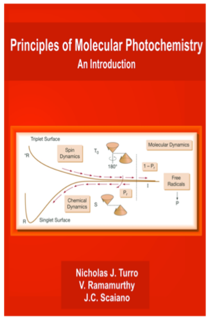
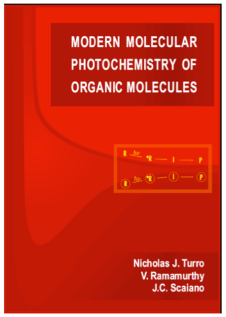
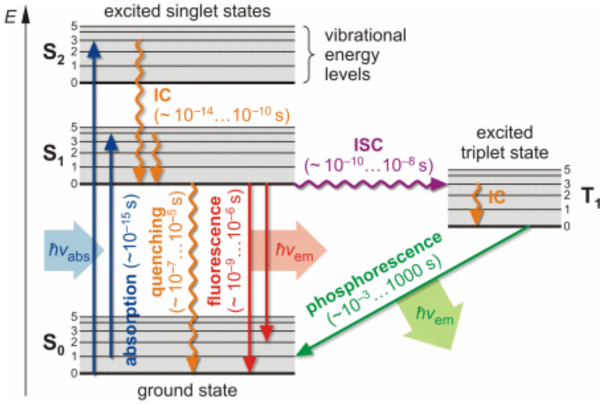
Electron and Energy Transfer

Chapter 7 (pp.383-481)







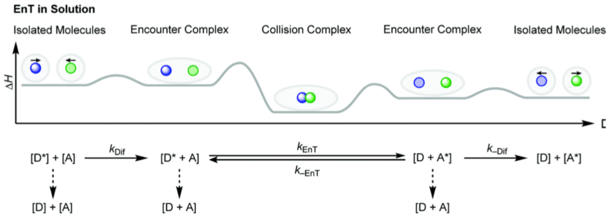
$$D^* \quad + \quad A \quad \xrightarrow{k_{diff}} \quad \{D^*A\}$$

$$\{D^*A\} \quad \longrightarrow \quad \{DA^*\}$$

$$\{DA^*\} \quad \xrightarrow{k_{-diff}} \quad D \quad + \quad A^*$$

$$k_{DIF} = \frac{8RT}{3000\eta}$$

Steps involved in energy transfer in solution



Scenario A:
fast energy transfer
$k_{\mathrm{EnT}} >> k_{\mathrm{Dif}}$
$\Downarrow$
diffusion-limited overall rate
$k_{\mathrm{obs}} \approx k_{\mathrm{Dif}}$

Scenario B:
slow energy transfer
$k_{\mathrm{EnT}} << k_{\mathrm{Dif}}$
$\Downarrow$
energy-transfer-limited overall rate
$k_{\mathrm{obs}} \propto k_{\mathrm{EnT}}$

Diffusion

$$k_{DIF} = \frac{8RT}{3000\eta}$$

η is the viscosity of the solvent (in units of Poise, P)
R is the gas constant (8.31×10^7 erg/mol or 1.99 cal mol^{-1} K^{-1}).

For typical non-viscous organic solvents (benzene, acetonitrile, hexane) at room temperature η is ~ 1-10 cP

k_{DIF} has a value of around 10^9-10^{10} M^{-1}s^{-1}.

Possibilities

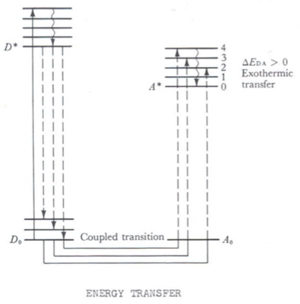
$$^1D^* + A \longrightarrow D + {}^1A^*$$

~~$^1D^* + A \longrightarrow D + {}^3A^*$~~

~~$^3D^* + A \longrightarrow D + {}^1A^*$~~

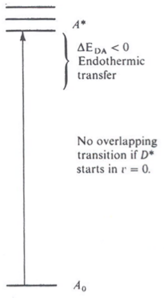
$$^3D^* + A \longrightarrow D + {}^3A^*$$

Energy Requirement



Allowed

$E_D > E_A$



Forbidden

$E_D < E_A$

Mechanisms

- Radiative Energy Transfer
  - Trivial ET
- Non-Radiative Energy Transfer
  - Resonance ET
  - Exchange ET

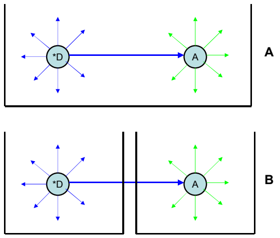
Trivial Energy Transfer

$$^*D \longrightarrow D + h\nu$$
$$h\nu + A \longrightarrow {}^*A$$

Depends On:

- The quantum yield (Φ_e^D) of emission of *D
- The number of A molecules (concentration) in the path of photons emitted by *D
- The light absorbing ability (extinction coefficient, ε_A) of A
- The overlap of the emission spectrum of *D and the absorption spectrum of A, with consideration given to the extinction coefficient, ε_A, of A at the wavelength of overlap.

Trivial energy transfer (*radiative* energy transfer)

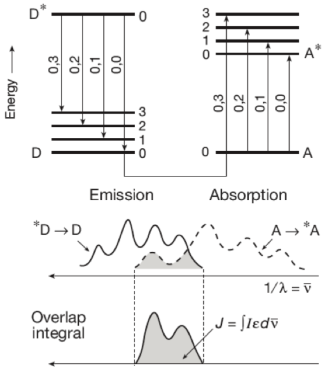


$$D^* \longrightarrow D + h\nu$$
$$A + h\nu \longrightarrow A^*$$

- no electronic interaction between D* and A
- D* emits a quantum of light which is absorbed by A

A physical encounter between A and D* is not required, the photon must only be emitted in an appropriate direction and the medium must be transparent in order to allow transmission.

Criteria for Trivial Energy Transfer: Spectral Overlap



$$J = \int_0^\infty \underset{\substack{\uparrow \\ \text{emitted light intensity}}}{I_D}(\bar{\nu})\,\overset{\substack{\text{extinction coefficient of A} \\ \downarrow}}{\varepsilon_A}(\bar{\nu})\,d\bar{\nu}$$

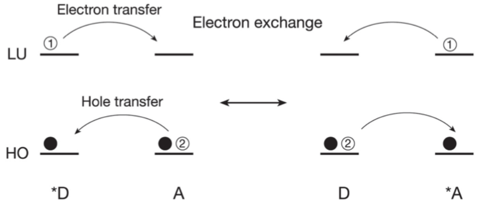
This overlap integral also can be used for energy transfer.

Non-Radiative Energy Transfer

Exchange Energy Transfer

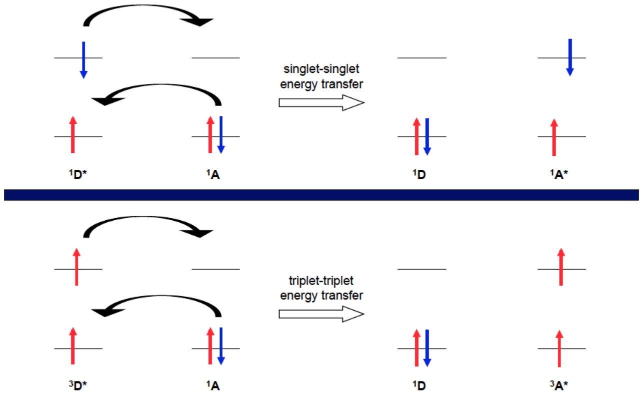
Dexter Energy Transfer

Collisional Energy Transfer



k_{ET} (exchange) = $KJ \exp(-2\, r_{DA}/L)$

S-S and T-T Exchange Energy Transfer



Criteria for Exchange Energy Transfer

$$k_{ET}\,(\text{exchange}) = KJ\exp(-2r_{DA}/L)$$

- Spin
- Energy matching
- Distance
- Orientation

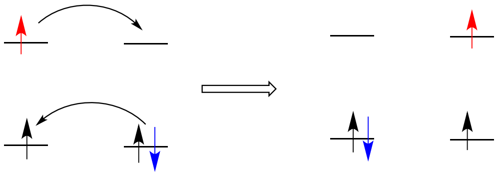
where K is related to the specific orbital interactions such as the dependence of orbital overlap to the instantaneous orientations of *D and A.

J is the normalized spectral overlap integral, where normalized means that both the emission intensity (I_D) and extinction coefficient (ε_A) have been adjusted to unit area on the wavenumber scale. It is important that J, by being normalized does not depend on the actual magnitude of ε_A.

r_{DA} is the donor-acceptor separation relative to their van der Waals radii, L

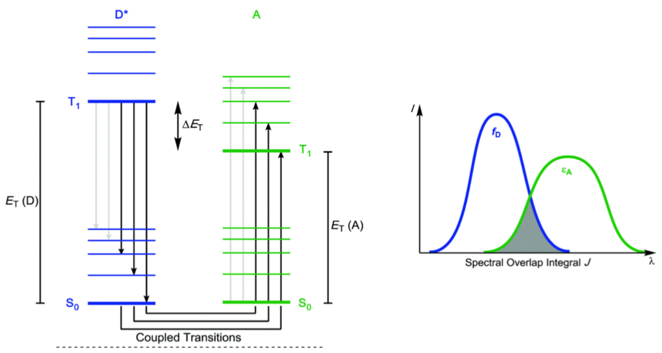
Triplet-Triplet Energy Transfer

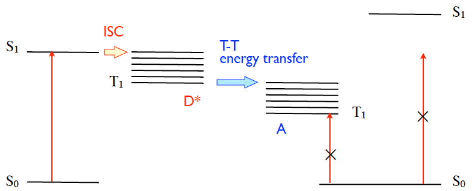
$$^3D^* + A \longrightarrow D + {}^3A^*$$



$$k_{ET}\,(\text{exchange}) = KJ\exp(-2\,r_{DA}/L)$$

Criteria for T-T Energy Transfer: Energy Criterion





benzophenone (n-π*) 370 nm

naphtalene (π-π*) 290 nm

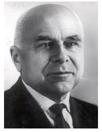
Sensitized Phosphorescence in Rigid Solution at 77°K

Donor	Acceptor	R_c(Å)
Benzaldehyde	Naphthalene	12
	1-Chloronaphthalene	12
	1-Bromonaphthalene	12
Benzophenone	Naphthalene	13
	1-Chloronaphthalene	13
	1-Bromonaphthalene	13
	1-Iodonaphthalene	13
m-Iodobenzaldehyde	Naphthalene	11
	1-Bromonaphthalene	11
Triphenylamine	Naphthalene	13
Carbazole	Naphthalene	15
Phenanthrene	Naphthalene	13
	1-Chloronaphthalene	14
	1-Bromonaphthalene	14

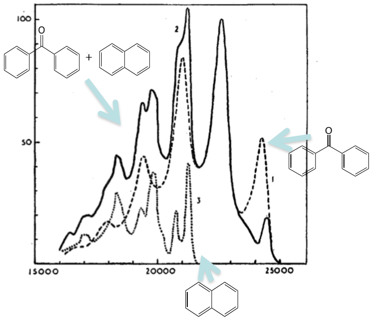
Organic Glass
at 77° K

Sensitized Phosphorescence at 77 ° K

A. Terenin and V. Ermolaev,
Doklady, Acad. Sc., U.S.S.R., *85*, 547, **1952**;
Trans. Faraday Soc., *52*, 1042, **1956**


A. Terenin


V. L. Ermolaev



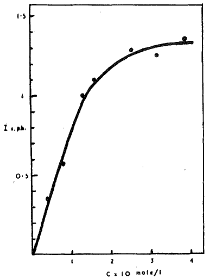
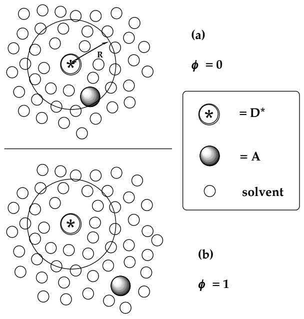


Fig. 3.—Phosphorescence intensity of naphthalene, sensitized by benzophenone against naphthalene concentration.

Energy Transfer in the Absence of Diffusion

The Perrin Formulation of Quenching. The Quenching Sphere



There exists a volume in space, termed a "quenching sphere", about *D whose radius is R; if a quencher molecule, A, is within this quenching sphere, then *D is deactivated with 100% efficiency.

If A molecule is outside of the quenching sphere, it does not quench *D at all.

According to the Perrin model, the measured lifetime of *D molecules that are not in the quenching sphere will be the same as the lifetime for *D in the absence of A.

A bit of history: Glass at 77° K to Solution at RT

Sensitized phosphorescence of aromatic compounds
A. N. Terenin and V. Ermolaev, *Doklady, Acad. Sc., U.S.S.R.*, *85*, 547, **1952**

Sensitized phosphorescence in organic solutions at low temperature: Energy transfer between triplet states
A. N. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, *52*, 1042, **1956**

Quenching of biacetyl fluorescence in solution
H. L. J. Backstrom and K. Sandros, *J. Chem. Phys.* **1955**, 2197

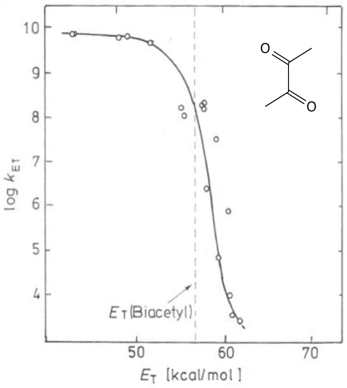
The quenching of long-lived fluorescence of biacetyl in solution
H. L. J. Backstrom and K. Sandros, *Acta Chemica Scand.* **1958**, *12*, 823

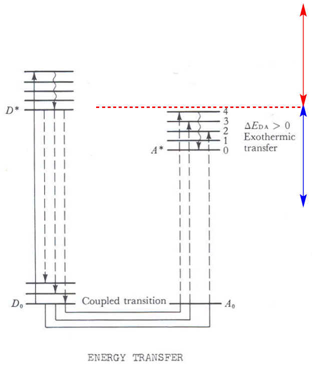
Transfer of triplet state energy in fluid solution: Sensitized Phopshorescence and its application to the determination of triplet state lifetimes
H. L. J. Backstrom and K. Sandros, *Acta Chemica Scand.* **1960**, *14*, 48

Energy transfer from the triplet state
G. Porter and F. Wilkinson, *Proc. Royal Soc. A*, **1961**, *264*, 1

Triplet-Triplet ET in Solution

H. L. J. Backstrom and K. Sandros, *Acta Chemica Scand. 12*, 823 (**1958**)





Triplet-Triplet ET in Solution
Correlation of rate with triplet energy gap

G. Porter and F. Wilkinson,
Proc. Royal Soc. A, 264, 1 (**1961**)

G. Porter

TABLE 6.5. *Rate Constants for Triplet–Triplet Energy Transfer*(56)

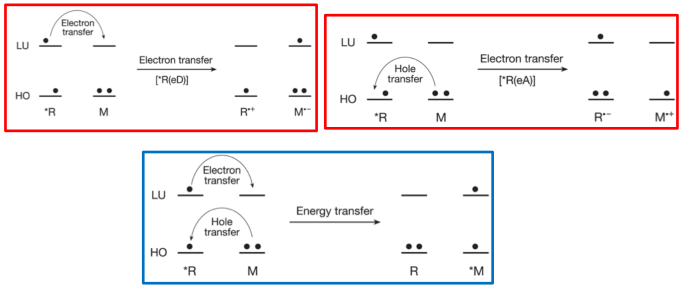
Donor	Acceptor	Solvent	ΔE_t, kcal/mole	k_{et}, M^{-1} sec^{-1}
Triphenylene	Naphthalene	Hexane	6.30	$1.3 \pm 0.8 \times 10^9$
Phenanthrene	1-Iodonaphthalene	Hexane	3.15	$7 \pm 2 \times 10^9$
Phenanthrene	1-Iodonaphthalene	Ethylene glycol	3.15	$2.1 \pm 0.2 \times 10^8$
Phenanthrene	1-Bromonaphthalene	Hexane	2.57	$1.5 \pm 0.8 \times 10^8$
Naphthalene	1-Iodonaphthalene	Ethylene glycol	2.29	$2.8 \pm 0.3 \times 10^8$
Phenanthrene	Naphthalene	Hexane	0.86	$2.9 \pm 0.7 \times 10^6$
Naphthalene	Phenanthrene	Hexane	−0.86	$\leq 2 \times 10^4$
Naphthalene	Benzophenone	Benzene	−8.90	$\leq 1 \times 10^4$

Similarity between energy and electron transfer

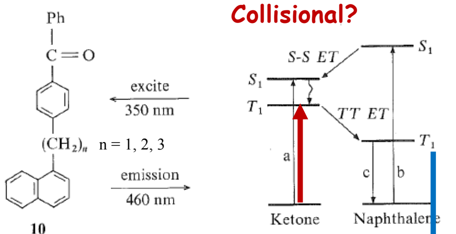
Exchange Energy Transfer

Dexter Energy Transfer

Collisional Energy Transfer



Collisional?



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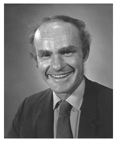


G. S. Hammond

Mixture of B & N

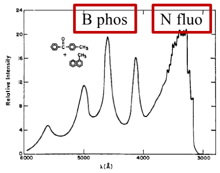


Figure 7. Emission spectrum of an equimolar (5 × 10⁻³ M) mixture of 1-methylnaphthalene and 4-methylbenzophenone in EPA glass under 3130-Å. irradiation.

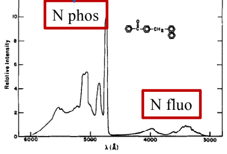
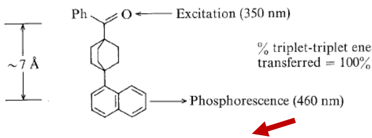
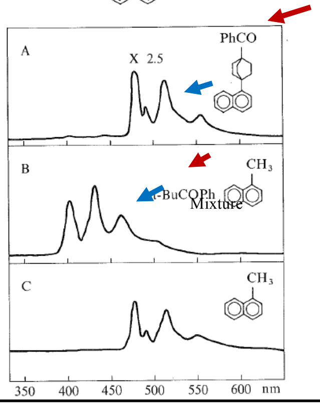


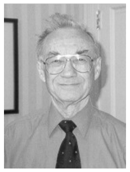
Figure 9. Total emission spectrum of 1.

Intramolecular Electronic Energy Transfer between Nonconjugated Chromophores in Some Model Compounds, G. S. Hammond et. al, *JACS*, **1965**, *87*, 2322

Collisional?







