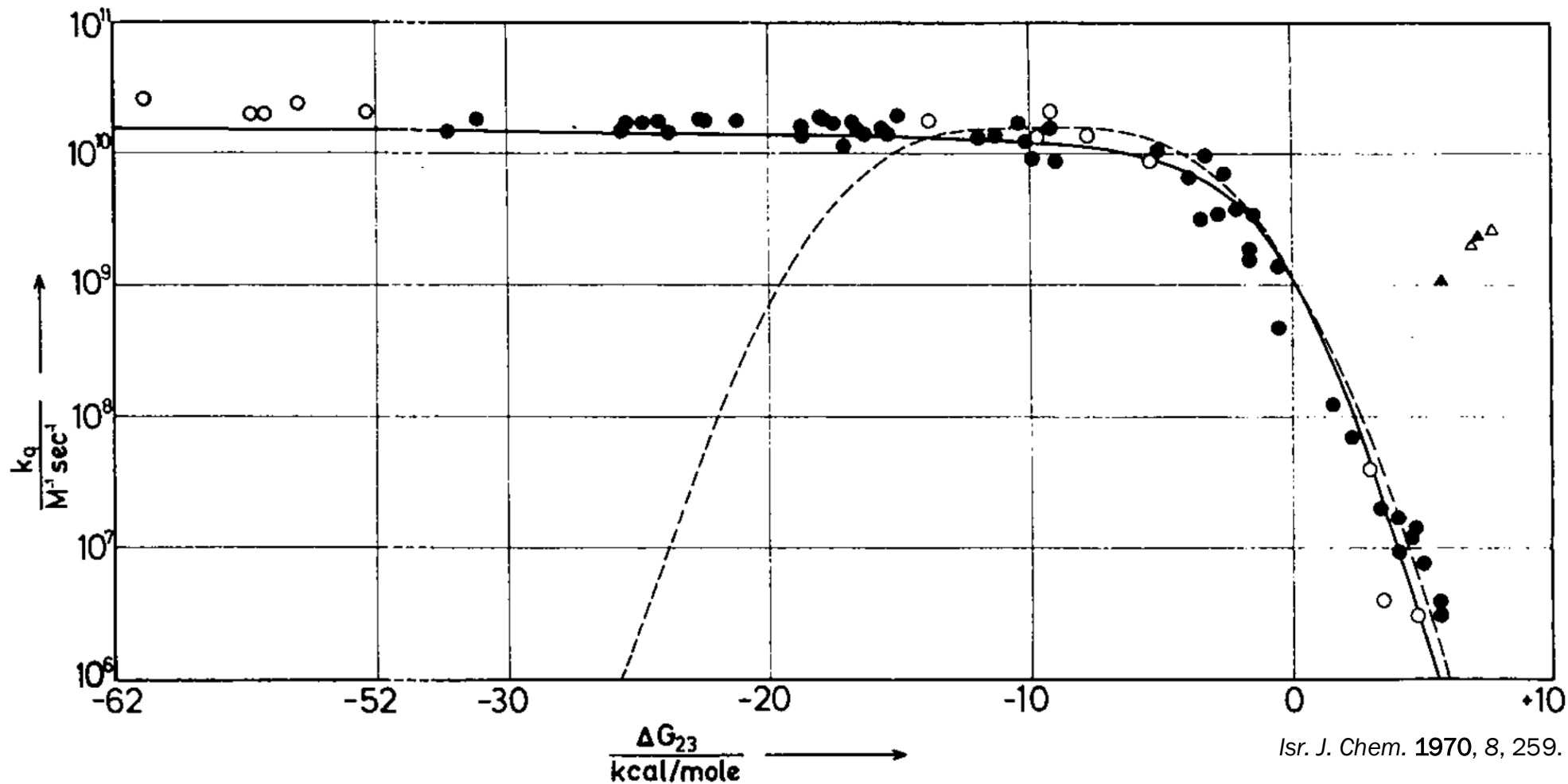
Photoinduced electron transfer, like all redox reactions, can be envisioned as two half-reactions. The ensuing analysis reveals the energy of a PET process in terms of redox potentials.

**Example.** Excited naphthalene + 1,4-dicyanobenzene in acetonitrile ( $E_{coul} \approx 0.2$  kcal/mol)



# Kinetics Meets Thermodynamics

The two kinetic cases just described can clearly be seen on a plot of  $k$  as a function of the free energy of PET (Rehm-Weller plot).



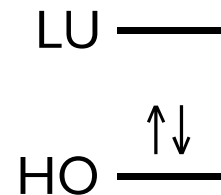
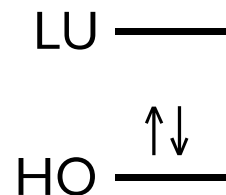
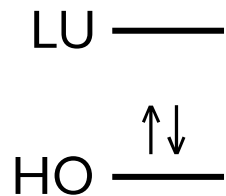
# Electron-poor Sensitizers: Patterns in Structure and Reactivity

Electron Transfer to/from Excited Electronic States

# Ionization Potential and Electron Affinity

**Ionization potential (IP)** is simply the oxidation potential of an electron donor D with respect to vacuum. **Electron affinity (EA)** is the reduction potential of an electron acceptor A.

vacuum —————

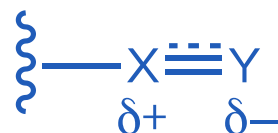


What structural factors affect IP and EA?

