Organic Chemistry of Exciplexes

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Denmark Group Meeting

March 18th, 2025

Presentation Overview

- Excimer/Exciplex first occurrences, Spectroscopic insights
- Total Synthesis
- Perspective

Not Discussed:

- Excimer/Exciplexes in materials or rigid media
- Kinetics and Diffusion Control in Excimer/Exciplex reactions

Presentation Overview

- Excimer/Exciplex first occurrences, Spectroscopic insights

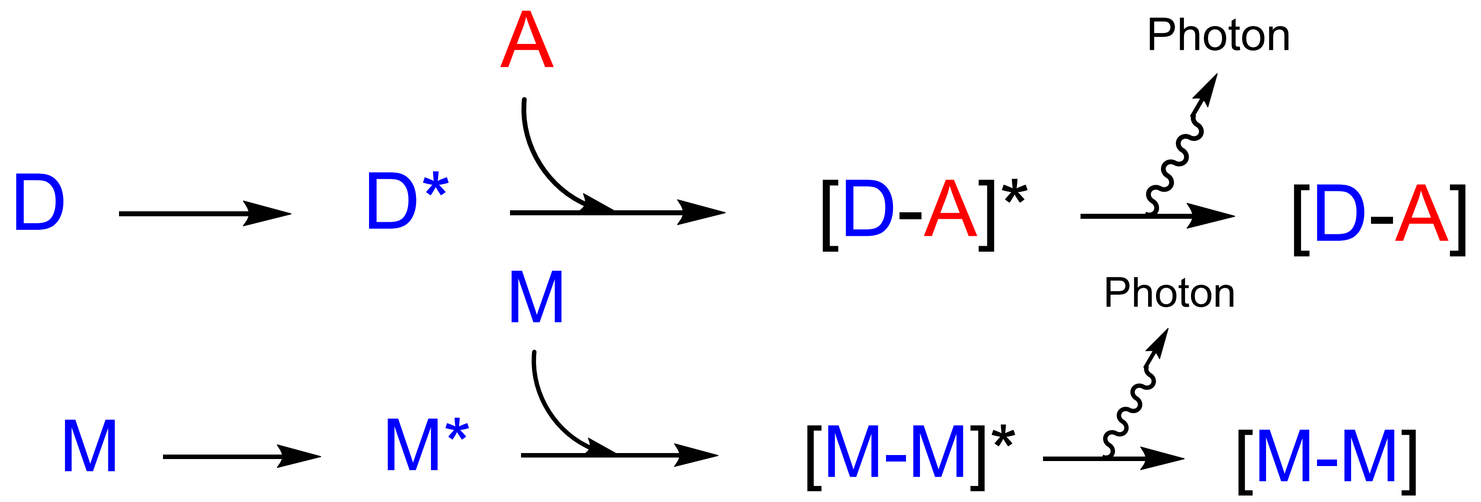
Definitions

Exciplex: A complex formed by the interaction of an excited molecular entity with a ground state counterpart of a different structure

Usually consists of a donor and an acceptor as contact ion pairs

Excimer: Dimers with associated excited electronic states, dissociative ground states