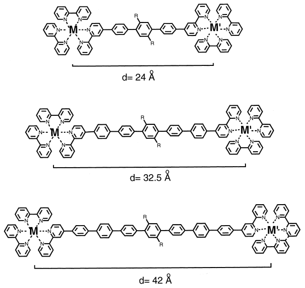
H. E. Zimmerman

Electron and Energy Transfer---
H. E. Zimmerman et. al., *JACS*, **1971**, *93*, 3638

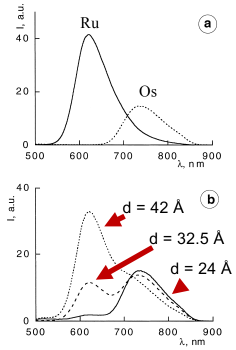
"For TT -ET close approach is not invariably required"

Recorded in methylcyclohexane-isopentane glass at 77 ° K

T-T Energy transfer at a distance: Need not be collisional



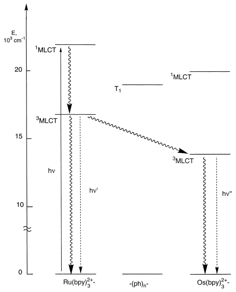
M = M'= Ru : $[Ru(bpy)_3\text{-}(ph)_n\text{-}Ru(bpy)_3]^{4+}$
M = M'= Os : $[Os(bpy)_3\text{-}(ph)_n\text{-}Os(bpy)_3]^{4+}$
M = Ru; M'= Os : $[Ru(bpy)_3\text{-}(ph)_n\text{-}Os(bpy)_3]^{4+}$
n = 3, 5, 7
R = n-hexyl

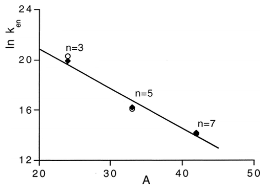


Photonic Wires of Nanometric Dimensions. Electronic Energy Transfer in Rigid ---- B. Schlicke, P. Belser, L. De Cola, E. Sabbioni and V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 4207

T-T Energy transfer at a distance: Need not be collisional

	at 298 K	at 77 K
$[Ru(bpy)_3\text{-}(ph)_3\text{-}Os(bpy)_3]^{4+}$	6.7×10^8	4.5×10^8
$[Ru(bpy)_3\text{-}(ph)_5\text{-}Os(bpy)_3]^{4+}$	1.0×10^7	1.1×10^7
$[Ru(bpy)_3\text{-}(ph)_7\text{-}Os(bpy)_3]^{4+}$	1.3×10^6	1.4×10^6





Marcus inverted curve in triplet-triplet energy transfer

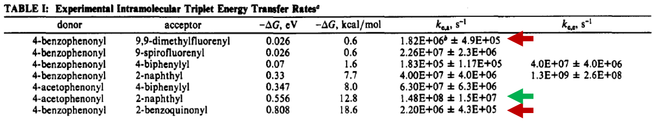
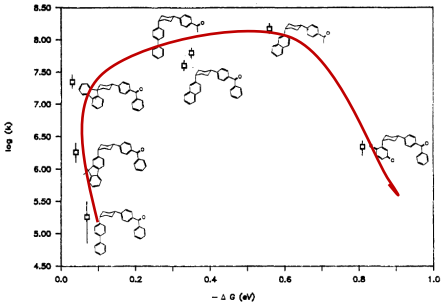


TABLE I: Experimental Intramolecular Triplet Energy Transfer Rates[a]

donor	acceptor	$-\Delta G$, eV	$-\Delta G$, kcal/mol	$k_{e,a}$, s^{-1}	$k_{e,e}$, s^{-1}
4-benzophenonyl	9,9-dimethylfluorenyl	0.026	0.6	1.82E+06[b] ± 4.9E+05	
4-benzophenonyl	9-spirofluorenyl	0.026	0.6	2.26E+07 ± 2.3E+06	
4-benzophenonyl	4-biphenylyl	0.07	1.6	1.83E+05 ± 1.17E+05	4.0E+07 ± 4.0E+06
4-benzophenonyl	2-naphthyl	0.33	7.7	4.00E+07 ± 4.0E+06	1.3E+09 ± 2.6E+08
4-acetophenonyl	4-biphenylyl	0.347	8.0	6.30E+07 ± 6.3E+06	
4-acetophenonyl	2-naphthyl	0.556	12.8	1.48E+08 ± 1.5E+07	
4-benzophenonyl	2-benzoquinonyl	0.808	18.6	2.20E+06 ± 4.3E+05	



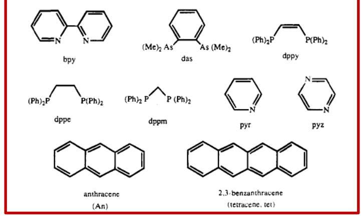
M. Sigman and G. Closs,
J. Phys. Chem. **1991**, 95, 5012-5017

Marcus relationship during T-T energy transfer

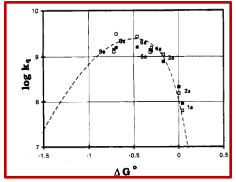
TABLE 1: Complexes and Quenchers[a]

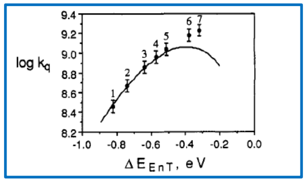
label	complex	label	quencher
1	$Os(bpy)_3^{2+}$	**a**	anthracene (An)
2	$Os(bpy)_2(pyz)_2^{2+}$	**b**	2,3-benzanthracene (tet)
3	$Os(bpy)_2(das)^{2+}$		
4	$Os(bpy)_2(dppm)^{2+}$		
5	$Os(bpy)_2(dppe)^{2+}$		
6	$Os(bpy)_2(CO)(pyr)^{2+}$		
7	$Os(bpy)(das)_2^{2+}$		
8	$Os(bpy)_2(CO)(MeCN)^{2+}$		
9	$Os(bpy)(dppy)_2^{2+}$		

[a] Structures are shown in Figure 1.

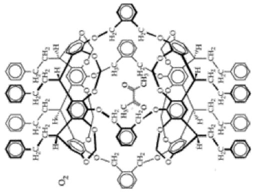


$$Os(bpy)_3^{2+*} + An \rightarrow Os(bpy)_3^{2+} + {}^3An$$





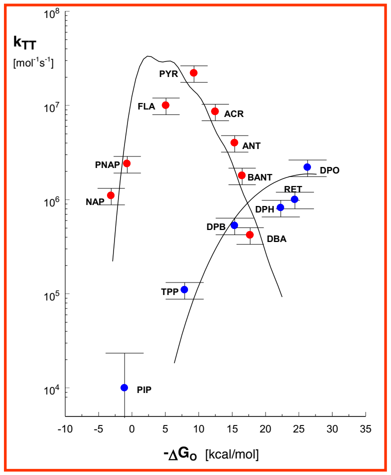
T. J. Meyer et. al., *J. Am. Chem. Soc.* **1991**, *113*, 5113
K. Schanze et. al., *J. Am. Chem. Soc.* **1992**, *114*, 1897



Triplet Energy Transfer through the Walls of Hemicarcerands: Temperature Dependence and the Role of Internal Reorganization Energy,
P. Piotrowiak et. al. *J. Am. Chem. Soc.* **1998**, *120*, 12626.

acceptor	triplet energy,[a] kcal/mol	$-\Delta G°$,[b] kcal/mol	$E_{a,corrected}$,[c] kcal/mol	k_{ET}, $M^{-1} s^{-1}$	
				1•biacetyl	[biacetyl]
		Aryl Acceptors			
naphthalene* [h] (NAP)	61.0	−3.1	4.6	1.1×10^6	$[2.0 \times 10^6]$[d]
2-phenylnaphthalene* (PNAP)	58.6	−0.7	3.0	2.4×10^6	$[6.5 \times 10^8]$[e]
fluoranthene* (FLA)	52.8	5.1	−0.2	1.0×10^7	$[5.2 \times 10^9]$[e]
pyrene* (PYR)	48.6	9.3	−0.9	2.2×10^7	$[6.0 \times 10^9]$[d]
acridine* (ACR)	45.4	12.5	−1.4	8.6×10^6	$[9.0 \times 10^9]$[d]
anthracene (ANT)	42.5	15.4	−2.0	4.0×10^6	$[8.0 \times 10^9]$[d]
9-bromoanthracene (BANT)	41.4	16.5	−4.9	1.8×10^6	$[6.6 \times 10^9]$[e]
9,10-dibromoanthracene (DBA)	40.2	17.7	−4.4	4.2×10^5	$[1.2 \times 10^9]$[e]
		Alkene Acceptors			
cis-piperylene[f] (PIP)	59.0	−1.1	5.2	1.0×10^4	$[1.6 \times 10^7]$[e]
1,3-cyclohexadiene (CHD))	52.4	5.5	4.2	2.0×10^4	$[2.9 \times 10^8]$[e]
triphenylethylene (TPP)	50.0	7.9	2.9	1.1×10^5	$[1.6 \times 10^8]$[e]
1,4-diphenyl-1,3-butadiene (DPB)	42.5	15.4	0.9	5.3×10^5	$[9.0 \times 10^8]$[e]
cycloheptatriene (CHP)	38.0	19.9	5.0	3.4×10^4	$[3.0 \times 10^9]$[e]
1,6-diphenyl-1,3,5-hexatriene* (DPH)	35.6	22.3	1.7	8.2×10^5	$[9.0 \times 10^8]$[e]
all-E-retinol* (RET)	33.5	24.4	1.1	1.0×10^6	$[4.8 \times 10^7]$[e]
1,8-diphenyl-1,3,5,7-octatetraene* (DPO)	31.6	26.3	1.7	2.2×10^6	$[4.3 \times 10^8]$[e]
oxygen $^1\Sigma$	37.5	20.4	−1.9	1.7×10^4	$[4.3 \times 10^8]$[g]

Free energy dependence of energy transfer between incarcerated biacetyl and acceptors in solution

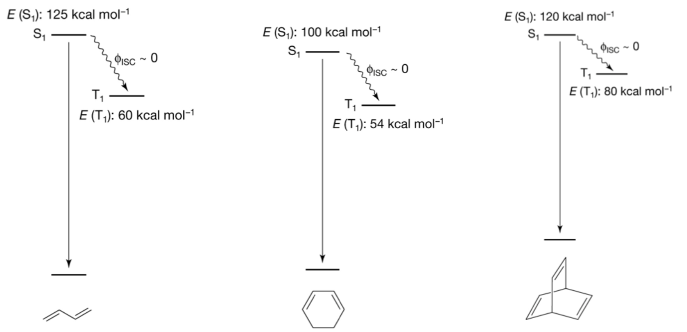


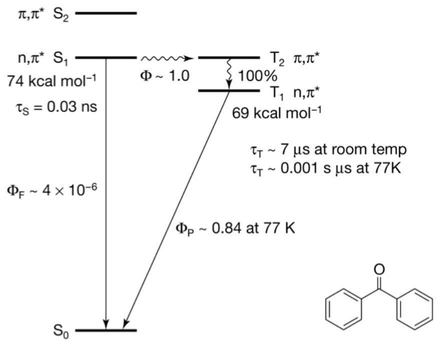
Value of triplet-triplet energy transfer in organic photochemistry

Sensitizers: Generation of reactive triplets

Quenchers: Identification of reactive triplet

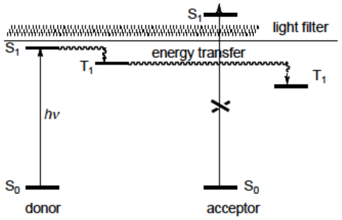
Need for Triplet Sensitization



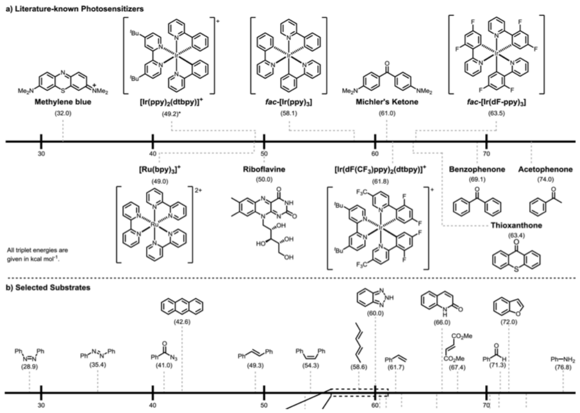


Sensitizers

- Should be able to excite the sensitizer alone even in presence of acceptor.
- Sensitizer should have high intersystem crossing efficiency (S$_1$ to T$_1$).
- Sensitizer should have triplet energy higher than the acceptor.
- Sensitizer should be photostable.



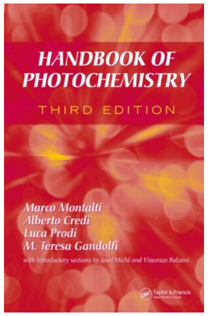
Examples of Triplet Sensitizers

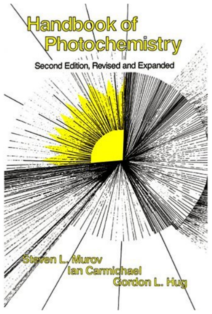


F. Glorius et. al., *Chem. Soc. Rev.*, **2018**, *47*, 7190

Table 10.3 Important Parameters for Triplet Photosensitizers

Compound	E_S (kcal mol^{-1})	E_T (kcal mol^{-1})	τ_S (s)	τ_T (s)	Conf. T_1	Φ_{ST}
Benzene	110	84	$\sim 10^{-7}$	10^{-6}	π,π^*	0.2
Acetone	~ 85	~ 78	10^{-9}	10^{-5}	n,π^*	1.0
Xanthone		74			π,π^*	1.0
Acetophenone	~ 79	74	10^{-10}	10^{-4}	n,π^*	1.0
4-CF_3Acetophenone		71			n,π^*	1.0
Benzophenone	~ 75	69	10^{-11}	10^{-4}	n,π^*	1.0
Triphenylene	83	67	$\sim 5 \times 10^{-8}$	10^{-4}	π,π^*	0.9
Thioxanthone	78	~ 65				
Anthraquinone		62			n,π^*	1.0
4-Ph-benzophenone	77	61		10^{-4}	π,π^*	1.0
Michler's ketone		61				1.0
Napthalene	92	61	10^{-7}	10^{-4}	π,π^*	0.7
2-Acetonaphthalene	78	59		10^{-4}	π,π^*	1.0
1-Acetonaphthalene	76	57		10^{-4}	π,π^*	1.0
Chrysene	79	57	5×10^{-8}		π,π^*	0.8
Biacetyl	~ 60	55	10^{-8}	10^{-3}	n,π^*	1.0
Benzil	~ 59	54	$\sim 10^{-8}$	10^{-4}	n,π^*	1.0
Camphorquinone	~ 55	50	$\sim 10^{-8}$		n,π^*	1.0
Pyrene	77	49	$\sim 10^{-6}$		π,π^*	0.3
Anthracene	76	47	$\sim 5 \times 10^{-9}$	10^{-4}	π,π^*	0.7
9,10-Dichloroanthracene	~ 74	40	$\sim 5 \times 10^{-9}$	10^{-4}	π,π^*	0.5
Perylene	66	~ 35	5×10^{-9}		π,π^*	0.005


HANDBOOK OF PHOTOCHEMISTRY
THIRD EDITION
Marco Montalti
Alberto Credi
Luca Prodi
M. Teresa Gandolfi
with introductory sections by Josef Michl and Vincenzo Balzani


Handbook of Photochemistry
Second Edition, Revised and Expanded
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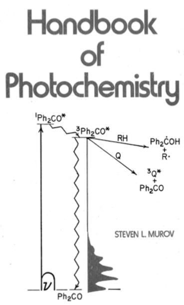
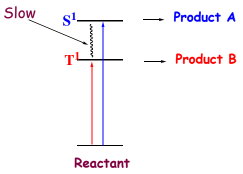
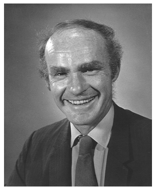
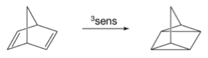
Ian Carmichael
Gordon L. Hug


Handbook of Photochemistry
STEVEN L. MUROV

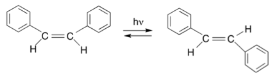



G. S. Hammond

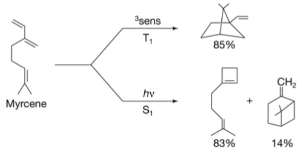
JACS, JPC, **1959-1970**
Review: Deactivation of excited states
L. M. Stephenson and G. S. Hammond, *Angew. Chem. Int. Ed.*, **1969**, *8*, 261.



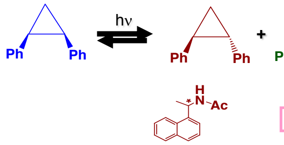
Turro, 61



Saltiel, 62



Liu, 64

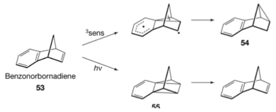


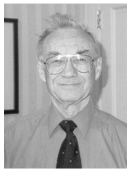
Cole, 65

ee = 6.7%

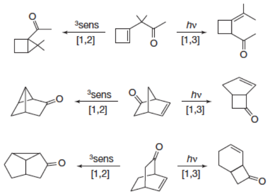
Ciganek, DuPont, 1966

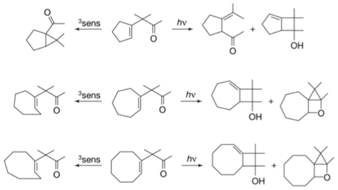
Kellog, DuPont, 1969




H. E. Zimmerman

JACS, **1973**, *95*, 3977 & 4606; **1970**, *92*, 4366.





Hammond at ?

Zimmerman at ?