# Electron-withdrawing Groups

**Electron-withdrawing groups (EWGs)** pull electron density from an attached pi system via resonance, induction, or a combination of both.

General structure of  
resonance-withdrawing groups



Orbital analysis shows EWGs increase ionization potential and electron affinity.

Examples with resonance structures

vacuum —————

LU ———

HO ———  
↑↓

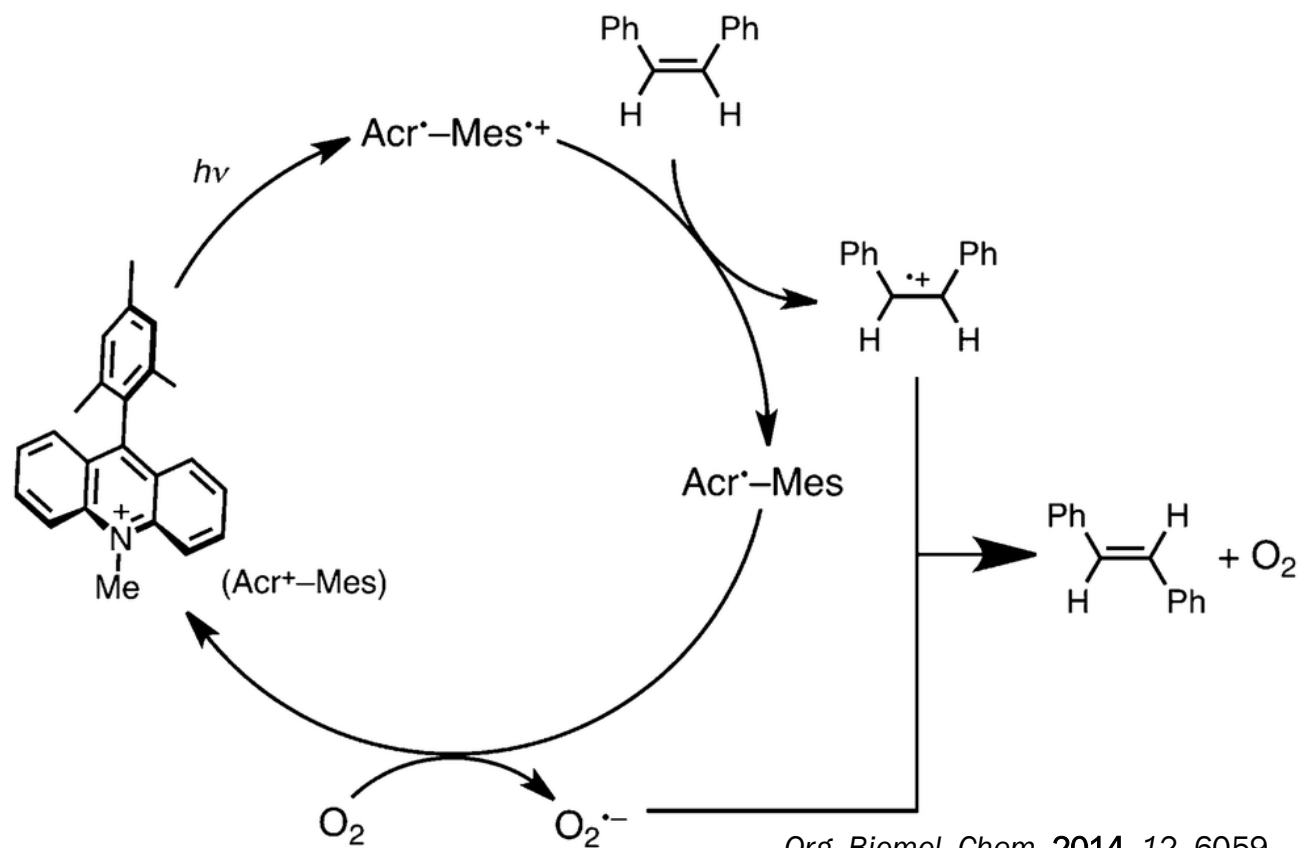
LU ———

HO ———  
↑↓

# Electron-poor Chromophores

Electron-poor chromophores with high electron affinity often promote the formation of radical cations or neutral carbon radicals from organometallic reagents.

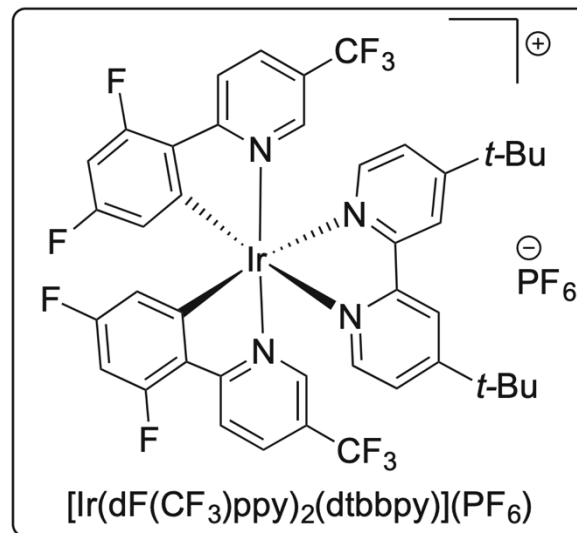
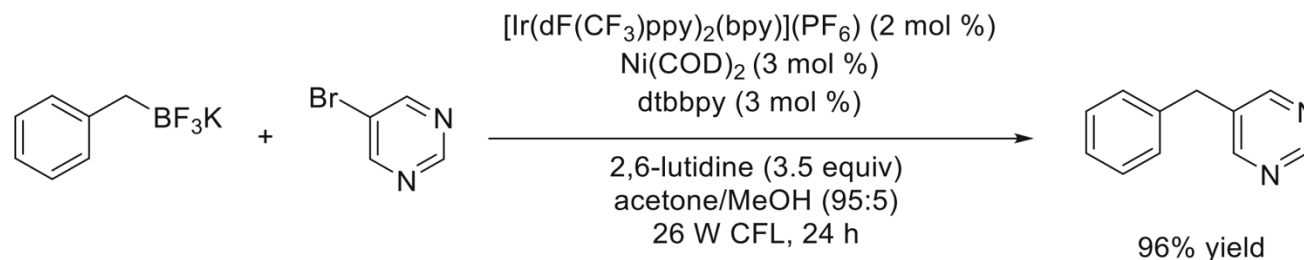
## Radical cations from an organic photoredox catalyst