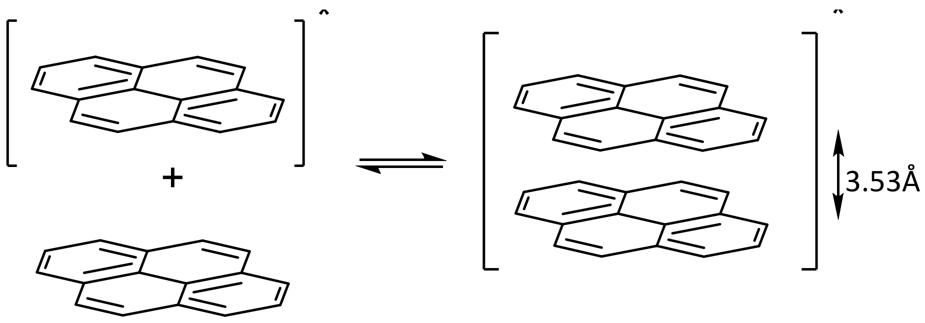
Excited states shared between dimers



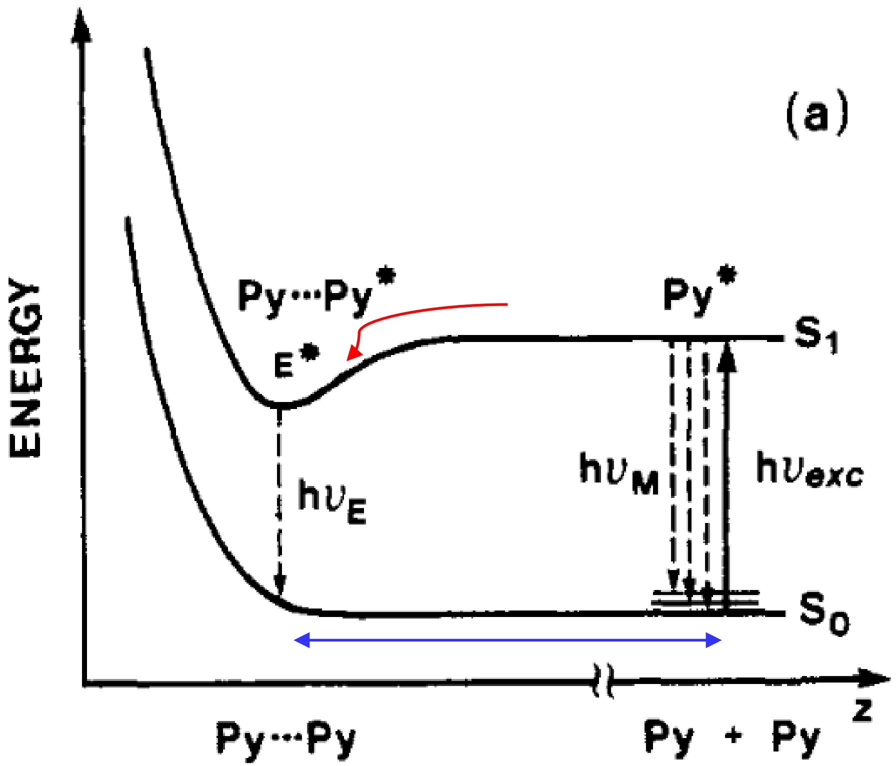
J., Waluk (**2020**). *Conformational Analysis of Molecules in Excited States*, Wiley

J. B. Birks, *Rep. Prog. Phys*. **1975**, 38, 903

Pyrene Excimer



Py* + Py [Py-Py]*



Ground state excimer has no energy gain to dimerization

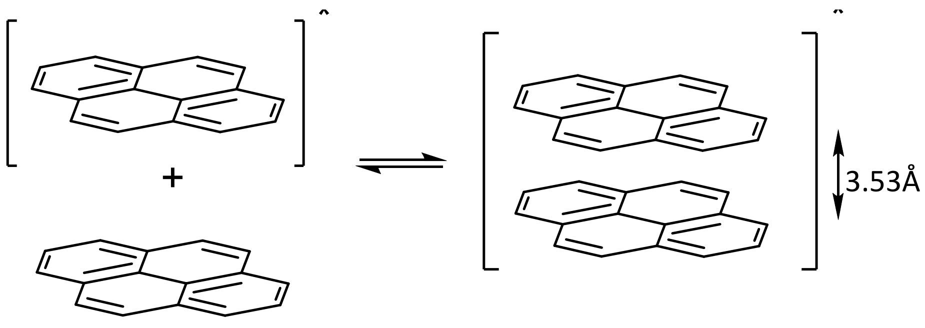
One excited monomer binding with a ground state monomer has net energy gain

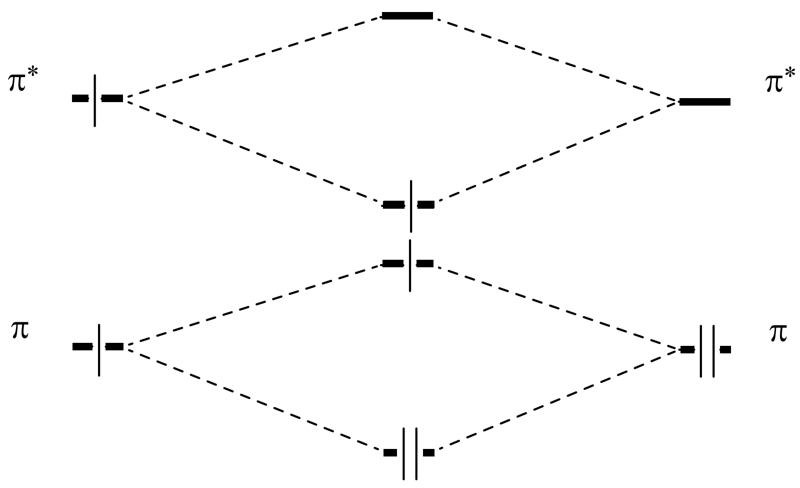
F. M. Winnik, *Chem. Rev.* **1993**, 93. 587-614