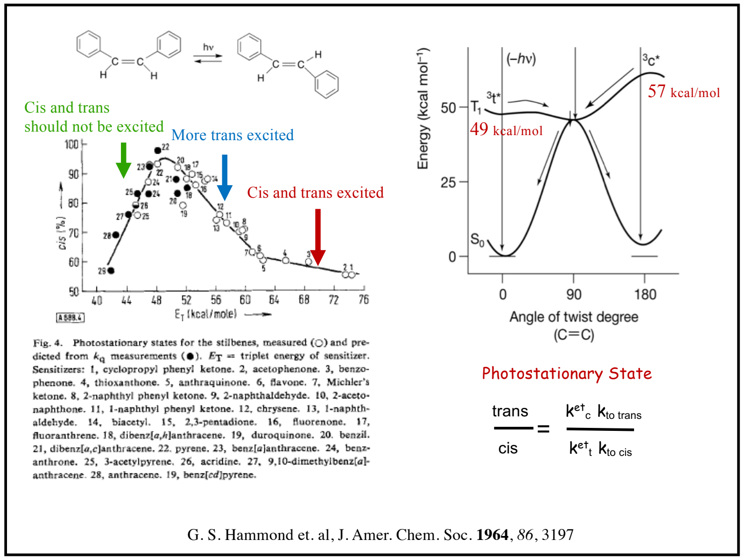
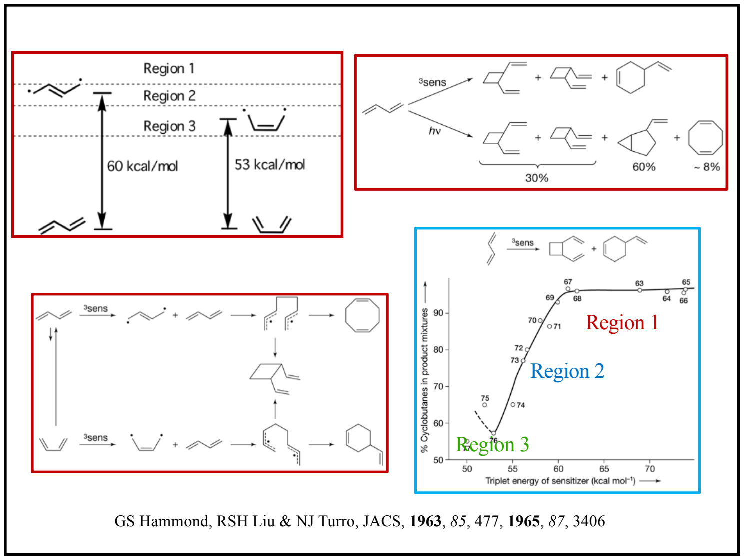


Fig. 4. Photostationary states for the stilbenes, measured (○) and predicted from k_q measurements (●). E_T = triplet energy of sensitizer. Sensitizers: 1, cyclopropyl phenyl ketone. 2, acetophenone. 3, benzophenone. 4, thioxanthone. 5, anthraquinone. 6, flavone. 7, Michler's ketone. 8, 2-naphthyl phenyl ketone. 9, 2-naphthaldehyde. 10, 2-acetonaphthone. 11, 1-naphthyl phenyl ketone. 12, chrysene. 13, 1-naphthaldehyde. 14, biacetyl. 15, 2,3-pentadione. 16, fluorenone. 17, fluoranthrene. 18, dibenz[*a,h*]anthracene. 19, duroquinone. 20. benzil. 21, dibenz[*a,c*]anthracene. 22. pyrene. 23, benz[*a*]anthracene. 24, benzanthrone. 25, 3-acetylpyrene. 26, acridine. 27, 9,10-dimethylbenz[*a*]-anthracene. 28, anthracene. 19, benz[*cd*]pyrene.

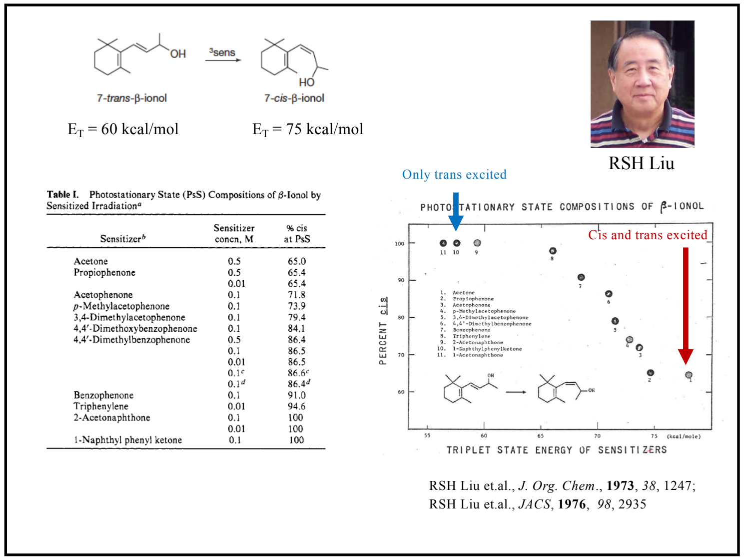
Photostationary State

$$\frac{\text{trans}}{\text{cis}} = \frac{k^{et}_c \; k_{\text{to trans}}}{k^{et}_t \; k_{\text{to cis}}}$$

G. S. Hammond et. al, J. Amer. Chem. Soc. **1964**, *86*, 3197



GS Hammond, RSH Liu & NJ Turro, JACS, **1963**, *85*, 477, **1965**, *87*, 3406



E_T = 60 kcal/mol

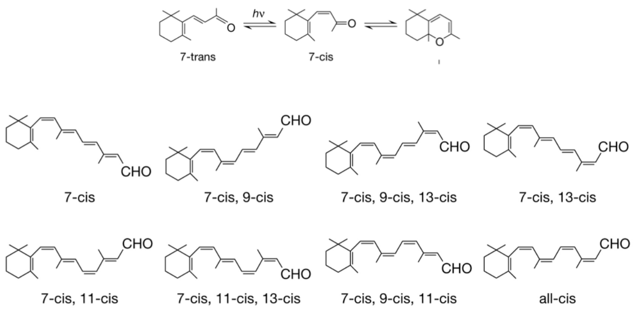
E_T = 75 kcal/mol

RSH Liu

Table I. Photostationary State (PsS) Compositions of β-Ionol by Sensitized Irradiation[a]

Sensitizer[b]	Sensitizer concn, M	% cis at PsS
Acetone	0.5	65.0
Propiophenone	0.5	65.4
	0.01	65.4
Acetophenone	0.1	71.8
p-Methylacetophenone	0.1	73.9
3,4-Dimethylacetophenone	0.1	79.4
4,4′-Dimethoxybenzophenone	0.1	84.1
4,4′-Dimethylbenzophenone	0.5	86.4
	0.1	86.5
	0.01	86.5
	0.1[c]	86.6[c]
	0.1[d]	86.4[d]
Benzophenone	0.1	91.0
Triphenylene	0.01	94.6
2-Acetonaphthone	0.1	100
	0.01	100
1-Naphthyl phenyl ketone	0.1	100

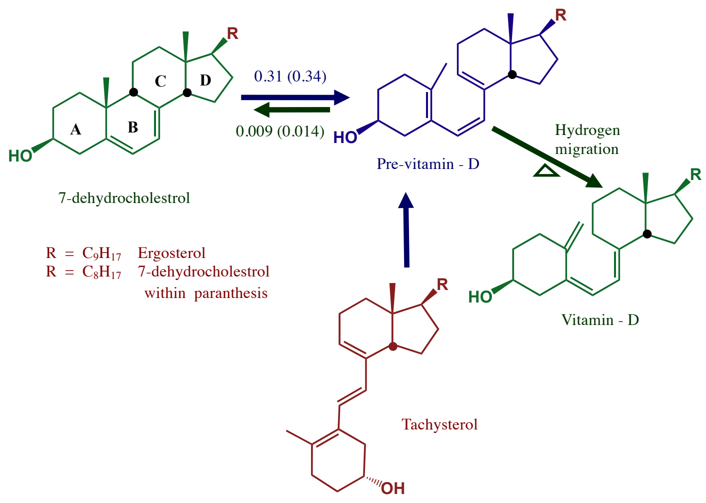
RSH Liu et.al., *J. Org. Chem.*, **1973**, *38*, 1247;
RSH Liu et.al., *JACS*, **1976**, *98*, 2935



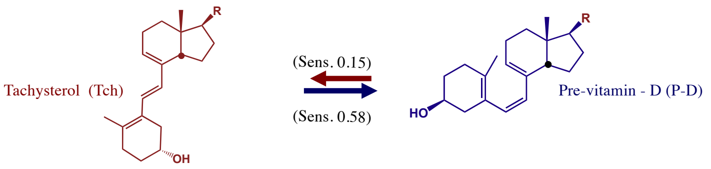
Doubly Hindered 7,11-Dicis Isomers of Retinal. Synthesis, Properties, and Interaction with Cattle Opsin, RSH Liu et.al., *J. Am. Chem. Soc.*, **1979**, *101*, 5078.

Vitamin A Isomers 12. 7-*cis*,9-*cis*,11-*cis*-Retinal, all-*cis*-Vitamin A, and 7-*cis*,9-*cis*,11-*cis*-12-Fluororetinal, RSH Liu et.al., *J. Am. Chem. Soc.*, **1983**, *105*, 2923.

Photochemistry and Synthesis of Stereoisomers of Vitamin A, RSH Liu et.al., *Tetrahedron*, 1984, **40**, 1931.



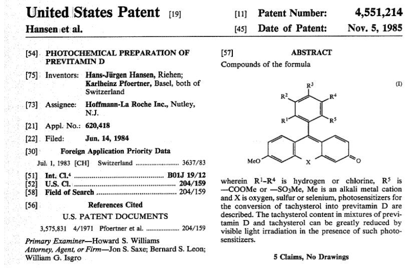
R = C_9H_{17} Ergosterol
R = C_8H_{17} 7-dehydrocholestrol
within paranthesis



Sensitizer	E_T KJ Mol^{-1}	(P-D/Tch)
Benzopheonone	286.3	2.6
Anthraquinone	260.8	2.1
2-Naphthylphenylketone	247.8	1.5
Benzil	225.0	1.8
9-Fluorenone	222.8	4.4
Benzanthrone	196.5	5.6
7,12-Dimethylbenzanhracene	185.2	16.3

Initial ratio (P-D/Tch)= 0.5; solvent=ethyl ether.

Photosensitized Isomerization of Previtamin D2 and Tachysterol------,
RSH Liu et. al., *Nouv. J. Chim*., 1978, **2**, 637, 1978.



United States Patent [19]
Hansen et al.

[11] **Patent Number:** **4,551,214**
[45] **Date of Patent:** **Nov. 5, 1985**

[54] **PHOTOCHEMICAL PREPARATION OF PREVITAMIN D**

[75] Inventors: **Hans-Jürgen Hansen,** Riehen; **Karlheinz Pfoertner,** Basel, both of Switzerland

[73] Assignee: **Hoffmann-La Roche Inc.,** Nutley, N.J.

[21] Appl. No.: **620,418**

[22] Filed: **Jun. 14, 1984**

[30] **Foreign Application Priority Data**

Jul. 1, 1983 [CH] Switzerland 3637/83

[51] **Int. Cl.**^{4} **B01J 19/12**
[52] **U.S. Cl.** **204/159**
[58] **Field of Search** 204/159

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,575,831 4/1971 Pfoertner et al. 204/159

Primary Examiner—Howard S. Williams
Attorney, Agent, or Firm—Jon S. Saxe; Bernard S. Leon; William G. Isgro

[57] **ABSTRACT**

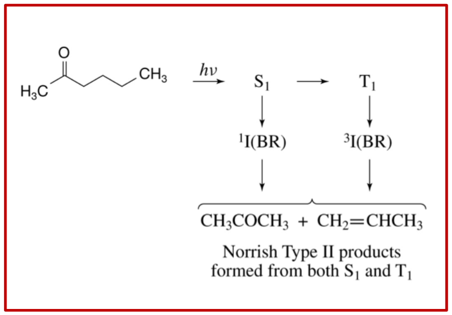
Compounds of the formula

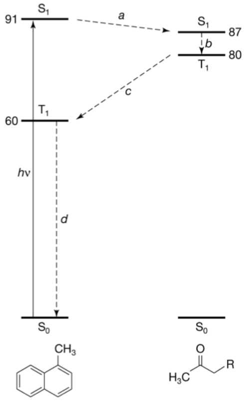
(I)

wherein R^1-R^4 is hydrogen or chlorine, R^5 is —COOMe or —SO_3Me, Me is an alkali metal cation and X is oxygen, sulfur or selenium, photosensitizers for the conversion of tachysterol into previtamin D are described. The tachysterol content in mixtures of previtamin D and tachysterol can be greatly reduced by visible light irradiation in the presence of such photosensitizers.

5 Claims, No Drawings

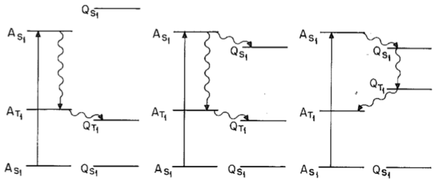
Identifying the reactive state





Quenchers

- ❖ Quencher should have absorption away from that of the reactant (donor).
- ❖ Quencher should have the triplet energy lower and the singlet energy higher than the reactant.
- ❖ Quencher should quench the reactant only be TT transfer, not by any other process.
- ➢ Quencher should be photostable.



T_1 quenching S_1 and T_1 quenching S_1 quenching

Stern-Volmer Equation

$$\Phi_f^0 = \frac{k_f}{k_f + k_d} = \frac{k_f}{\frac{1}{\tau_0}} = k_f \tau_0$$

In absence of quencher

$$\Phi_f = \frac{k_f}{k_f + k_d + k_q[Q]} = \frac{k_f}{\frac{1}{\tau_0} + k_q[Q]}$$

In presence of quencher

$$\frac{\Phi_f^0}{\Phi_f} = \frac{\frac{k_f}{\frac{1}{\tau_0}}}{\frac{k_f}{\frac{1}{\tau_0} + k_q[Q]}} = 1 + k_q \tau_0 [Q]$$

Dividing these equations

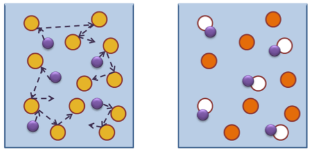
$$\frac{\Phi_f^0}{\Phi_f} = \frac{I_f^0}{I_f} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$

Stern-Volmer Equation

The Photochemistry Portal
photochemistry.wordpress.com

Types of quenching: Static and dynamic

Dynamic



Dynamic Quenching
Increasing quencher ● concentration increases probability of collision

Static Quenching (Association)
Increasing quencher concentration ● increases probability of association

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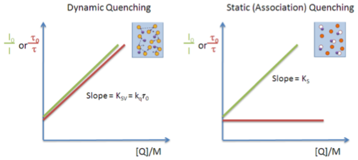
Static



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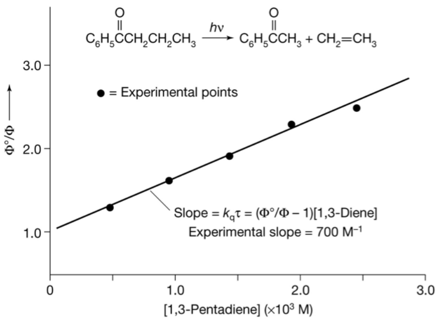
Identification of the reactive state (T₁)

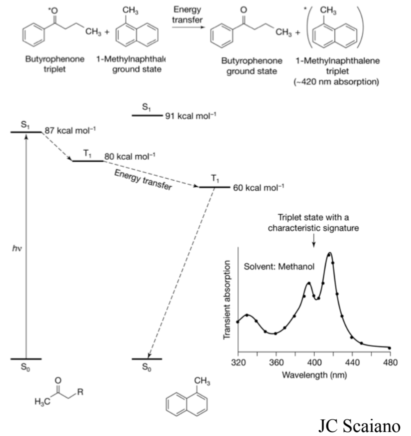
Stern-Volmer plot



$$C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow{h\nu} C_6H_5\overset{O}{\overset{\|}{C}}CH_3 + CH_2{=}CH_2$$

PJ. Wagner and GS Hammond, *JACS*, **1966**, *88*, 1245

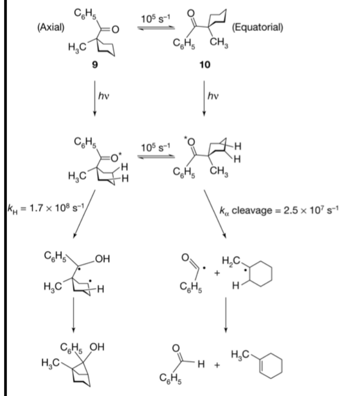
Identification of the reactive state (T₁)

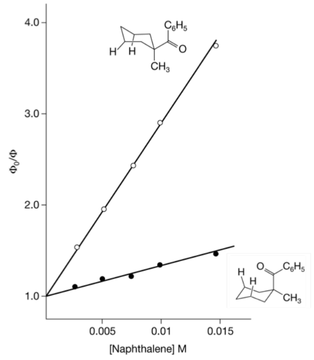


JC Scaiano

Probing the mechanism through quenching

FD Lewis et.al., *JACS*, **1974**, *96*, 6090





$$\frac{\Phi_f^0}{\Phi_f} = \frac{I_f^0}{I_f} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q]$$ Stern-Volmer Equation

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Sensitization from upper triplet (T₂)

RSH Liu et. al., *J. Am. Chem. Soc.*, **1969**, *91*, 1492.

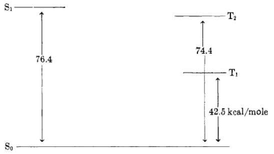
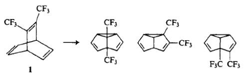


Figure 1. Energy diagram of anthracene.



Sensitizer	E_{T_1}[a]	Φ **1**[c]
Xanthone	74.2	+
Acetophenone	73.6	0.9
Benzophenone	68.5	1.03
Michler's ketone	61.0	...
2-Acetonaphthone	59.3	0.037
9-Fluorenone	51[e]	0.0001
Benzanthrone	47.0	...
Acridine	45.3	...
Anthracene (An)	42.5[f]	+
9,10-Dibromo-An	40.2[f]	0.0081
9,10-Dichloro-An	40.2[f]	0.0035
9,10-Dimethyl-An	?	0.0006
9-Bromo-10-methyl-An	?	0.0068

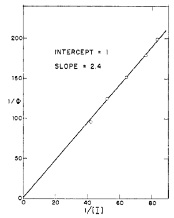


Figure 2. A Stern-Volmer plot of the 9,10-dibromoanthracene-sensitized reaction of **1**.

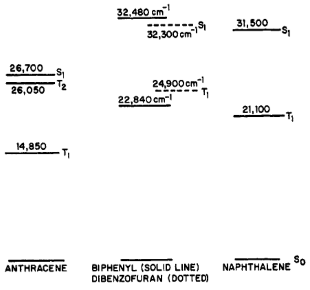
Table IV. Comparison of Quantum Yields of Reaction of **1** from Single and Double Sensitizer Experiments[a]

Sensitizers (concn, *M*)	Concn of **1**	Quantum yield
9-Fluorenone (0.0167)	0.033	0.0001[b]
9,10-Dibromo-An (6.67 × 10⁻⁴)	0.033	0.0038
9-Fluorenone (0.0167) + 9,10-dibromo-An (6.67 × 10⁻⁴)[c]	0.033	0.002
9,10-Dibromo-An (2.00 × 10⁻³)	0.033	0.0037

[a] In *n*-hexane. [b] Limit of detection. [c] Approximately 80% light absorbed by fluorenone.

Sensitization from upper triplets (T₂)

RSH Liu et. al., *J. Am. Chem. Soc.*, **1969**, *91*, 250.



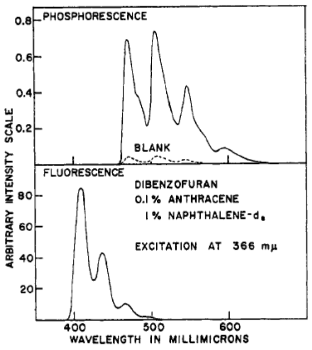
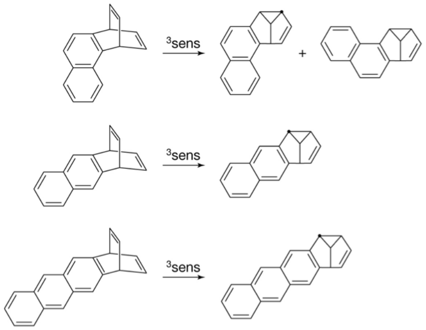


Figure 2. Phosphorescence and fluorescence at 77°K of a 0.1-mm dibenzofuran crystal doped with 0.1% anthracene and 1% naphthalene-d_8 using 366-mμ excitation. The dotted line is the phosphorescence of a similar DBF crystal doped only with naphthalene-d_8. While the absolute intensity units are arbitrary, the relative units have meaning.