# Electron-poor Chromophores

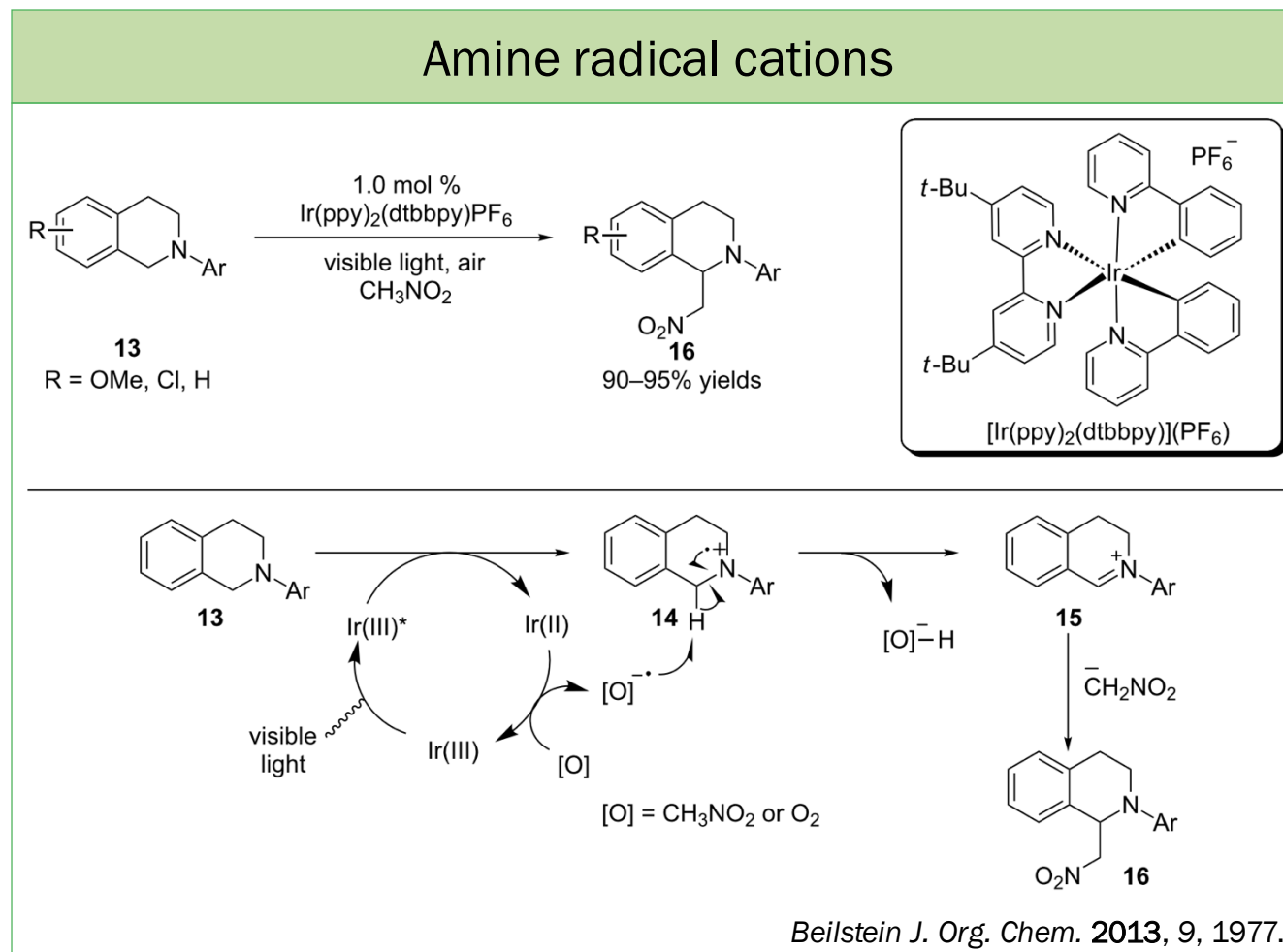
Electron-poor chromophores with high electron affinity often promote the formation of radical cations or neutral carbon radicals from organometallic reagents.

## Carbon radicals from organometallic reagents



# Electron-poor Chromophores

When paired with molecules with low ionization potential (e.g. amines or weak inorganic bases such as  $\text{CO}_3^{2-}$ ), even “electron-neutral” sensitizers can serve as electron donors.