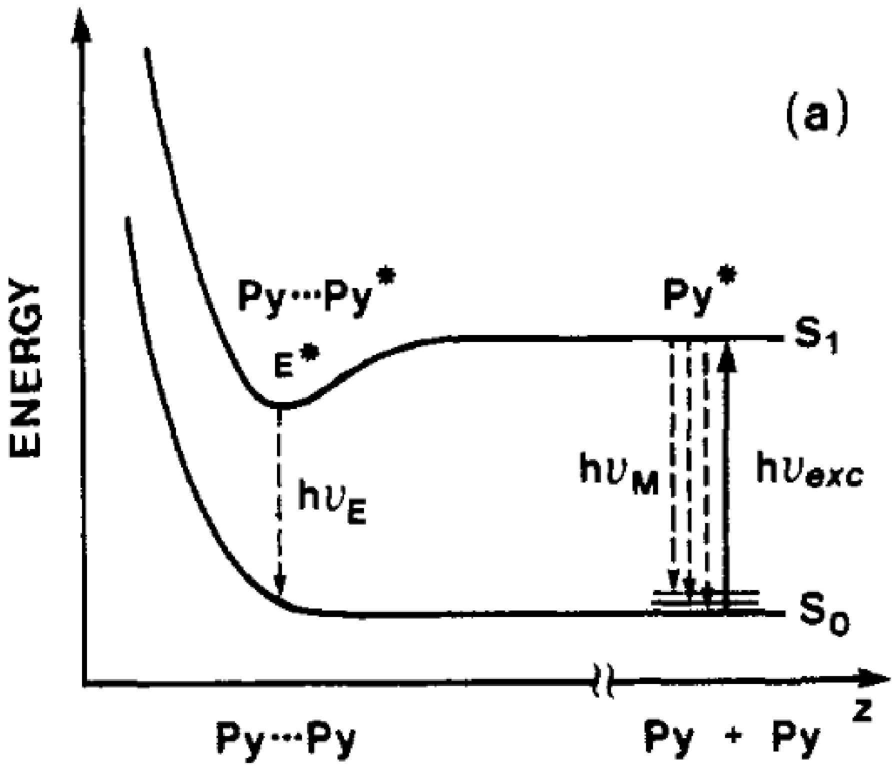
J. B. Birks, *Rep. Prog. Phys.* **1975**, 38, 903