Importance of T₂ recognized in photoreactions



H. E. Zimmerman et.al, JACS, **1970**, *92*, 4366,
1973, *95*, 3977 & 4606.

References

Deactivation of excited states, L. M. Stephenson and G. S. Hammond, *Angew. Chem. Int. Ed*., **1969**, *8*, 261.

Energy Transfer and Organic Photocehmistry, A. Lamola & N. J. Turro, Wiley, **1969**

Dual catalysis strategies in photochemical synthesis, T. P. Yoon et.al., *Chem. Rev*., **2016**, *116*, 10011

Energy transfer catalysis mediated by visible light: Principles, applications and directions, F. Glorius et. al., *Chem. Soc. Rev*., **2018**, *47*, 7190

Visible-light induced organic photochemical reactions through energy transfer pathways, Q-Q. Zhou-----W-J. Xiao, *Angew. Chem. Int. Ed*., **2019**, *58*, 1586.

Delayed Fluorescence

Triplet–Triplet Annihilation

Up-conversion

Triplet Fusion

Antistokes delayed fluorescence

Sensitized antistokes delayed fluorescence

Beginnings of Delayed Fluorescence

B. Stevens & E. Hutton, Nature, **1960**, *186*, 1046

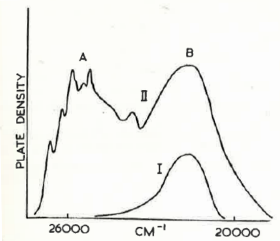


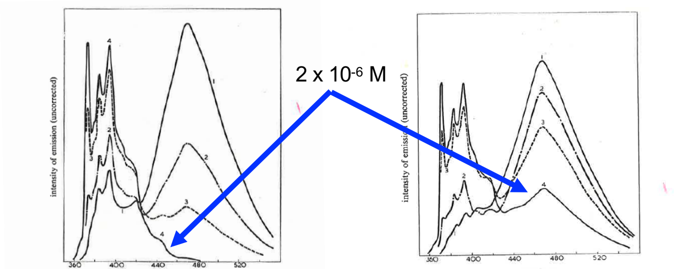
Fig. 1. Spectrum of slow fluorescence of pyrene in solution photographed through phosphoroscope (I), and of total fluorescence (II) consisting of violet (monomer) and blue (dimer) bands A and B

Lifetime: 1.8 ± 0.2 ms

Origin unclear

Origin of delayed fluorescence identified

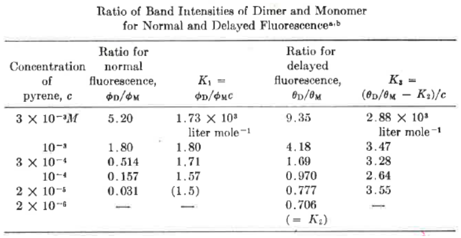
CA Parker & CG Hatchard, Trans. Faraday Soc., 1963, 59, 284



2 x 10^{-6} M

Fig. 18. Normal fluorescence of pyrene in ethanol.[42] (1) 3 × $10^{-3}M$, (2) $10^{-3}M$, (3) 3 × $10^{-4}M$, (4) 2 × $10^{-6}M$. The instrumental sensitivity settings for curves 1 and 4 were approximately 0.6 and 3.7 times that for curves 2 and 3. The short wavelength ends of the spectra in the more concentrated solutions are distorted by self-absorption.

Fig. 19. Delayed fluorescence of pyrene in ethanol.[42] (1) 3 × $10^{-3}M$, (2) $10^{-3}M$, (3) 3 × $10^{-4}M$, (4) 2 × $10^{-6}M$. The instrumental sensitivity settings were approximately 1000 times greater than those for the corresponding curves in Figure 18. The short wavelength ends of the spectra in the more concentrated solutions are distorted by self-absorption.



Ratio of Band Intensities of Dimer and Monomer for Normal and Delayed Fluorescence[a,b]

Concentration of pyrene, c	Ratio for normal fluorescence, ϕ_D/ϕ_M	$K_1 = \phi_D/\phi_M c$	Ratio for delayed fluorescence, θ_D/θ_M	$K_3 = (\theta_D/\theta_M - K_2)/c$
$3 \times 10^{-3}M$	5.20	1.73×10^3 liter mole^{-1}	9.35	2.88×10^3 liter mole^{-1}
10^{-3}	1.80	1.80	4.18	3.47
3×10^{-4}	0.514	1.71	1.69	3.28
10^{-4}	0.157	1.57	0.970	2.64
2×10^{-5}	0.031	(1.5)	0.777	3.55
2×10^{-6}	—	—	0.706 (= K_2)	—

Delayed Fluorescence

Anthracene, Phenanthrene, Naphthalene, Benzpyrene etc.

CA Parker & CG Hatchard, *Proc. Chem. Soc*., **1962**, 147

CA Parker & CG Hatchard, *Proc. R. Soc. London. Ser.A*. **1962**, *269*, 574

CA Parker & CG Hatchard, Nature, **1963**, *200*, 331

"The intensity of the emission is proportional to the square of the rate of light absorption."

Pyrene CA Parker & CG Hatchard, Trans. Faraday Soc., 1963, 59, 284

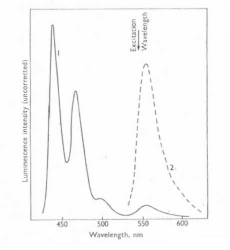
"The delayed fluorescence produced by triplet-triplet quenching is sharply different from that form eosin. To facilitate distinction between the two types we suggest the one be called E-type (esoin) and the other P-type (pyrene)."

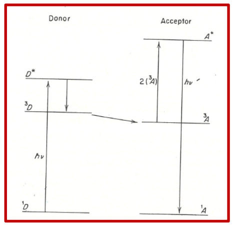
Sensitized Anti-Stokes Delayed Fluorescence

Sensitized Anti-Stokes Delayed Fluorescence, CA Parker, CG Hatchard,
Proc. Chem. Soc.: Lond. **1962**, 386.

Emit
Perylene

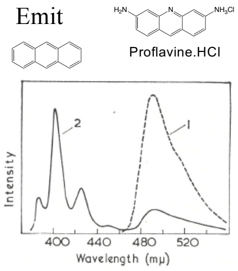
Excite
Eosin



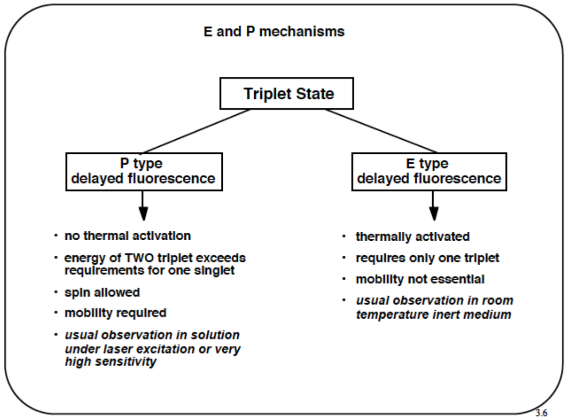


Emit

Excite



Two types of delayed fluorescence



E and P mechanisms

Triplet State

P type delayed fluorescence

- no thermal activation
- energy of TWO triplet exceeds requirements for one singlet
- spin allowed
- mobility required
- *usual observation in solution under laser excitation or very high sensitivity*

E type delayed fluorescence

- thermally activated
- requires only one triplet
- mobility not essential
- *usual observation in room temperature inert medium*

3.6

P-type delayed fluorescence

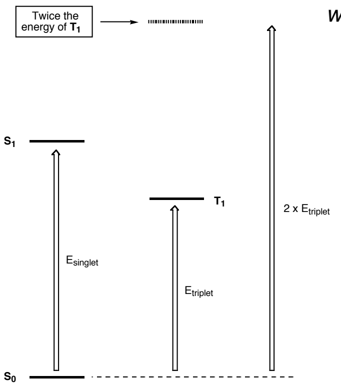
The process in which the first excited singlet state is populated by interaction of two molecules in the triplet state (triplet-triplet annihilation) thus producing one molecule in the excited singlet state

In this biphotonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence.

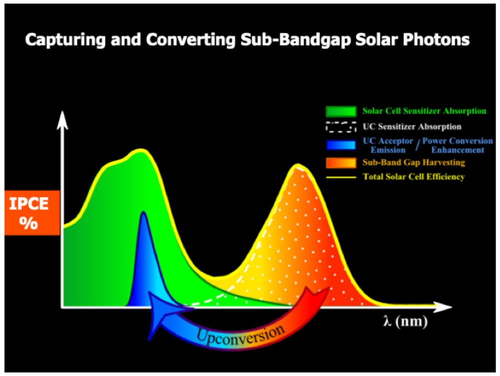
Triplet-Triplet Annihilation

$$^*D(T_1) + {}^*D(T_1) \xrightarrow{k_{TTA}} {}^*D(S_1) + D(S_0)$$

with $\Delta H < 0$



Photochemical Upconversion: Sensitized TTA (Sensitized Triplet Fusion)



Not every collision leads to energy transfer

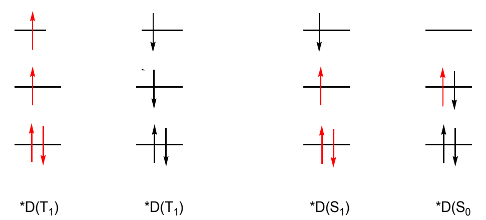
Spin statistics for the interactions of two triplets

	T_n	$T_{n.}$	Total spin $S = T_n + T_n$	Arrow notation	Multipilicity $= (2S + 1)$	Name of final state, Symbol
Case 1	T_{+1} (↑↑)	T_{-1} (↓↓)	0	↑↓↑↓	1	Singlet, S
Case 2	T_{+1} (↑↑)	T_0 (↓↑)	+1	↑↑↓↑	3	Triplet, T
Case 3	T_{+1} (↑↑)	T_{+1} (↑↑)	+2	↑↑↑↑	5	Quintet, Q

Exchange Energy Transfer

$$^*D(T_1) \;+\; ^*D(T_1) \xrightarrow{k_{TTA}} \; ^*D(S_1) \;+\; D(S_0)$$

with $\Delta H < 0$



Initial states

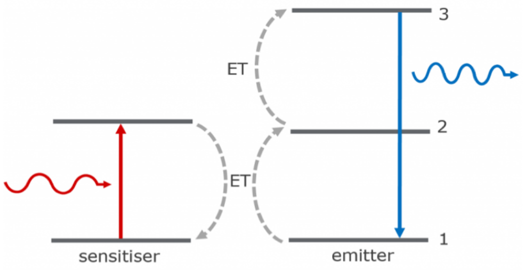
Final states

$^*D(T_1)$ $^*D(T_1)$ $^*D(S_1)$ $^*D(S_0$

Properties of TTA in Solution
Direct light absorption

- The rate constants for TTA, k_{TTA}, are generally very large.
- With laser light excitation, triplet state concentrations in excess of 10^{-5} M can be readily achieved. Typical products $k_{TTA}[D^*(T_1)]$ may then be around or over 10^5 s^{-1}. Thus, any triplet with lifetime of a few microseconds (a common situation) will undergo at least some TTA in fluid solution.
- The high sensitivity with which fluorescence can be detected makes TTA an easily observable process even when it is not the major mechanism for triplet decay.

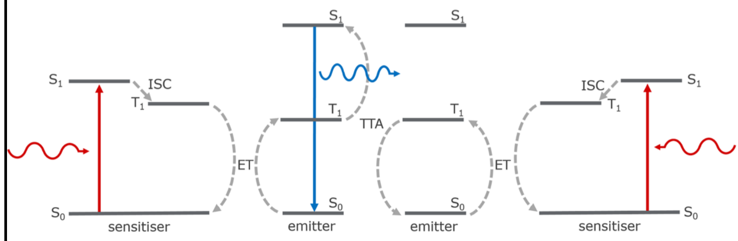
Red Light to Blue Light



Sequential energy transfer upconversion

Goal: Go as much red and as much blue

Sensitized up-conversion
Red Light to Blue Light



Sensitized triplet-triplet annihilation up-conversion

MLCT Sensitized Up-conversion
Newer examples

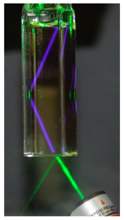
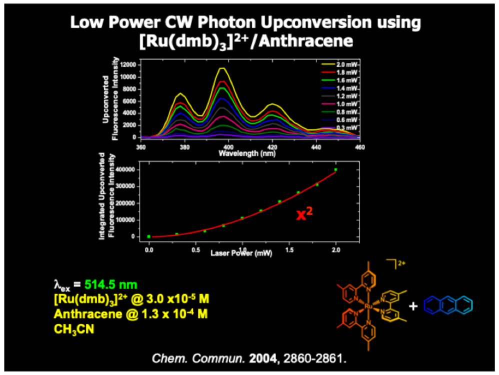


Fig. 1. Digital photograph of the upconverted fluorescence produced in a CH_3CN solution containing $[Ru(dmb)_3]^{2+}$ and DPA. Excitation was afforded by a commercial green laser pointer (λ_{ex} = 532 nm).



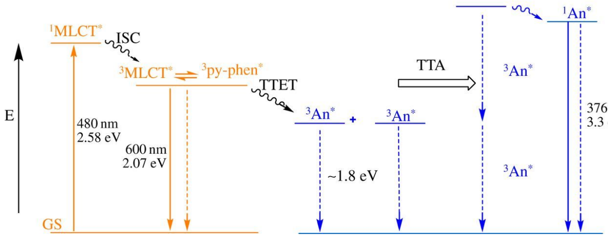
Low Power CW Photon Upconversion using $[Ru(dmb)_3]^{2+}$/Anthracene

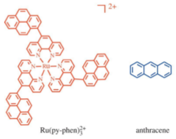
λ_{ex} = 514.5 nm
$[Ru(dmb)_3]^{2+}$ @ 3.0 x10⁻⁵ M
Anthracene @ 1.3 x 10⁻⁴ M
CH_3CN

Chem. Commun. **2004**, 2860-2861.

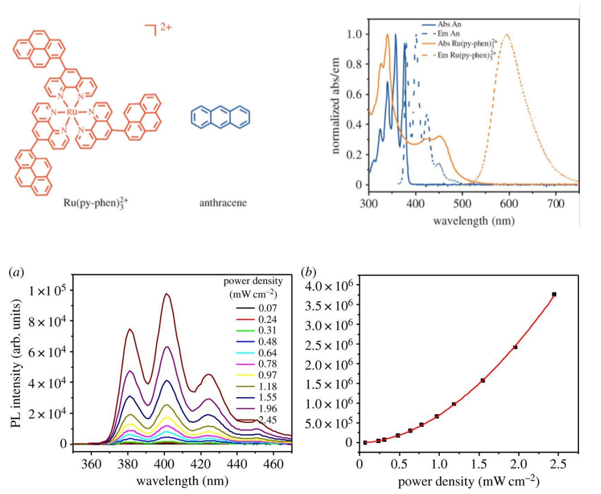
Anti-Stokes delayed fluorescencefrom metal–organic bichromophores, DV. Kozlov and FN. Castellano, Chem. Commun., **2004**, 2860–2861

Sensitized upconversion: Red Light to Blue Light
Newer examples

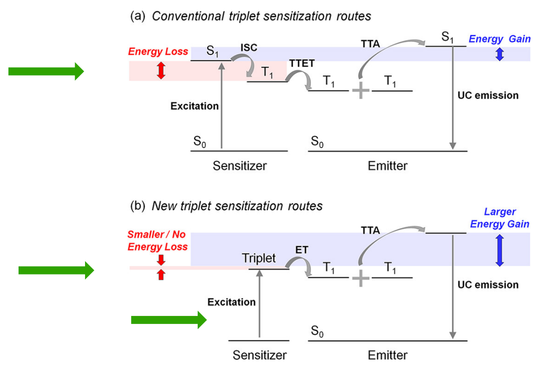




FN. Castellano et. al., Photon upconversion sensitized by a Ru(II)-pyrenyl chromophore. Phil. Trans. R. Soc. A, **2015,** 373: 20140322.



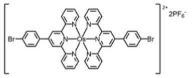
Goal: Control the loss of energy, Keep the S_1-T_1 gap small



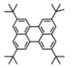
Direct S_0 to T_1 absorption saves energy loss.