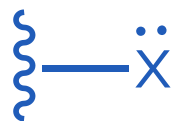
# Electron-rich Sensitizers: Patterns in Structure and Reactivity

Electron Transfer to/from Excited Electronic States

# Electron-donating Groups

**Electron-donating groups (EDGs)** inject electron density into an attached pi system via resonance, induction, or a combination of both.

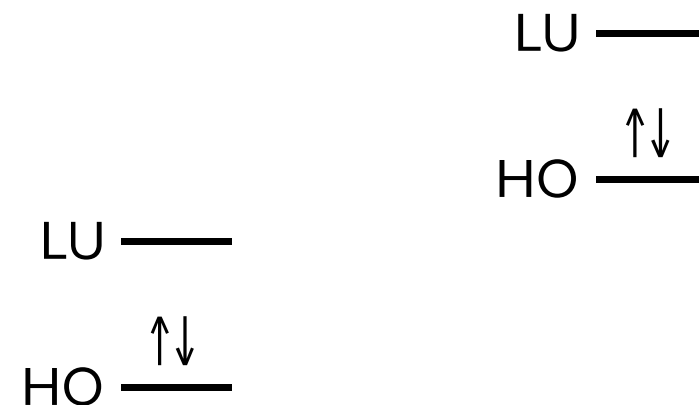
General structure of  
resonance-donating groups



Examples with resonance structures

Orbital analysis shows EDGs decrease ionization potential and electron affinity.

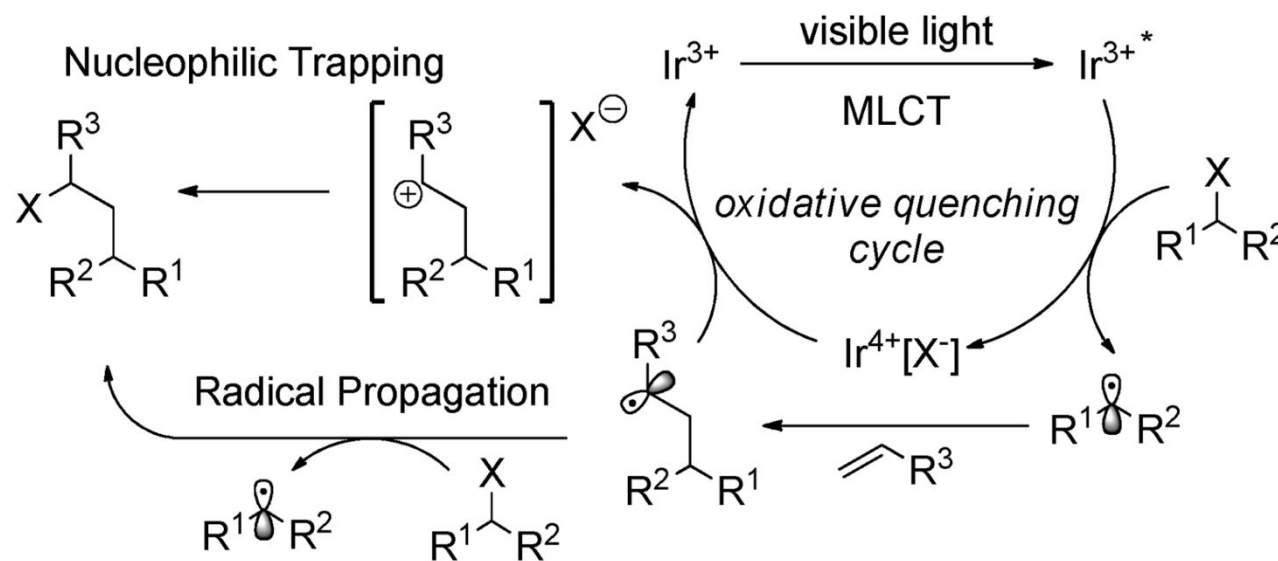
vacuum —————



# Electron-rich Chromophores

Electron-rich chromophores with low ionization potential often promote the formation of radical anions or neutral carbon radicals from organohalides.

## Atom transfer radical addition via oxidative quenching

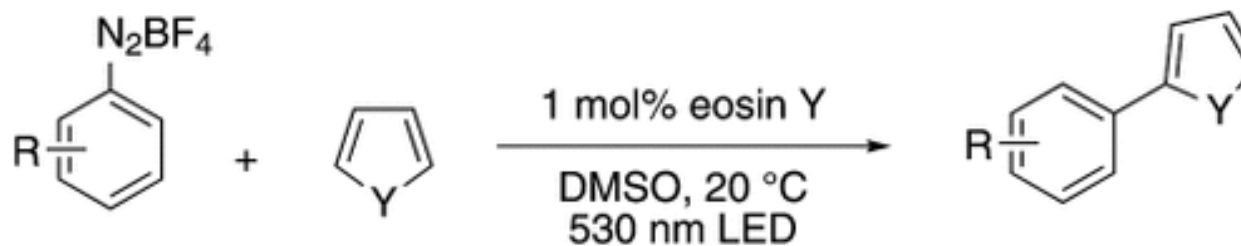


*J. Am. Chem. Soc.* **2011**, *133*, 4160.