D. A. Van Dyke; B. A. Pryor; P. G. Smith; M. R. Topp, *J. Chem. Educ*. **1998**, 75, 5, 615

Pyrene Excimer







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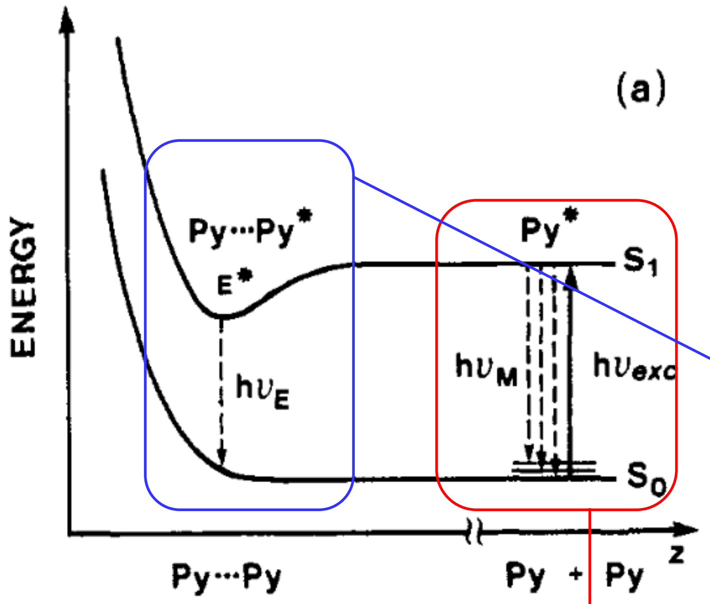
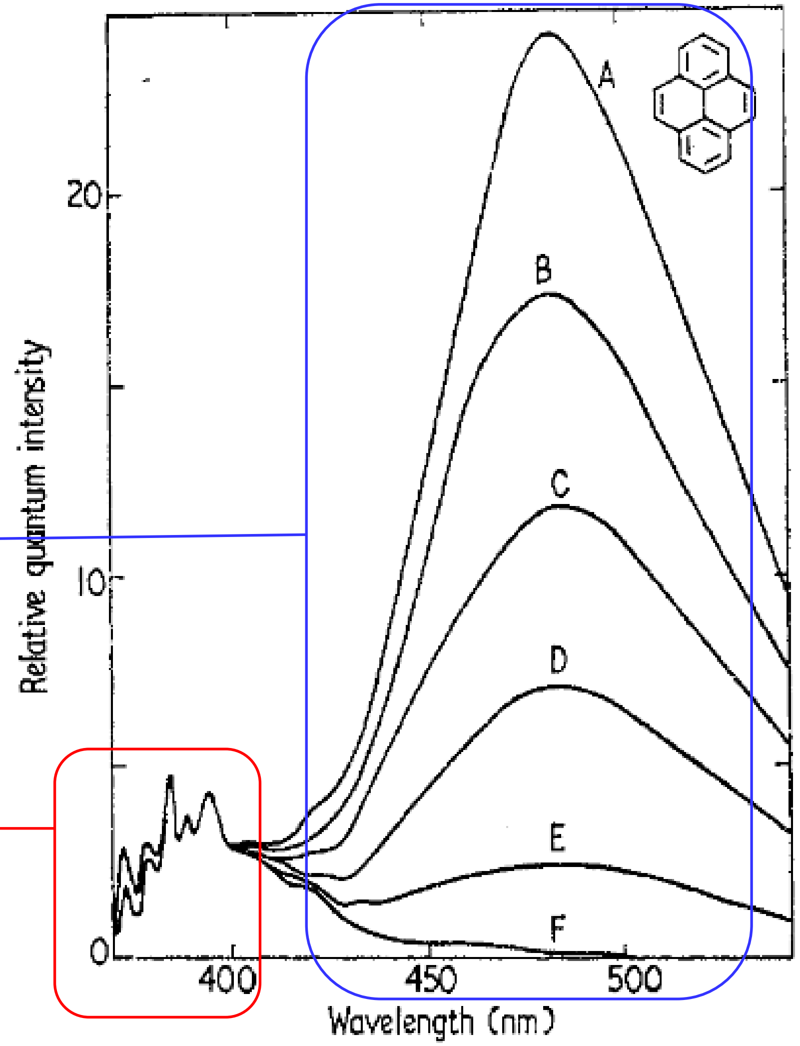