New Triplet Sensitization Routes for Photon Upconversion: Thermally Activated Delayed Fluorescence Molecules, Inorganic Nanocrystals, and Singlet-to-Triplet Absorption, N. Yanai, and N. Kimizuka, Acc. Chem. Res. **2017**, *50*, 2487-2495

NIR-to-blue TTA-UC



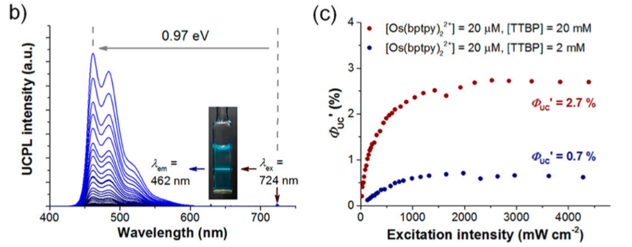
Os(bptpy)$_2^{2+}$



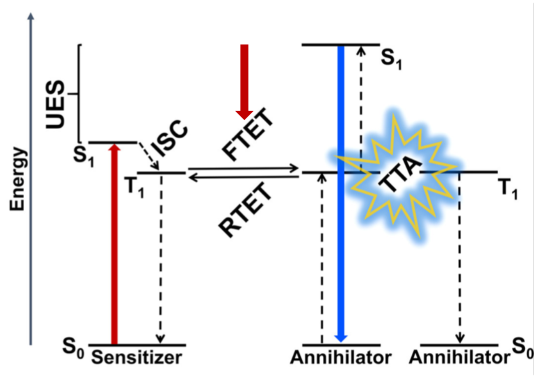
TTBP

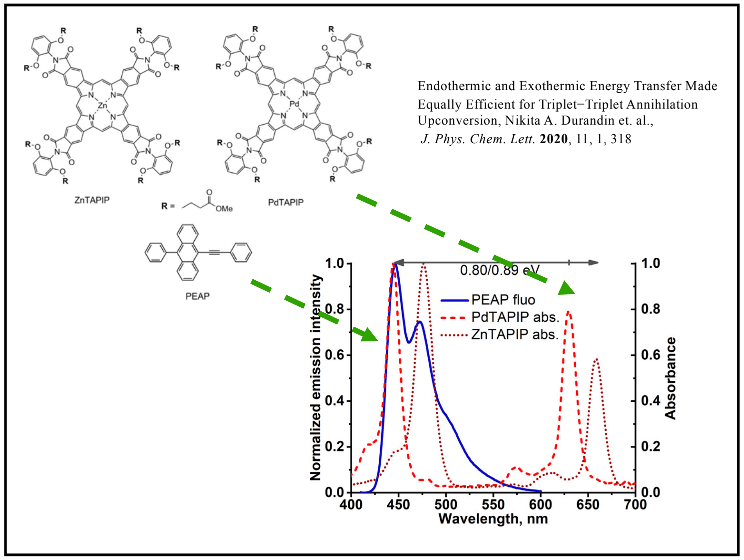
Sensitizer: **S_0 to T_1 absorption**, NIR, 724 nm

Emitter: Visible, Blue light, 450-600 nm



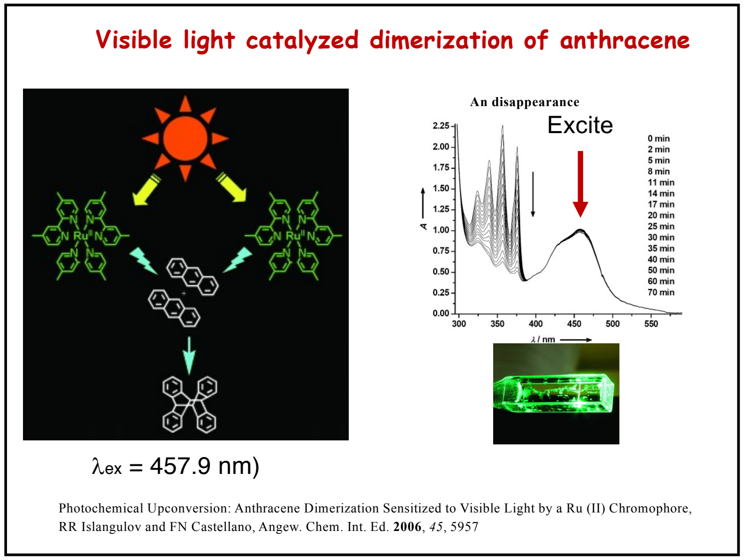
Goal: Control the loss of energy, Keep the T_1-T_1 gap small





Endothermic and Exothermic Energy Transfer Made Equally Efficient for Triplet−Triplet Annihilation Upconversion, Nikita A. Durandin et. al., *J. Phys. Chem. Lett.* **2020**, 11, 1, 318

Visible light catalyzed dimerization of anthracene

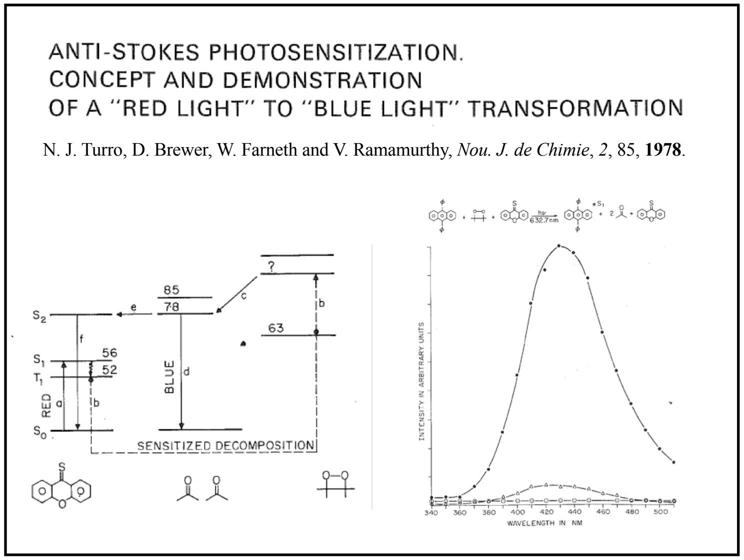


λex = 457.9 nm)

Photochemical Upconversion: Anthracene Dimerization Sensitized to Visible Light by a Ru (II) Chromophore, RR Islangulov and FN Castellano, Angew. Chem. Int. Ed. **2006**, *45*, 5957

ANTI-STOKES PHOTOSENSITIZATION. CONCEPT AND DEMONSTRATION OF A "RED LIGHT" TO "BLUE LIGHT" TRANSFORMATION

N. J. Turro, D. Brewer, W. Farneth and V. Ramamurthy, *Nou. J. de Chimie*, *2*, 85, **1978**.



Selected Reviews

C. A. Parker, Phosphorescence and Delayed Fluorescence from Solutions, Adv. Photochem., **1964**, *2*, 305

Photon upconversion based on sensitized triplet–triplet annihilation, T. N. Singh-Rachford, F. N. Castellano, Coordination Chemistry Reviews, **2010**, *254*, 2560–2573

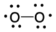
C. E. McCusker, F. N. Castellano, Materials Integrating Photochemical Upconversion, Top Curr Chem (Z) **2016**, 374, 19

Upconversion Luminescent Materials: Advances and Applications
J. Zhou, Q. Liu, W. Feng, Y. Sun, and F. Li, Chem. Rev. **2015**, *115*, 395

New perspectives for triplet–triplet annihilation based photon upconversion using all-organic energy donor & acceptor chromophores, A. Jean-Luc Ayitou et. al., Chem. Commun., **2018**, *54*, 5809.

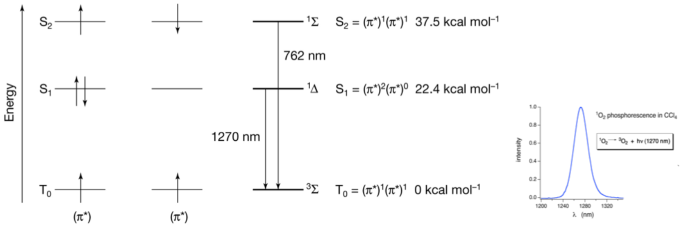
Singlet Oxygen

1

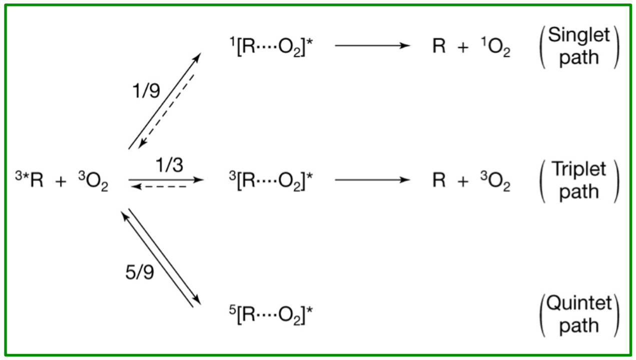


2

$$(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2pz})^2(\pi_{2py})^2(\pi_{2px})^2(\pi_{2px}{}^*)^1(\pi_{2py}{}^*)^1$$



$$\boxed{{}^*R(S_1) + {}^3O_2 \rightarrow {}^*R(T_1) + {}^1O_2\,({}^1\Delta)}$$



Representative rate constants and singlet oxygen efficiencies for the quenching of **excited singlets** by oxygen in acetonitrile at room temperature

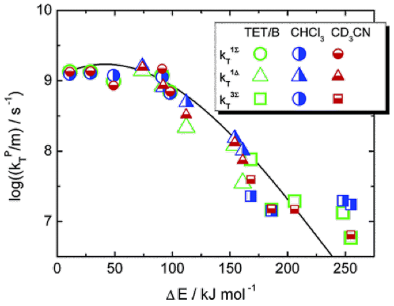
Substrate	Solvent	$(S\Delta^S)a$	k_q^S, 10^9 (M-1s-1)
Naphthalene	Acetonitrile	≤ 0.09	31
Phenanthrene	Acetonitrile	0	33
Triphenylene	Acetonitrile	≤ 0.02	37
Pyrene	Acetonitrile	0.30	29
Fluoranthene	Acetonitrile	0.30	6.6
Perylene	Acetonitrile	0.27	38
Tetracene	Acetonitrile	0.25	42
Anthracene	Acetonitrile	≤ 0.02	30

For the ET to be effective the singlet-triplet (S_1–T_1) energy gap of the donor must be greater than the energy gap between the ground and singlet state of oxygen (22.4 kcal/mol), the acceptor.

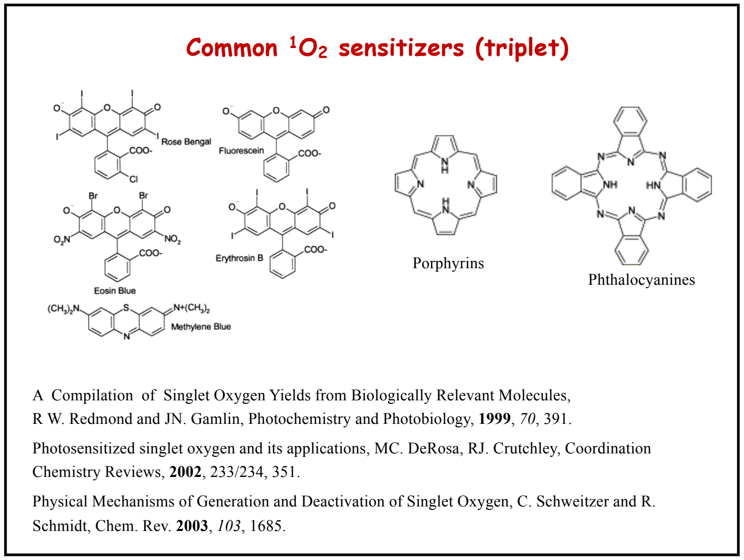
The π,π* triplet states of polynuclear aromatics are generally highly efficient at producing singlet oxygen, frequently with SΔ ≥ 0.8. The n,π* triplet states of ketones have low values of SΔ, for example for benzophenone SΔ is in the 0.3-0.4 range. Depends on the S_1–T_1 gap.

Energy Gap Law for Electronic Energy Transfer to O_2

R. Schmidt, *J. Phys. Chem. A* **2006**, *110*, 8, 2622



Marcus type relationship. Larger the excess energy (more than needed to generate singlet oxygen) slower the rate constant.

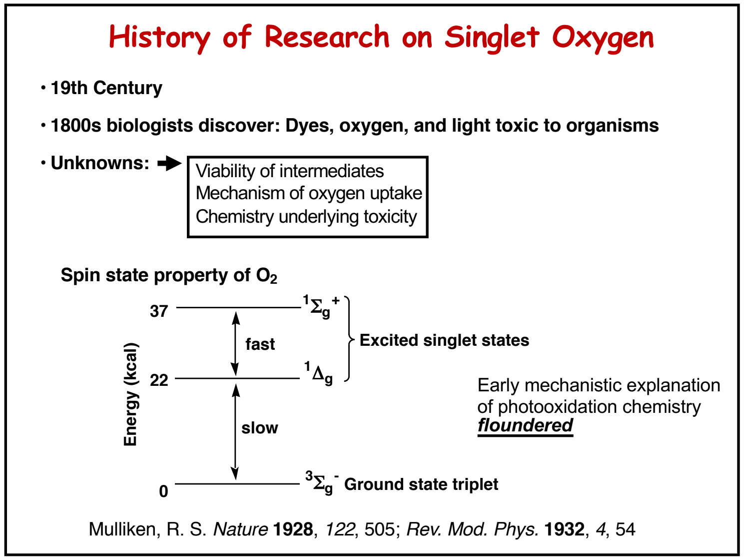


Common $^1O_2$ sensitizers (triplet)

A Compilation of Singlet Oxygen Yields from Biologically Relevant Molecules, R W. Redmond and JN. Gamlin, Photochemistry and Photobiology, **1999**, *70*, 391.

Photosensitized singlet oxygen and its applications, MC. DeRosa, RJ. Crutchley, Coordination Chemistry Reviews, **2002**, 233/234, 351.

Physical Mechanisms of Generation and Deactivation of Singlet Oxygen, C. Schweitzer and R. Schmidt, Chem. Rev. **2003**, *103*, 1685.



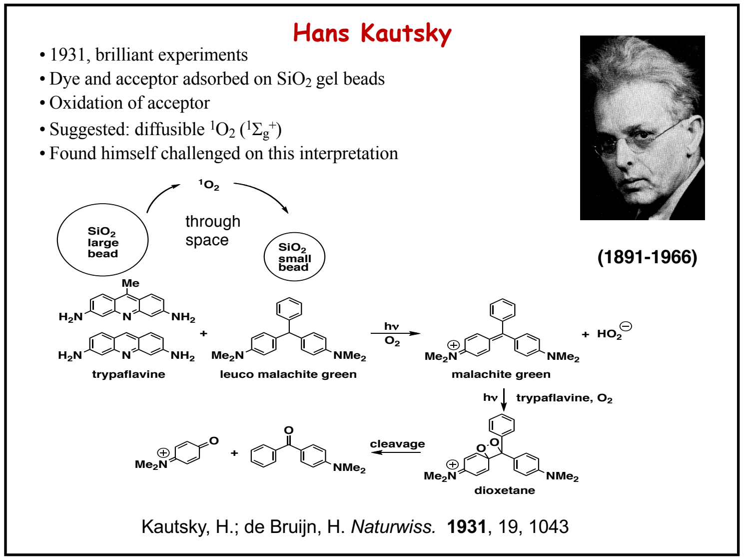
History of Research on Singlet Oxygen

- **19th Century**
- **1800s biologists discover: Dyes, oxygen, and light toxic to organisms**
- **Unknowns:** ➔
  Viability of intermediates
  Mechanism of oxygen uptake
  Chemistry underlying toxicity

Spin state property of O_2

Early mechanistic explanation of photooxidation chemistry ***floundered***

Mulliken, R. S. *Nature* **1928**, *122*, 505; *Rev. Mod. Phys.* **1932**, *4*, 54

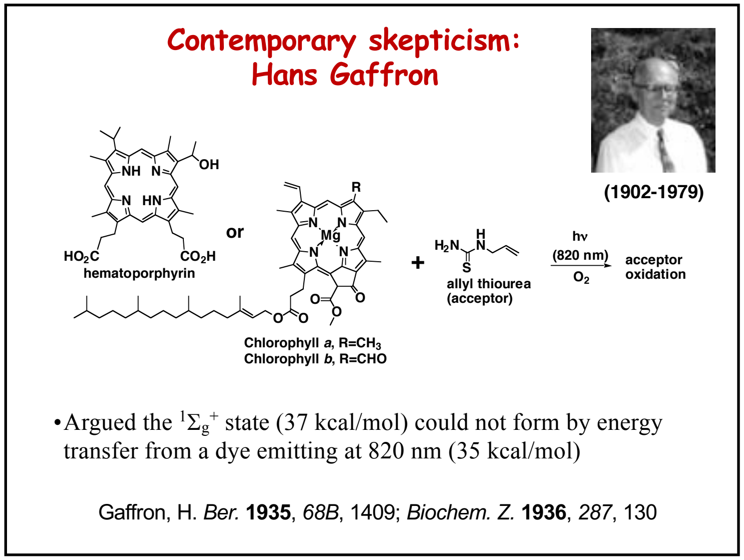


Hans Kautsky

- 1931, brilliant experiments
- Dye and acceptor adsorbed on SiO_2 gel beads
- Oxidation of acceptor
- Suggested: diffusible $^1O_2$ ($^1\Sigma_g^+$)
- Found himself challenged on this interpretation

(1891-1966)

Kautsky, H.; de Bruijn, H. *Naturwiss.* **1931**, 19, 1043



Contemporary skepticism: Hans Gaffron

(1902-1979)

- Argued the $^1\Sigma_g^+$ state (37 kcal/mol) could not form by energy transfer from a dye emitting at 820 nm (35 kcal/mol)

Gaffron, H. *Ber.* **1935**, *68B*, 1409; *Biochem. Z.* **1936**, *287*, 130

Contemporary Skepticism
GO Schenck

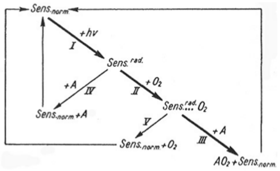
1940-1963

$^{\bullet}$Sens--OO$^{\bullet}$ (moloxide)

Papers on photooxidation were one-sided

Photooxidation attributed to sensitizer—oxygen adduct

Many discounted the contribution of $^1O_2$ ($^1\Delta_g$)



G. O. Schenck
(1913-2003)

References:

Schenck, G. O. *Naturwiss.* **1948**, *35*, 28

Blum, H. F. *Physiol. Rev.* **1945**, *25*, 483

Bowen, E. J. *Discussions Faraday Soc.* **1953**, *14*, 143

Terenin, A. N. *Akad. Nauk S.S.S.R.* **1955**, 85

Livingston, R. S. *Conf. Biol. Antioxidants Trans.* **1950**, *5*, 17

Singlet Oxygen

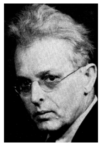
$^1\Sigma_g^+$ Singlet Oxygen as the reactive species

H. Kautsky et. al., Naturwissenschaften, **1931**, 19,1043

H.Kautsky, et. al., Dtsch. Chem. Ges., **1933**, 66, 1588.

H. Kautsky, Biochem. Z, **1937**, 291,271(1937)

H. Kautsky, Trans. Faraday Soc., **1939**, 35, 216.



H. Kautsky

G. O. Schenck

$^{\bullet}$Sens--OO$^{\bullet}$ (moloxide)

GO. Schenck, G. O. *Naturwiss.* **1948**, *35*, 28

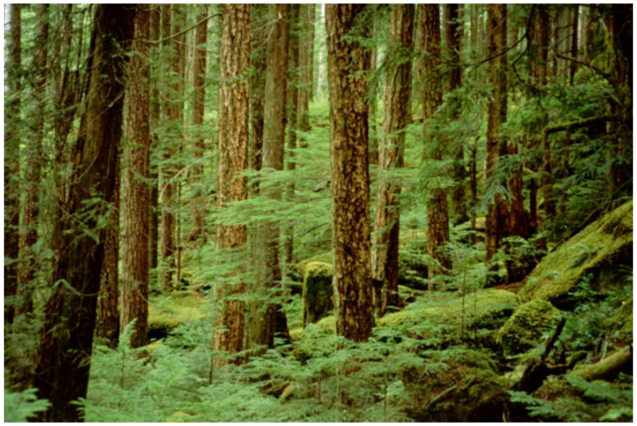
Singlet Oxygen

Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879

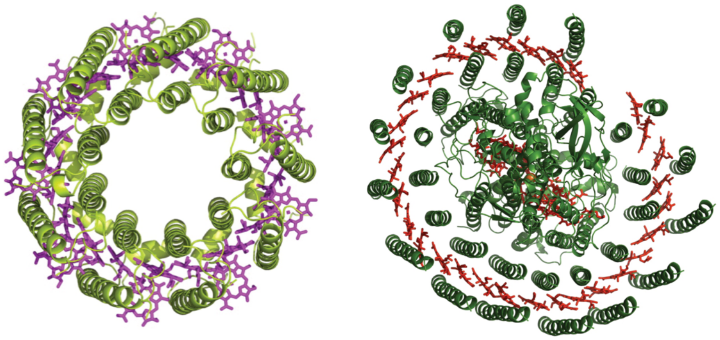
Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3880

S Wolf, CS Foote, J Rebek Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7770

C. S. Foote



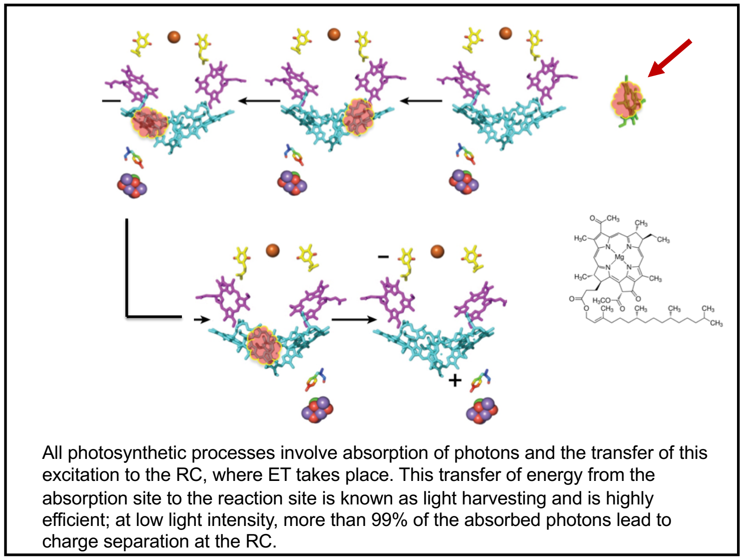
Plants that commonly grow in the shade benefit from having a variety of light-absorbing pigments. Each pigment can absorb different wavelengths of light, which allows the plant to absorb any light that passes through the taller trees.