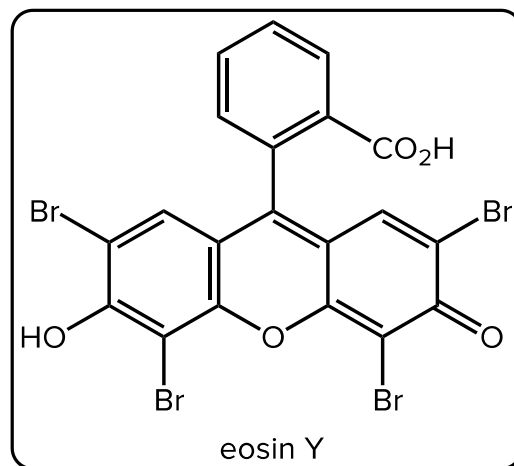
# Electron-rich Chromophores

When paired with molecules with high electron affinity (e.g. carbonyls, electron-poor arenes), even “electron-neutral” sensitizers can serve as electron donors.

## Arenediazoniums as precursors to aryl radicals



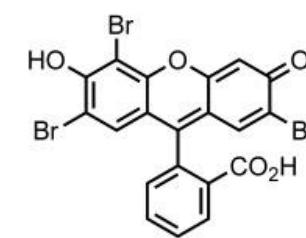
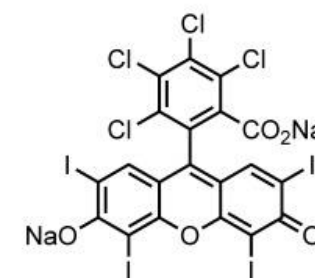
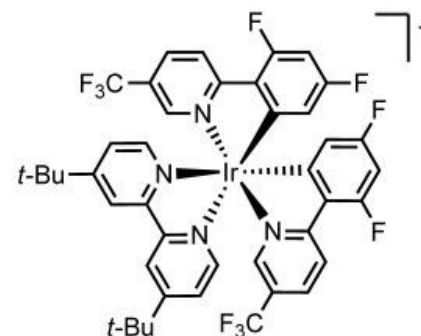
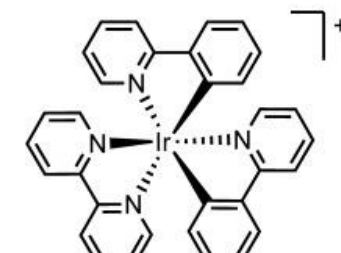
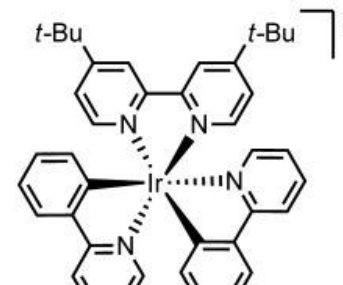
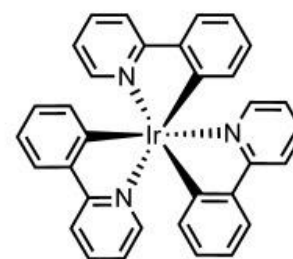
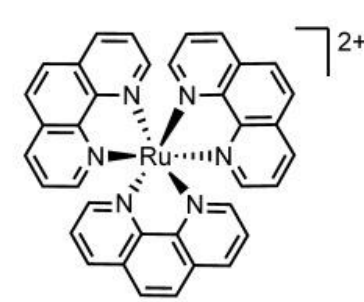
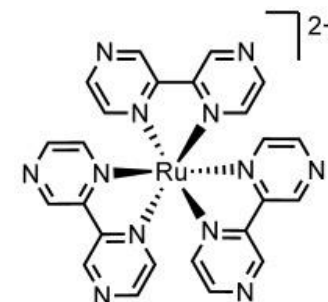
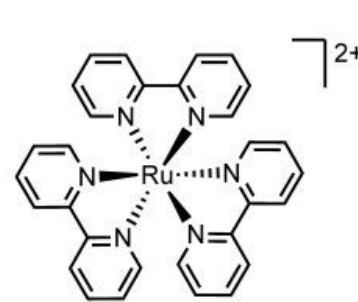
Y = O, S, NBoc



# Properties of Photoredox Catalysts

Using prior ideas, we can easily rationalize the redox properties of these photoredox catalysts.

Catalyst	$E_{00}$	$E_{red}$	$E^*_{red}$	$E_{ox}$	$E^*_{ox}$
Ru-1	2.1	-1.33	0.77	1.29	-0.81
Ru-2	2.0	-0.80	1.45	1.86	-0.26
Ru-3	2.1	-1.36	0.86	1.28	-0.94
Ir-1	2.5	-2.19	0.31	0.77	-1.73
Ir-2	2.2	-1.51	0.66	1.21	-0.96
Ir-3	2.1	-1.42	0.68	1.25	-0.85
Ir-4	2.6	-1.37	1.21	1.69	-0.89
RB	1.8	-0.78	0.99	1.09	-0.68
EoY	2.3	-1.14	1.18	0.72	-1.60
DCA	2.9	-0.83	2.07	1.89	-1.01
TiO <sub>2</sub>	3.0	-2.00	1.00	1.00	-2.00



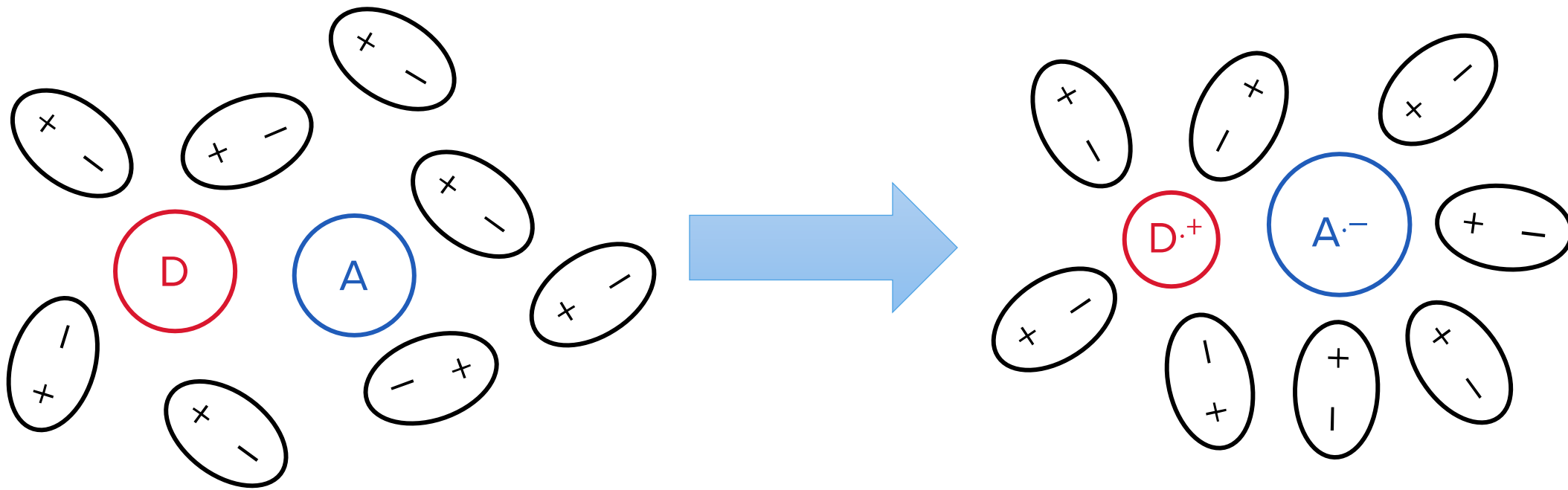


# Marcus Theory I

Electron Transfer to/from Excited Electronic States

# Electron Transfer: Molecular-scale View

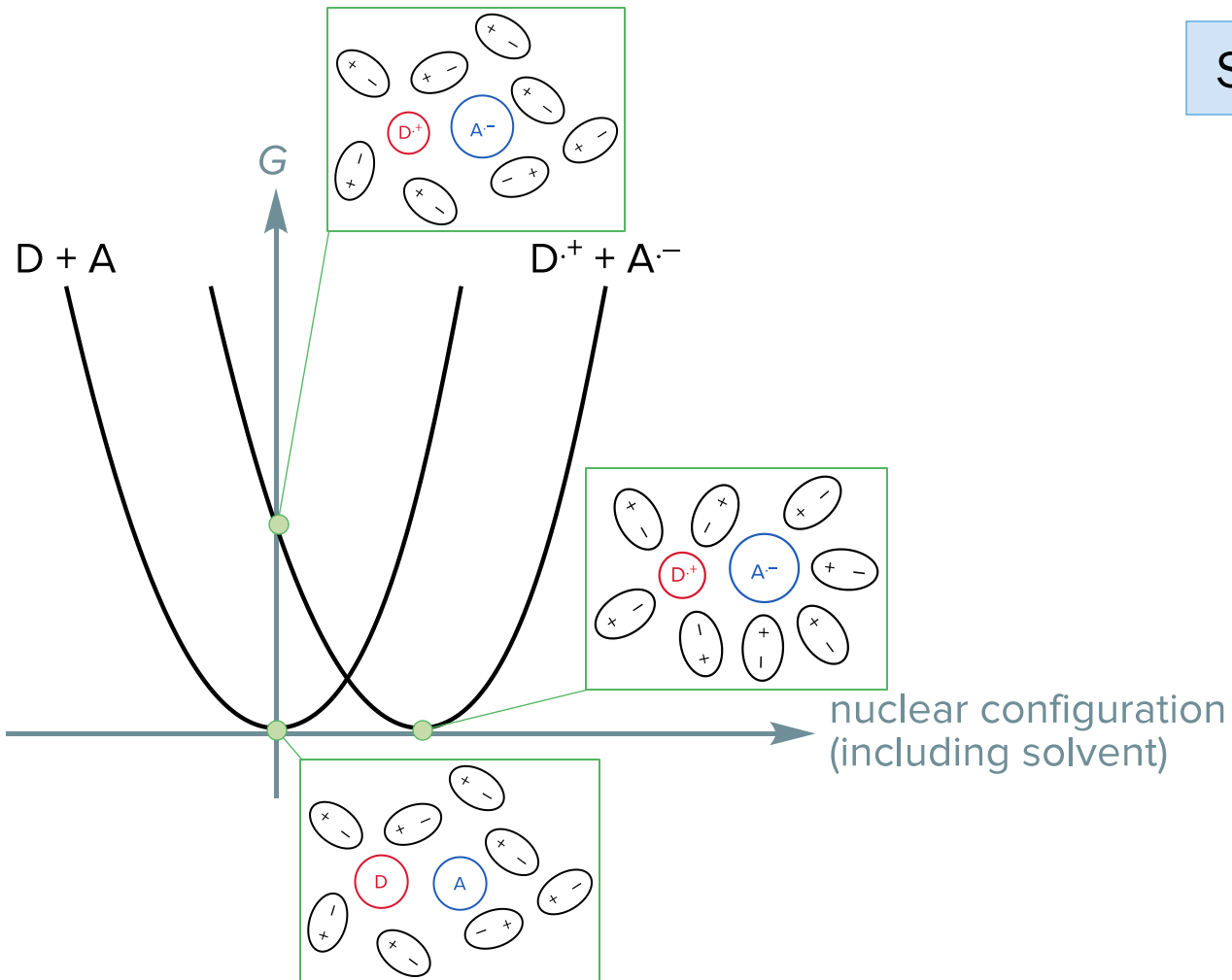
On the molecular level, electron transfer involves (1) *inner-sphere* reorganization of bonds and atoms in D and A and (2) *outer-sphere* reorganization of solvent molecules.