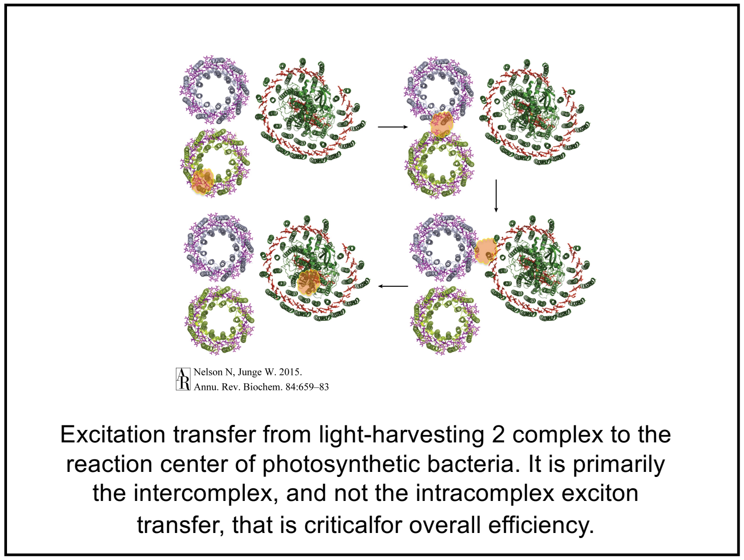
LH2

RC–LH1

LH1, light-harvesting 1 complex;
LH2, light harvesting 2 complex RC, reaction center.

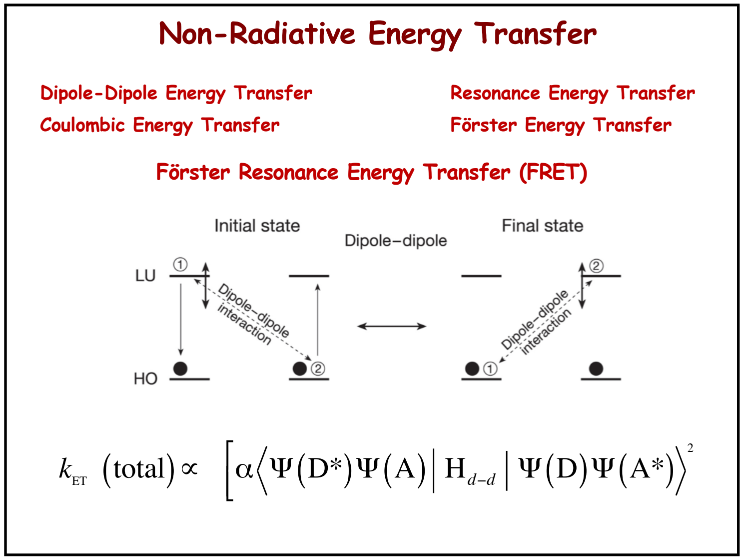


All photosynthetic processes involve absorption of photons and the transfer of this excitation to the RC, where ET takes place. This transfer of energy from the absorption site to the reaction site is known as light harvesting and is highly efficient; at low light intensity, more than 99% of the absorbed photons lead to charge separation at the RC.



Nelson N, Junge W. 2015.
Annu. Rev. Biochem. 84:659–83

Excitation transfer from light-harvesting 2 complex to the reaction center of photosynthetic bacteria. It is primarily the intercomplex, and not the intracomplex exciton transfer, that is criticalfor overall efficiency.

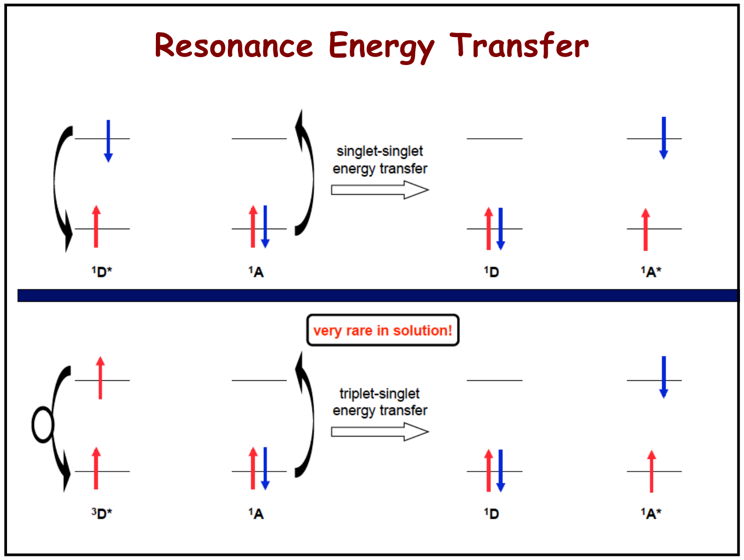


Non-Radiative Energy Transfer

Dipole-Dipole Energy Transfer
Coulombic Energy Transfer
Resonance Energy Transfer
Förster Energy Transfer

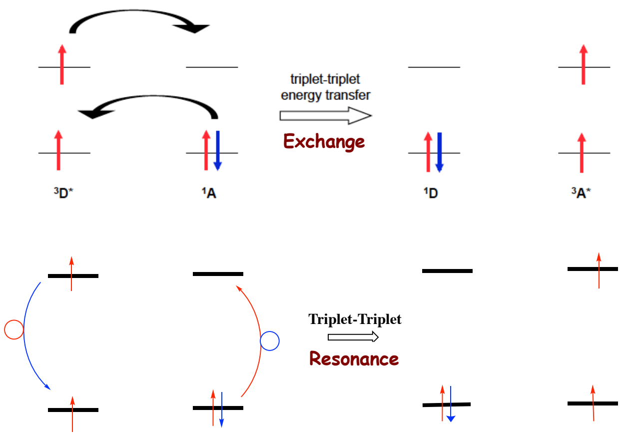
Förster Resonance Energy Transfer (FRET)

$$k_{ET}\ (\text{total}) \propto \left[\alpha\left\langle \Psi(D^*)\Psi(A)\,\middle|\, H_{d-d}\,\middle|\,\Psi(D)\Psi(A^*)\right\rangle^2\right.$$



Resonance Energy Transfer

Exchange *vs* Resonance (Triplet-Triplet)



History singlet-singlet energy transfer

Hg vapor to Na vapor

G. Cario and J. Franck, Z. Physik, 17, 202 (1923).

Hg vapor to H_2

Xe vapor to H_2

H. Calvert, Z. Physik, 78, 479 (1932)

Anthracene to Naphthalene crystals

A. Winterstein and K. Schon, Naturwiss., 22, 237 (1934)

E. J. Bowen, Nature, 142, 108 (1938)

Tryptaflavin to Rhodamine B in solution (> 70Å)

T. Forster, Z. Elektrochem., 63, 93 (1949)

1-Chloroanthracene to perylene

E. Bowen and B. Brocklehurst, Trans. Faraday Soc., 49,1131 (1953)

Milestones in the Theory of Resonance Energy Transfer

1918 J. Perrin proposed the mechanism of resonance energy transfer. A theoretical interpretation of energy transfer between molecules, involved fluorescence polarization in a solution of a single chemical species of fluorophore.

1922 G. Cario and J. Franck demonstrate that excitation of a mixture of mercury and thallium atomic vapors with 254nm (the mercury resonance line) also displayed thallium (sensitized) emission at 535nm.

1928 H. Kallmann and F. London developed the quantum theory of resonance energy transfer between various atoms in the gas phase. The dipole-dipole interaction and the parameter R_0 were used for the first time.

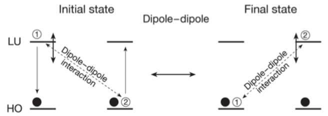
1932 F. Perrin published a quantum mechanical theory of energy transfer between molecules of the same specie in solution. Qualitative discussion of the effect of the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.

1941 W. Arnold and J.R. Oppenheimer, an abstract on FRET in photosynthesis and full article in 1950

1946-1949 T. Förster developed the first quantitative theory of molecular resonance energy transfer.

Förster Resonance Energy Transfer (FRET)

A Transmitter-Antenna Receiver-Antenna Mechanism



Beginning

End

$$k_{ET} \propto \left\langle \Psi_{D*}\Psi_A \left| \frac{\mu_D \mu_A}{r^3} f(\theta) \right| \Psi_D \Psi_{A*} \right\rangle^2$$

$$\propto \frac{1}{r^6}$$

Operator

Interaction energy (E) between two dipoles μ_A, μ_D at a separation r is given by

Transition dipole moment

$$E \propto \frac{\mu_A \mu_D}{r^3} f(\theta)$$

Distance

$$\Delta E\,({}^*D \rightarrow D) = \Delta E\,(A \rightarrow {}^*A)$$

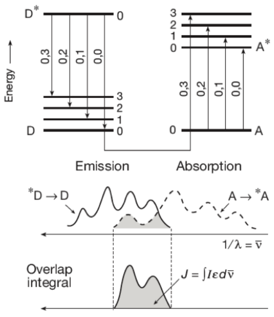
$$E \propto \frac{\mu_A \mu_D}{r^3} f(\theta) \longleftarrow \text{Operator}$$

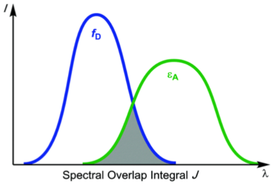
$$k_{ET}\,(\text{dipole - dipole}) \rightarrow \frac{k_D^{o} \int \varepsilon_A}{R_{DA}^{6}}$$

$$k_{ET}\,(\text{dipole - dipole}) = \alpha \frac{\kappa^2\, k_D^{o}}{R_{DA}^{6}}\; J\left(\varepsilon_A\right)$$

$$J = \frac{\int F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int F_D(\lambda)d\lambda}$$

$$k_{ET}\,(\text{dipole - dipole}) = \alpha \frac{\kappa^2\, k_D^{o}}{R_{DA}^{6}}\; J\left(\varepsilon_A\right)$$



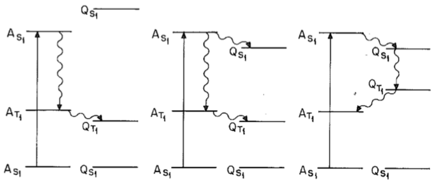


$$\int_0^{\infty} F_D(\nu)\epsilon_A(\nu)\,\frac{d\nu}{\nu^4} = \text{spectral overlap integral}$$

Triplet-Triplet Energy Transfer

Sensitizers and Quenchers

Organic Chemistry



S_1 and T_1 quenching
Not specific,not useful

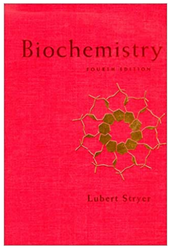
T_1 quenching
Sensitizer

S_1 quenching
Quencher

Singlet-Singlet Energy Transfer

FRET as a "Spectroscopic Ruler"

Biochemistry and Biology



$$k_{ET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

Lubert Stryer

Förster formulation

$$k_{ET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$k_{ET} = \frac{\phi_D\kappa^2}{\tau_D r^6}\,\frac{9000\ln 10}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda$$

ϕ_D : Fluorescence quantum yield of donor in absence of acceptor

κ^2 : Orientation factor

τ_D : Lifetime of donor in absence of acceptor

r : Donor – acceptor distance

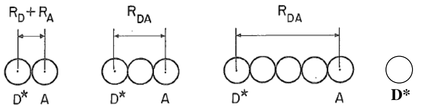
N_A: Avogadro number

n : Refractive index of the medium

$F_D(\lambda)$: Normalized fluorescence spectrum of donor

$\varepsilon_A(\lambda)$: Normalized absorption spectrum of acceptor

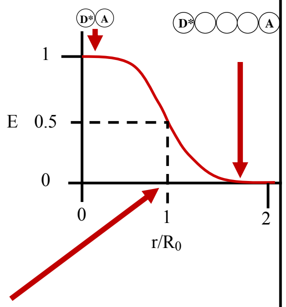
Definition of R_0



In the absence of acceptor: k[D*]

In the presence of acceptor: k[D*] + k_{ET} [D*][A]

We make an assumption that when r = R_0
k[D*] = k_{ET} [D*][A]



At $r_{DA} = R^o_{DA}$:

The deactivation of excited state would be
k_{ET} [D*] + k[D*] [A] = 2 k[D*]

What happens to Förster formulation at R_0

$$k_{ET} = \frac{\phi_D\kappa^2}{\tau_D r^6}\,\frac{9000\ln 10}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda$$

When r = R_o the rate of energy transfer equals the rate of deactivation.

$$k_{ET} = k_D = \tau_D^{-1}$$

$$\tau_D^{-1}\quad \boxed{\cancel{k_{ET}} = \frac{\phi_D\kappa^2}{\tau_D \underset{R_0}{\cancel{r^6}}}\,\frac{9000\ln 10}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda}$$

Replacing r with R_0 and rearranging the above eqn.

$$R_0^6 = \frac{\phi_D\kappa^2 \; 9000\ln 10}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda$$

R_0 can be calculated using this eqn.

For each D-A pair the # is fixed

$$k_{ET} = \frac{1}{\tau_D r^6}\boxed{\frac{\phi_D\kappa^2}{1}\,\frac{9000\ln 10}{128\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda}$$

$$R_0^6 = \frac{\phi_D\kappa^2 \; 9000\ln 10}{28\pi^5 N_A n^4}\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda$$

$$k_{ET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

R_0 = Forster distance

R_0 is constant for a particular donor – acceptor pair in a given solvent

What one needs to estimate 'r'?

$$k_{ET}(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

One can get 'r', if we can measure

- k_{ET} (Rate constant of energy transfer)
- τ_D (Lifetime of donor in absence of acceptor)
- R_0 is calculated.

What is k_{ET}

$$D \xrightarrow{h\upsilon} D^*$$

$$D^* \xrightarrow{k} D$$

$$D^* \xrightarrow{k_F} D + h\upsilon$$

$$\boxed{D^* + A \xrightarrow{k_{ET}} D + A^*}$$

$$A^* \xrightarrow{k_A} A$$

Follow the fluorescence of the donor

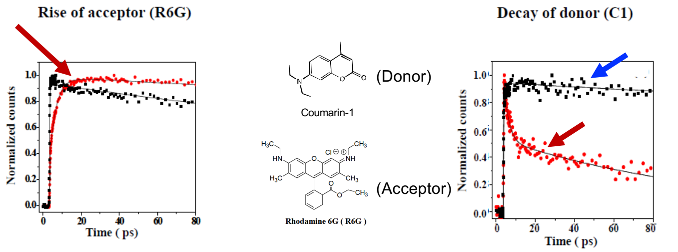
$$\Phi^F = \frac{k_F}{k_F + k}$$

$$\Phi_A{}^F = \frac{k_F}{k_F + k + k_{ET}}$$

$$\frac{\Phi_F}{\Phi_A{}^F} = \frac{k_F + k + k_{ET}}{k_F} \times \frac{k_F}{k_F + k}$$

$$\boxed{\frac{\Phi_F}{\Phi_A{}^F} = 1 + \frac{k_{ET}}{k_F + k} = 1 + \tau\, k_{ET}}$$

Singlet-Singlet Energy Transfer



Inverse rise time of acceptor fluorescence is: k_{ET}

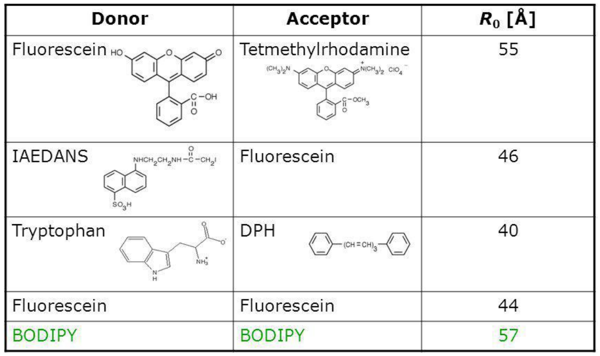
$$k_{ET} = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$\boxed{k_{ET} = \frac{1}{\tau_{DA}} - \frac{1}{\tau_D}}$$

System	$\tau^A{}_{rise}$	$\tau_D{}^0$	R_0	R_{DA}
$C480@OA_2$ +R6G	1.5 ps	4900 ps	48.8 Å	13±1 Å
$C153@OA_2$ +R6G	1.0 ps	7400 ps	55.7 Å	13±1 Å
$C1@OA_2$ +R6G	3.5 ps	4300 ps	42.5 Å	13±1 Å

Förster radius - examples

Some typical donor-acceptor pairs commonly used in structural mapping of proteins, and their values of R_0:



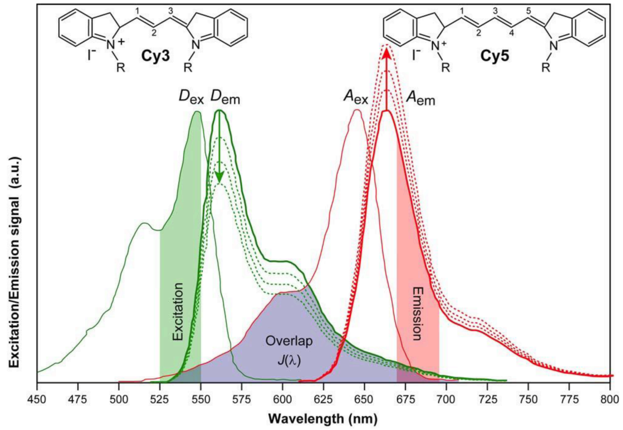
Donor	Acceptor	R_0 [Å]
Fluorescein	Tetmethylrhodamine	55
IAEDANS	Fluorescein	46
Tryptophan	DPH	40
Fluorescein	Fluorescein	44
BODIPY	BODIPY	57

$$R_0^6 = \frac{\phi_D \kappa^2}{} \frac{9000 \ln 10}{128 \pi^5 N_A n^4} \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