Do inner- and outer-sphere motions happen in concert or does inner-sphere electron transfer happen first?

# Libby Theory of Electron Transfer

The energy released as solvent adjusts to  $D^+$  and  $A^-$  is called *reorganization energy* ( $\lambda$ ). Libby posited that  $\lambda$  must be fully invested before the product PES is reached.



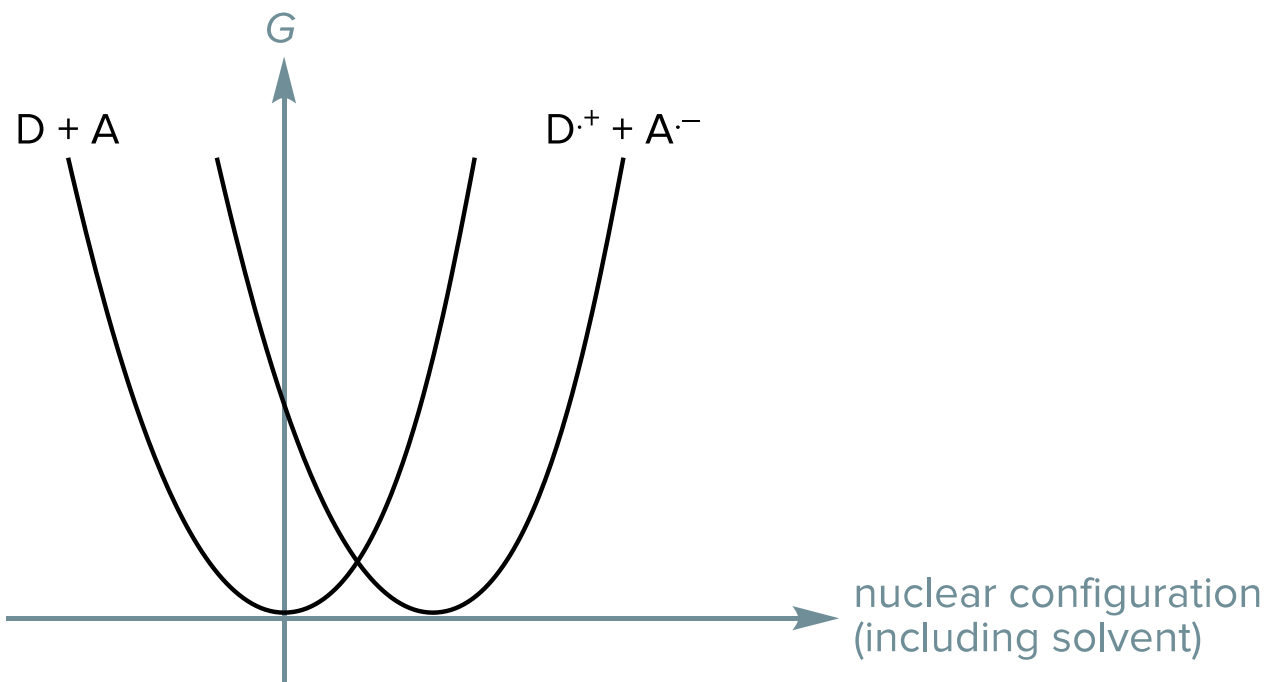
Self-exchange reaction ( $\Delta G^\circ = 0$ )

Hypothesis:  $\Delta G^\ddagger = \lambda$



# Marcus Theory of Electron Transfer

If solvent molecules move in concert with the transferred electron, the activation energy is lower than that predicted by the Libby model. The resulting picture is the foundation of Marcus theory.



Self-exchange reaction ( $\Delta G^\circ = 0$ )

Hypothesis:  $\Delta G^\ddagger = \lambda/4$

What happens if  $\Delta G^\circ \neq 0$ ?



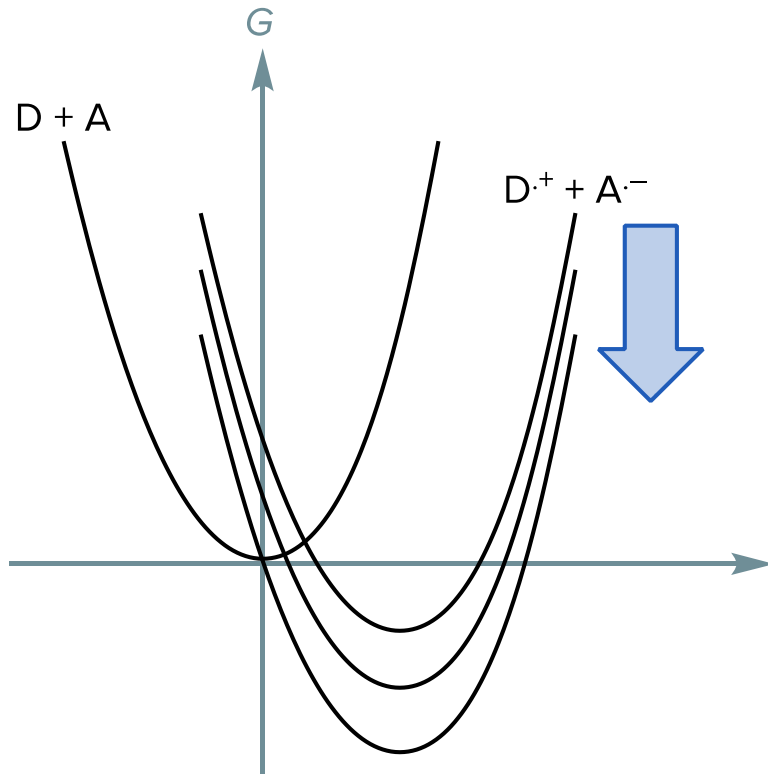
# Marcus Theory II

Electron Transfer to/from Excited Electronic States

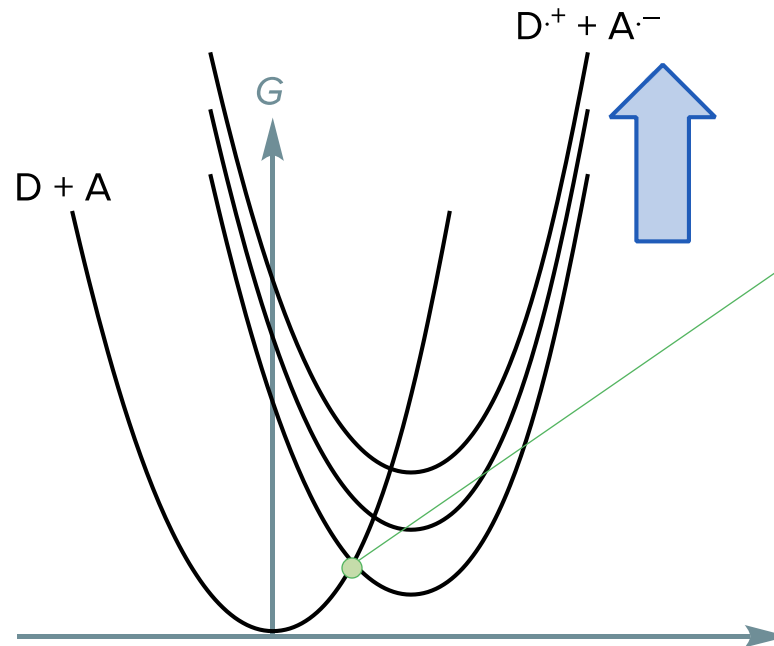
# Marcus Theory of Electron Transfer

Endergonic ET reactions behave as expected:  $\Delta G^\ddagger$  increases as  $\Delta G^\circ$  increases.  
Until  $\Delta G^\circ = -\lambda$ , exergonic ET reactions also behave as expected.

Exergonic electron transfer



Endergonic electron transfer



$$G_{DA} = x^2$$

$$G_{D^+A^-} = (x - \sqrt{\lambda})^2 + \Delta G^\circ$$

Where the  $G$  values are equal...

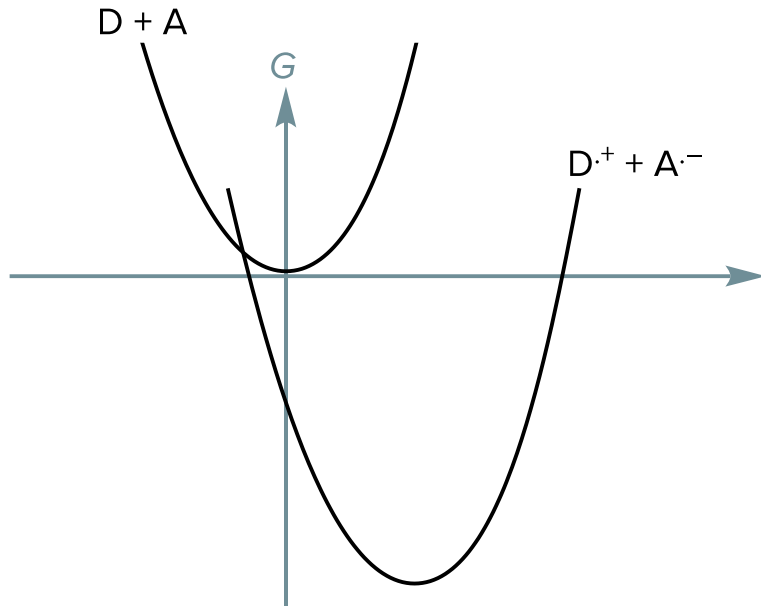
$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

# Marcus Theory of Electron Transfer

Something very strange happens when  $\Delta G^\circ < -\lambda$ . The activation energy of electron transfer starts to increase as the reaction becomes more exergonic!

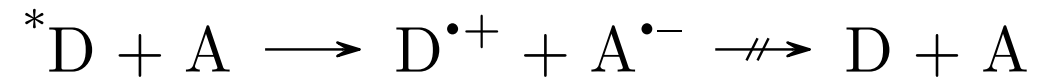
$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

Very exergonic electron transfer



Maximal rate of electron transfer when  $\Delta G^\circ = -\lambda$

Good news for photoinduced electron transfer...



Reactions for which  $\Delta G^\circ < -\lambda$  are said to be in the *Marcus inverted region*.

# Rehm and Weller Revisited

The inverted region is not visible in the data of Rehm and Weller even though we might expect it to be. Marcus was finally vindicated 30 years later!

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