Tab. 9.1. Examples of Förster critical radii

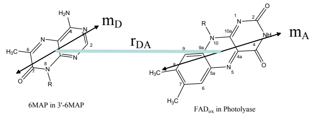
Donor	*Acceptor*	*R_0 (Å)*
Naphthalene	Dansyl	~22
Anthracene	Perylene	~31
Pyrene	Perylene	~36
Phenanthrene	Rhodamine B	~47
Fluorescein	Tetramethylrhodamine	~55
Fluorescein-5-isothiocyanate	Eosin maleimide	~60
Rhodamine 6G	Malachite green	~61
Tryptophan	Dansyl	~21
Tryptophan	ANS	~23
Tryptophan	Anthroyl	~25
Tryptophan	Pyrene	~28

Spectral Overlap



The Orientation Factor

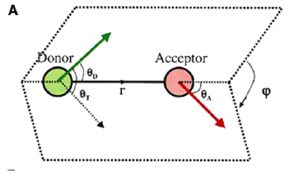
$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D \cos\theta_A)^2$$



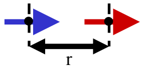
θ_T: $\angle$ m_D, m_A

θ_D: $\angle$ m_D, r_{DA}

θ_A: $\angle$ m_A, r_{DA}



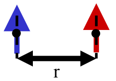
Case 1:



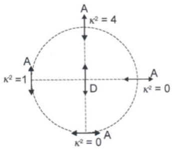
$\theta_A = 0$
$\theta_D = 0$
$\theta_T = 0$

$$\kappa^2 = (\cos 0 - 3\cos 0 \cos 0)^2 = 4$$

Case 2:

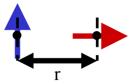


$\theta_A = 90$
$\theta_D = 90$
$\theta_T = 0$



$$\kappa^2 = (\cos 0 - 3\cos 90 \cos 90)^2 = 1$$

Case 3:



$\theta_A = 90$
$\theta_D = 90$
$\theta_T = 90$

$$\kappa^2 = (\cos 90 - 3\cos 90 \cos 90)^2 = 0$$

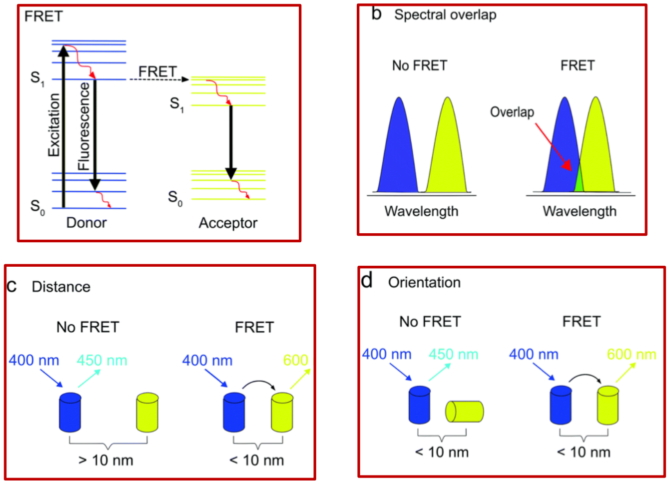
Case 4:

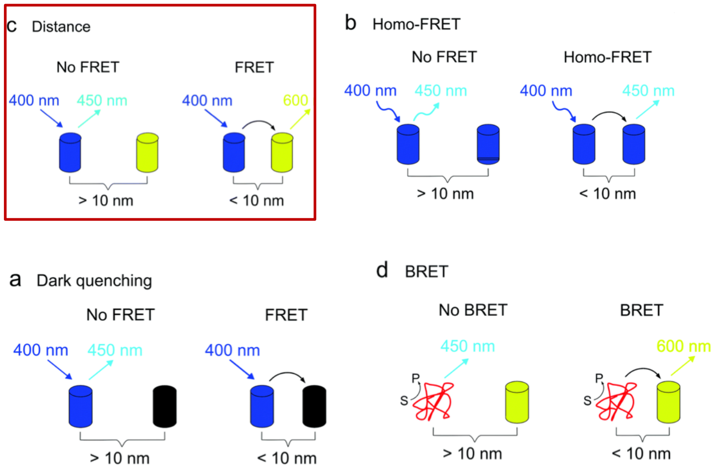
When the transition moment of donor and acceptor are normalized
The value of κ^2 can be taken as an average

$$\langle \kappa^2 \rangle = \frac{\int_0^{\pi} (\cos\theta_T - 3\cos\theta_D\cos\theta_A)^2 \, d\theta_T d\theta_D d\theta_A}{\int_0^{\pi} d\theta_T d\theta_D d\theta_A} = \frac{2}{3}$$

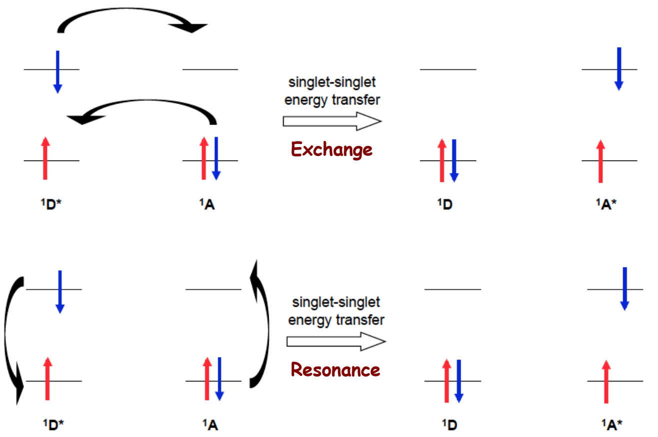
The rate of energy transfer between a donor and acceptor is given by where ***k*** is taken to be 2/3; this is an assumption, need not be true all the time.

$$k_{ET} = \frac{1}{\tau_D r^6} \frac{\phi_D \kappa^2}{1} \frac{9000 \ln 10}{128\pi^5 N_A n^4} \int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$





Exchange *vs* Resonance (Singlet-Singlet)



Differences between Förster (dipole-dipole interaction) and Dexter (electron exchange) energy transfer processes

- The rate of dipole-induced energy transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as $e^{-(2r/L)}$. Quantitatively, this means that k_{ET} (exchange) drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å)
- The rate of dipole-induced transfer depends on the oscillator strength of the $^*D \rightarrow D$ and $A \rightarrow {}^*A$ radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the $^*D \rightarrow D$ and $A \rightarrow {}^*A$ transitions

---

$$D^* + A \rightarrow D + A^*$$

$$k_{ET}\ (\text{total}) \propto \left[\alpha \langle \Psi(D^*)\Psi(A) | H_e | \Psi(D)\Psi(A^*) \rangle^2\right.$$

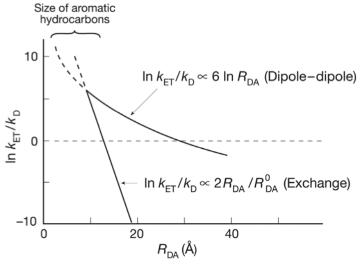
Electron exchange

$$\left. + \beta \langle \Psi(D^*)\Psi(A) | H_c | \Psi(D)\Psi(A^*) \rangle^2 \right]$$

Electron dipole-dipole interactions

$$k_{ET}\ (\text{exchange}) = KJ \exp(-2\, r_{DA}/L)$$

$$k_{ET\,(\text{Dipole-dipole})} \propto E^2 \approx \left(\frac{\mu_D \mu_A}{R_{DA}^3}\right)^2 = \frac{\mu_D^2 \mu_A^2}{R_{DA}^6}$$



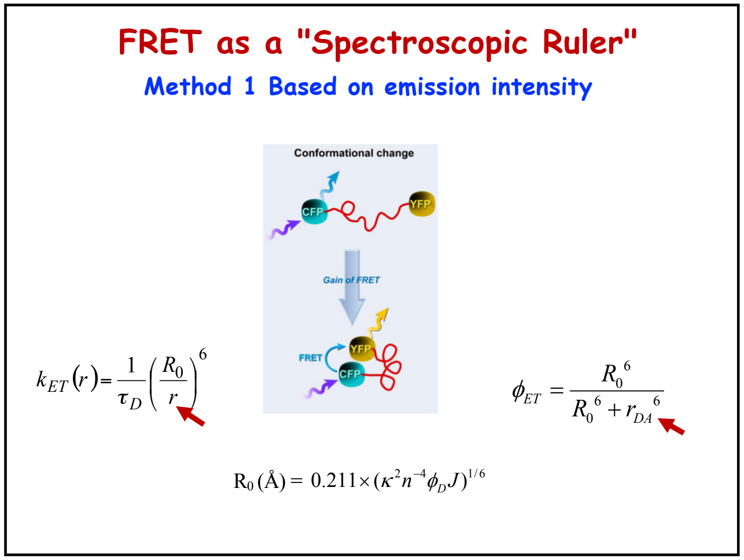
Distance dependence, when it can be measured accurately, is a basis for distinguishing energy transfer that occurs by dipole–dipole interactions from electron exchange interactions, since the latter generally falls off exponentially with the separation $\mathbf{R_{DA}}$

Dipole-dipole mechanism will be most favored for *D and A pairs such that:

- The $^*D \rightarrow D$ and $A \rightarrow {}^*A$ processes correspond to a large (spectral) overlap integral, *J*.
- The radiative rate constant, k°_D, is as large as possible.
- The magnitude of ε_A is as large as possible.
- There is a small spatial separation between *D and A.
- There will be a preferred orientation for which energy transfer is most favorable.

A Theory of Sensitized Luminescence in Solids, D. L. Dexter, *J. Chem. Phys.* 21, 836 (1953)

Transfer mechanisms of electronic excitation, Th. Forster, *Discussions Faraday Soc.* 27, 7, (1959)



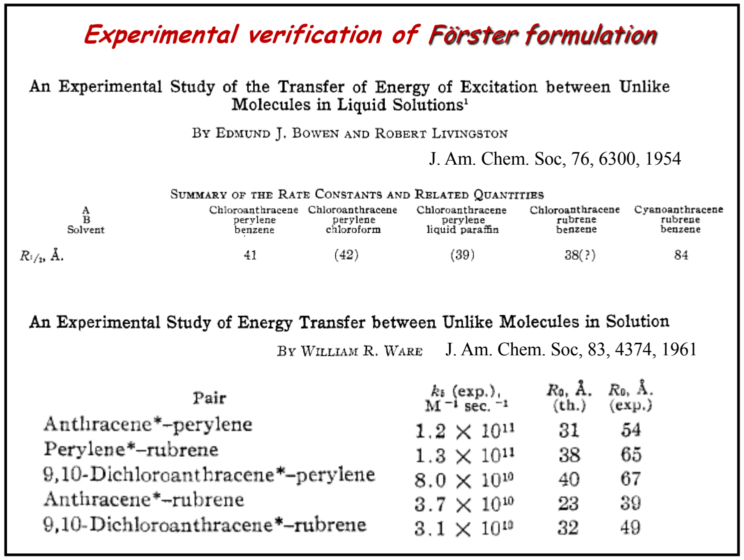
FRET as a "Spectroscopic Ruler"

Method 1 Based on emission intensity

$$k_{ET}(r)=\frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

$$\phi_{ET}=\frac{R_0^{\,6}}{R_0^{\,6}+r_{DA}^{\,6}}$$

$$R_0\,(\text{Å}) = 0.211\times(\kappa^2 n^{-4}\phi_D J)^{1/6}$$



Experimental verification of Förster formulation

An Experimental Study of the Transfer of Energy of Excitation between Unlike Molecules in Liquid Solutions[1]

By Edmund J. Bowen and Robert Livingston

J. Am. Chem. Soc, 76, 6300, 1954

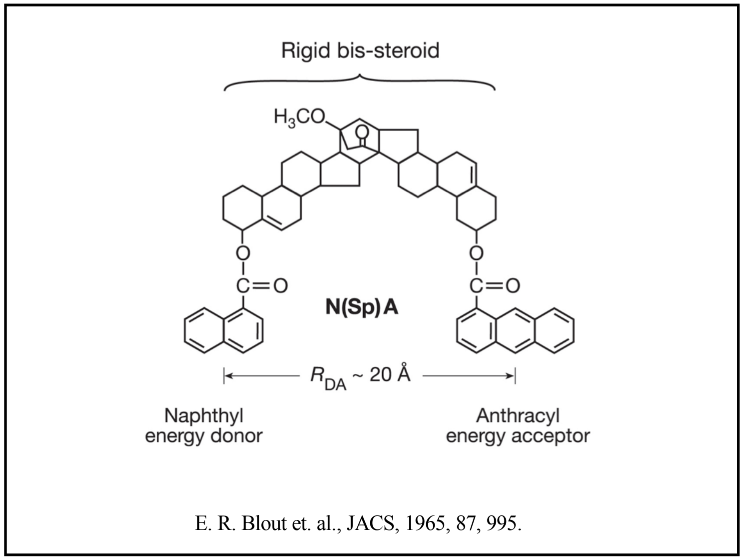
Summary of the Rate Constants and Related Quantities

A B Solvent	Chloroanthracene perylene benzene	Chloroanthracene perylene chloroform	Chloroanthracene perylene liquid paraffin	Chloroanthracene rubrene benzene	Cyanoanthracene rubrene benzene
$R_{1/2}$, Å.	41	(42)	(39)	38(?)	84

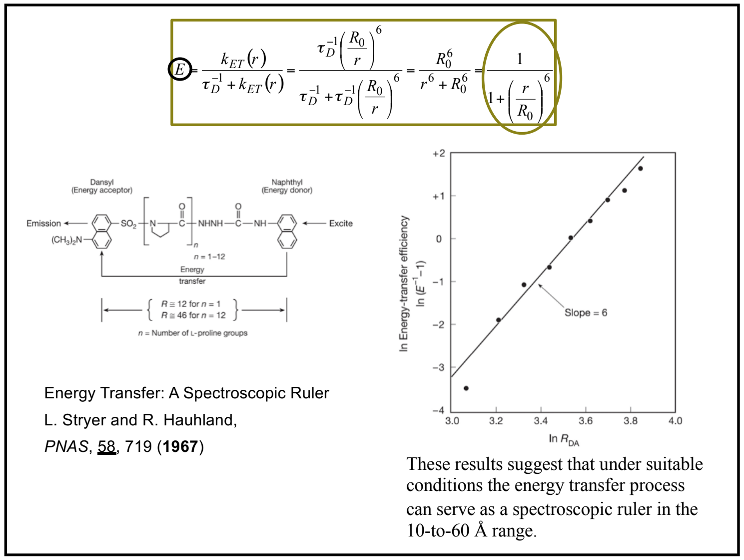
An Experimental Study of Energy Transfer between Unlike Molecules in Solution

By William R. Ware J. Am. Chem. Soc, 83, 4374, 1961

Pair	k_5 (exp.), M^{-1} sec.$^{-1}$	R_0, Å. (th.)	R_0, Å. (exp.)
Anthracene*–perylene	1.2×10^{11}	31	54
Perylene*–rubrene	1.3×10^{11}	38	65
9,10-Dichloroanthracene*–perylene	8.0×10^{10}	40	67
Anthracene*–rubrene	3.7×10^{10}	23	39
9,10-Dichloroanthracene*–rubrene	3.1×10^{10}	32	49



E. R. Blout et. al., JACS, 1965, 87, 995.



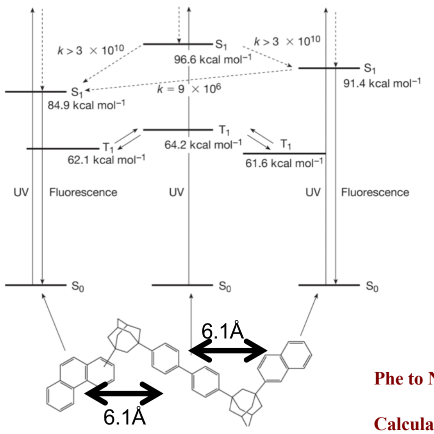
$$\boxed{E}=\frac{k_{ET}(r)}{\tau_D^{-1}+k_{ET}(r)}=\frac{\tau_D^{-1}\left(\frac{R_0}{r}\right)^6}{\tau_D^{-1}+\tau_D^{-1}\left(\frac{R_0}{r}\right)^6}=\frac{R_0^6}{r^6+R_0^6}=\frac{1}{1+\left(\frac{r}{R_0}\right)^6}$$

Energy Transfer: A Spectroscopic Ruler

L. Stryer and R. Hauhland,

PNAS, 58, 719 (**1967**)

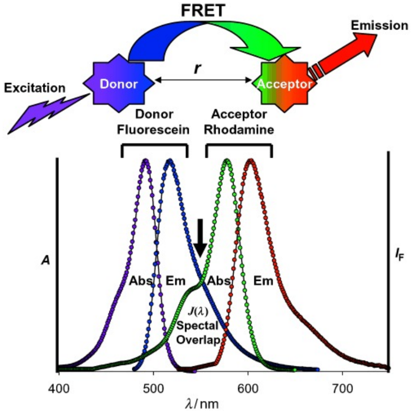
These results suggest that under suitable conditions the energy transfer process can serve as a spectroscopic ruler in the 10-to-60 Å range.



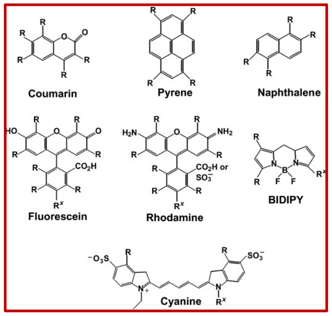
Phe to Naph distance

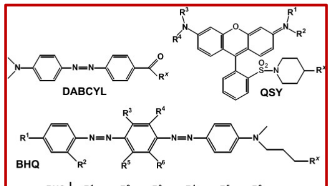
Calculated by FRET: 15.7Å

Estimated by modeling: 14.3Å



FRET pairs



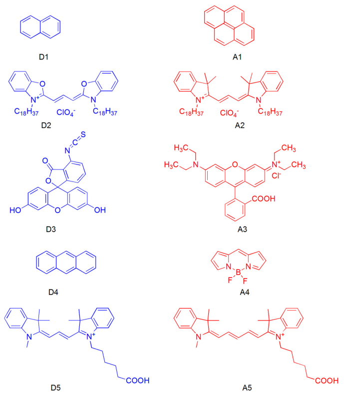


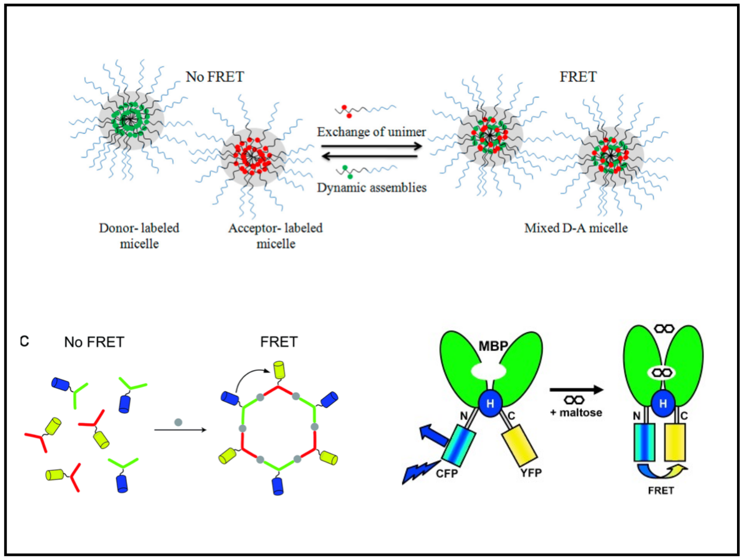
BHQ	R¹	R²	R³	R⁴	R⁵	R⁶
1	CH_3	NO_2	CH_3	H	H	OCH_3
2	NO_2	H	H	OCH_3	OCH_3	H
10	NaO_3S	H	H	NaO_3S	H	H

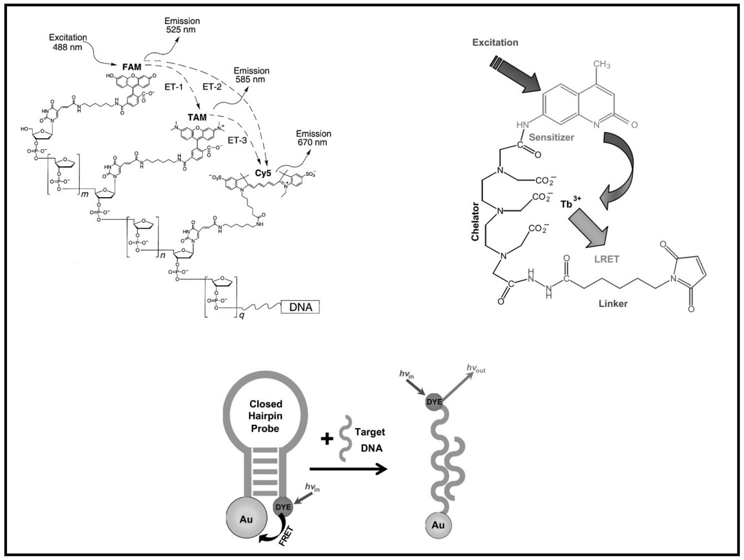
Donors

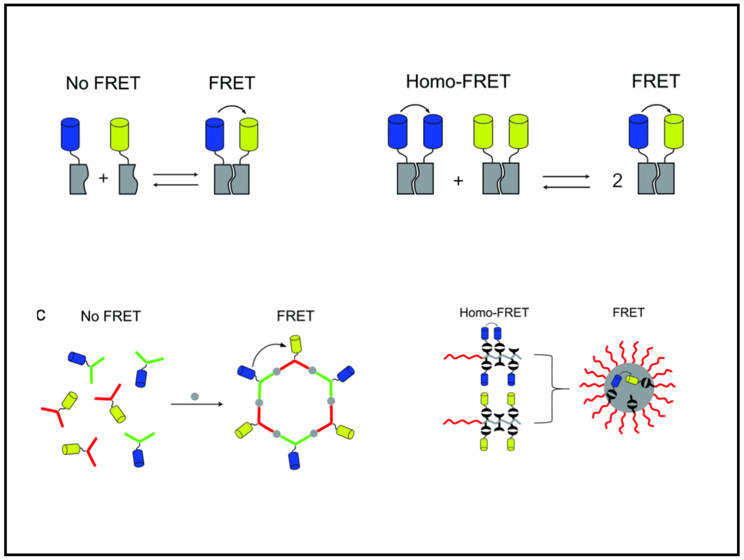
Acceptors

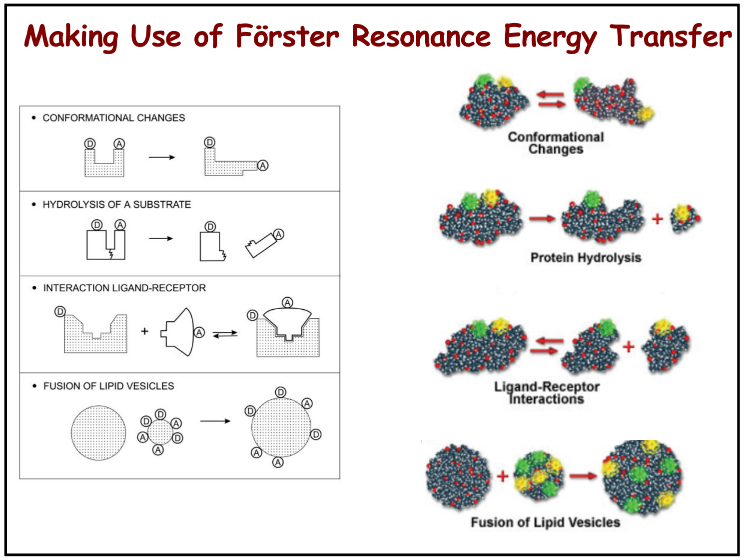
FRET pairs

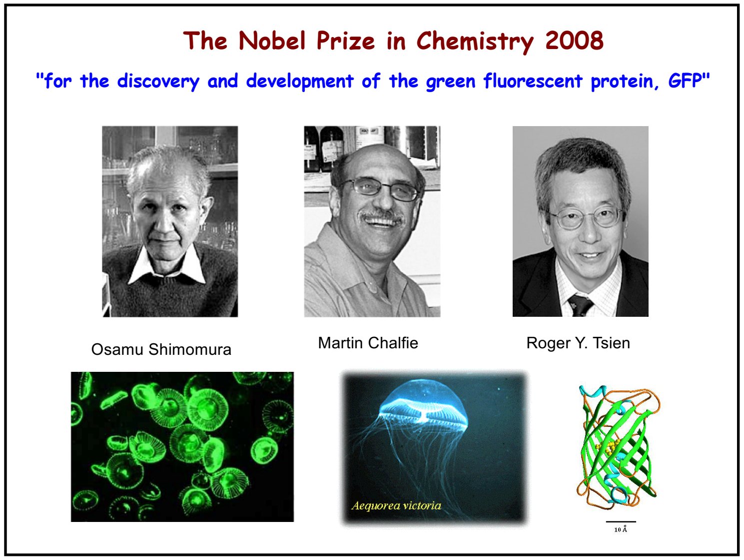









Making Use of Förster Resonance Energy Transfer



The Nobel Prize in Chemistry 2008

"for the discovery and development of the green fluorescent protein, GFP"

Osamu Shimomura

Martin Chalfie

Roger Y. Tsien

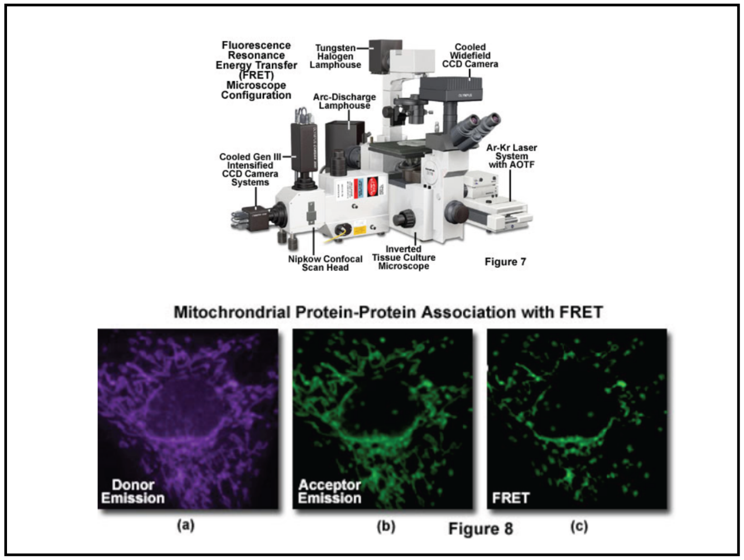
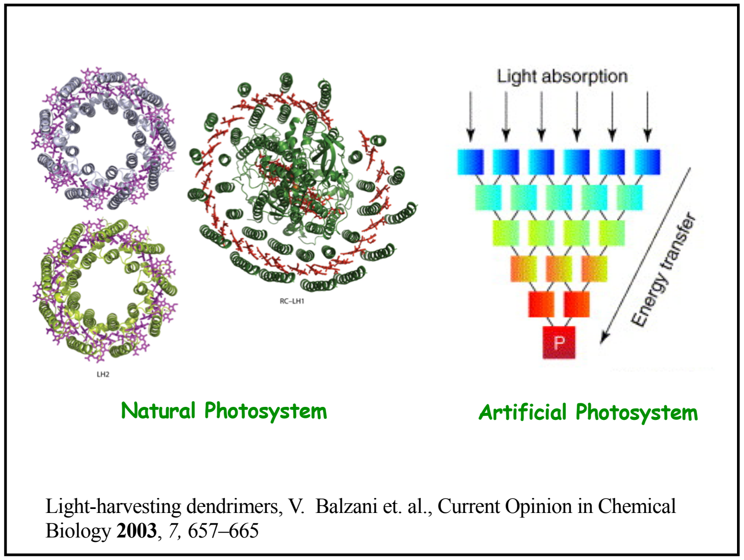


Figure 7

Mitochrondrial Protein-Protein Association with FRET

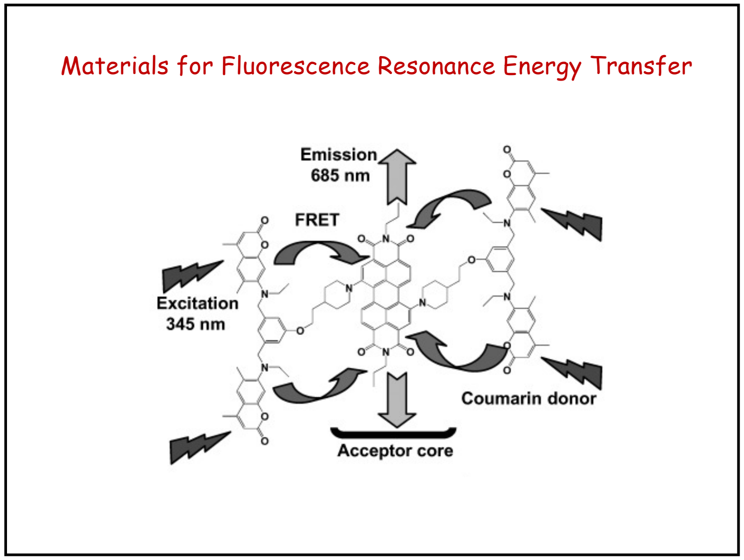
Figure 8



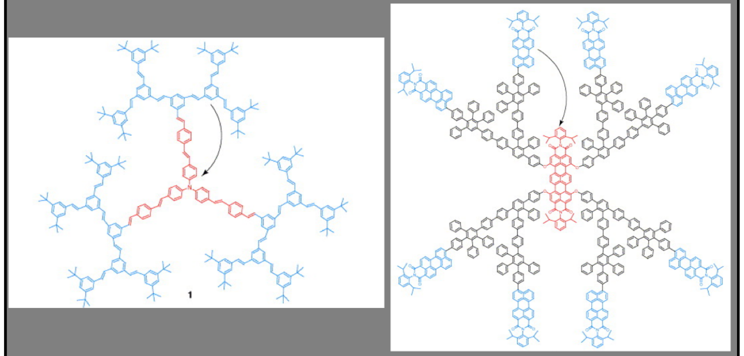
Natural Photosystem

Artificial Photosystem

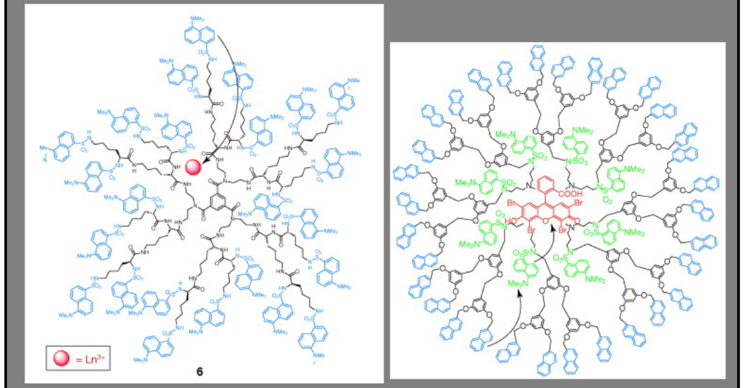
Light-harvesting dendrimers, V. Balzani et. al., Current Opinion in Chemical Biology **2003**, *7*, 657–665



Materials for Fluorescence Resonance Energy Transfer

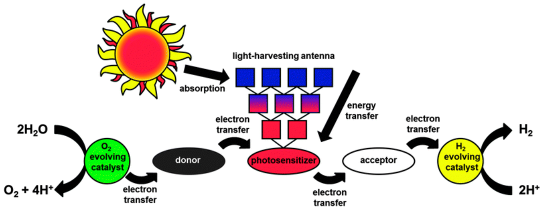


1



= Ln^{3+}

6



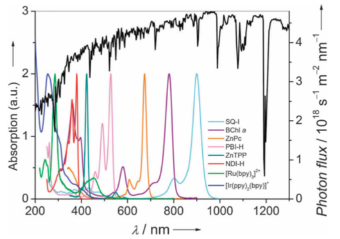
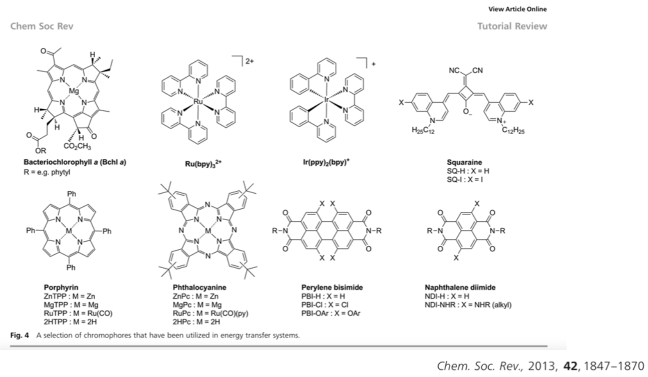


Fig. 5 Incident photon flux solar spectrum (ASTM 1.5 solar output spectra) and UV-Vis spectra of commonly selected chromophores plotted with normalized absorption to help visualize spectral overlap. See Table 1 for extinction coefficients.



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Chem Soc Rev

Tutorial Review

Bacteriochlorophyll *a* (Bchl *a*)
R = e.g. phytyl

Ru(bpy)$_3^{2+}$

Ir(ppy)$_2$(bpy)$^+$

Squaraine
SQ-H : X = H
SQ-I : X = I

Porphyrin
ZnTPP : M = Zn
MgTPP : M = Mg
RuTPP : M = Ru(CO)
2HTPP : M = 2H

Phthalocyanine
ZnPc : M = Zn
MgPc : M = Mg
RuPc : M = Ru(CO)(py)
2HPc : M = 2H

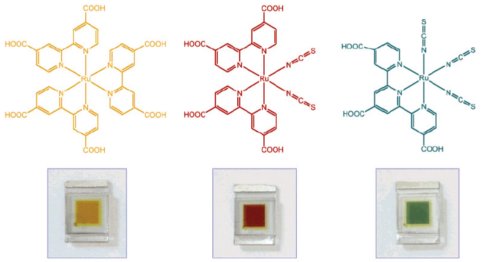
Perylene bisimide
PBI-H : X = H
PBI-Cl : X = Cl
PBI-OAr : X = OAr

Naphthalene diimide
NDI-H : X = H
NDI-NHR : X = NHR (alkyl)

Fig. 4 A selection of chromophores that have been utilized in energy transfer systems.

Chem. Soc. Rev., 2013, **42**, 1847–1870

Ru-Dyes For Dye-Sensitized Solar Cells



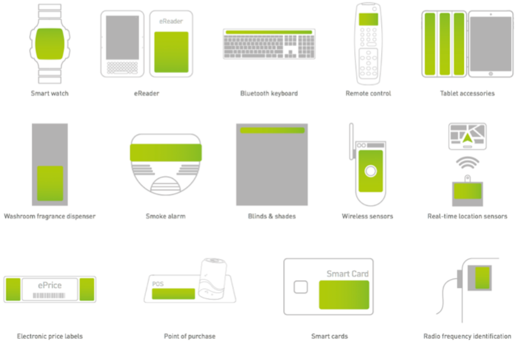
Michael Gratzel,
Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells,
Inorg. Chem., 44 (20), 6841-6851, 2005

DSC application – Portable electronics

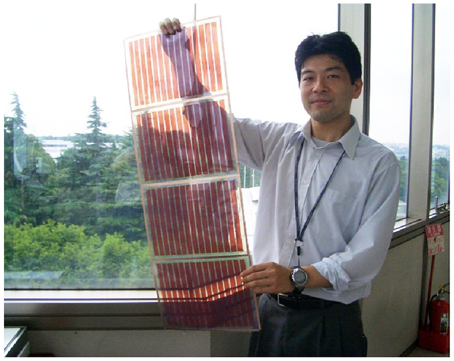
Consumer electronics

Sensors & Actuators

Retail



PECCell - flexi DSC



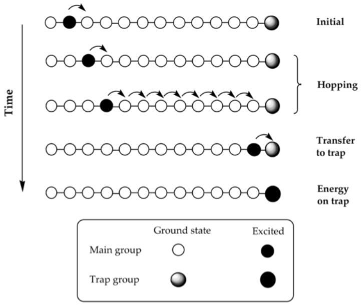
ECOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

DSC-based Portable Powerpack from G24i

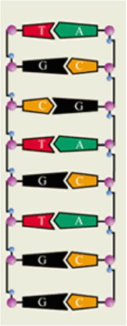
Laboratory for Photonics and Interfaces (LPI)

Large area DSC panels for outdoor and building integration

Long distance energy and electron migration



Energy transfer through space



Electron transfer through bond

Some Reflections on the Work of Theodor Forster
George Porter, Naturwissenschaften, **1976,** *63*, 207-211

THE HISTORY OF FRET: From conception through the labors of birth
R. M. Clegg, Reviews in Fluorescence, **2006**, 1-45

Materials for Fluorescence Resonance Energy Transfer Analysis: Beyond Traditional Donor–Acceptor Combinations
K.E. Sapsford, L. Berti, and I. L. Medintz, Angew. Chem. Int. Ed. **2006**, *45,4562* – 4588

Structure and Energy Transfer in Photosystems of Oxygenic Photosynthesis N. Nelson and W. Junge, Annu. Rev. Biochem. **2015**. *84*, 659–83

Investigating supramolecular systems using Forster resonance energy transfer
A. J. P. Teunissen, C, Pealrez-Medina, A. Meijerink and W. J. M. Mulder,
Chem. Soc. Rev., **2018**, *47*, 7027

Fluorescence Resonance Energy Transfer (FRET): A Powerful Tool for Probing Amphiphilic Polymer Aggregates and Supramolecular Polymers,
P. Rajdev, and S. Ghosh, J. Phys. Chem. B **2019**, *123*, 327–342

Thank you!

NSF