Broad fluorescence Non-discreet, which are Excimer emissions

Sharp fluorescence, allowed discreet transitions, characteristic in monomer Py



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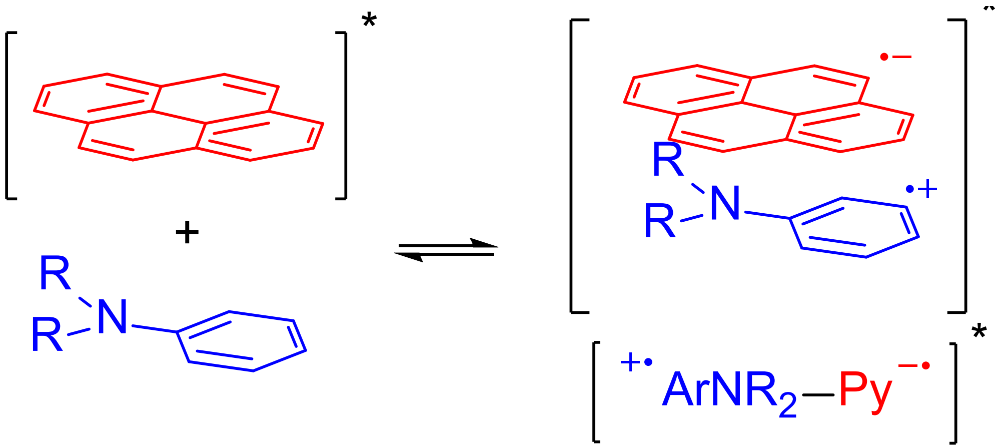
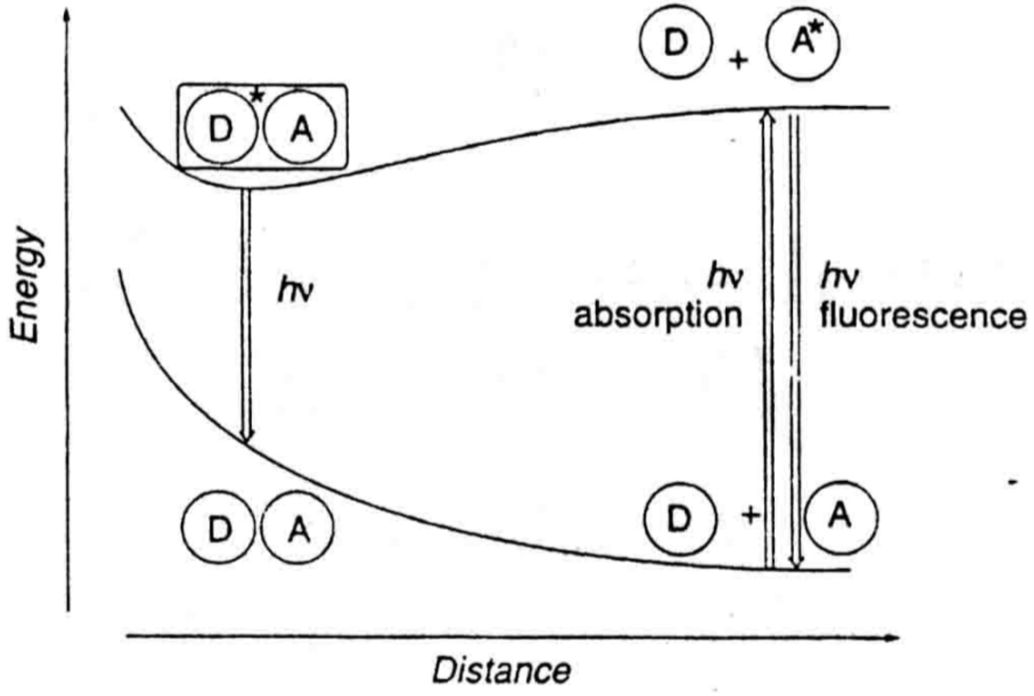
Exciplexes VS Excimers



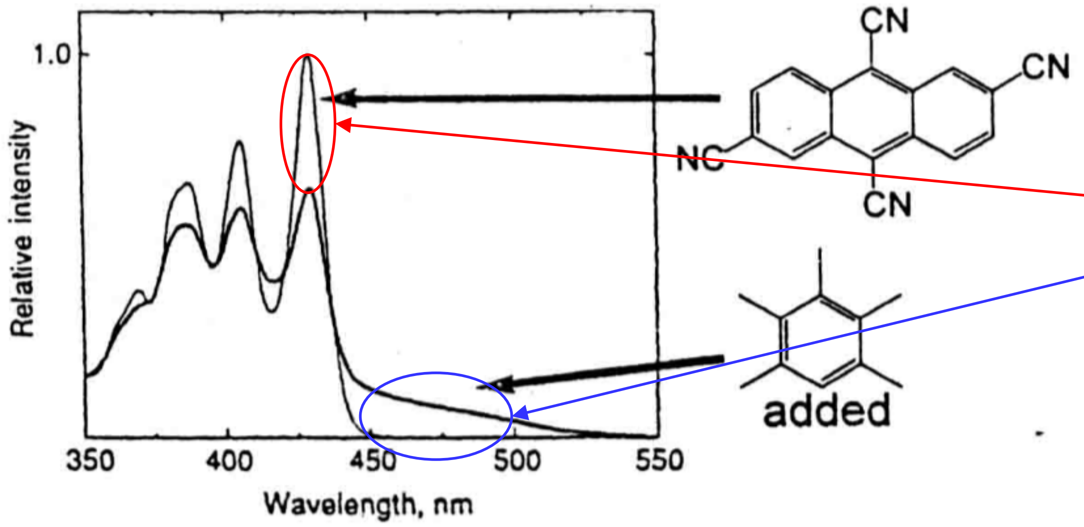


After a donor-acceptor complexation, an exciplex is formed, which can be described as a charged ion pair.

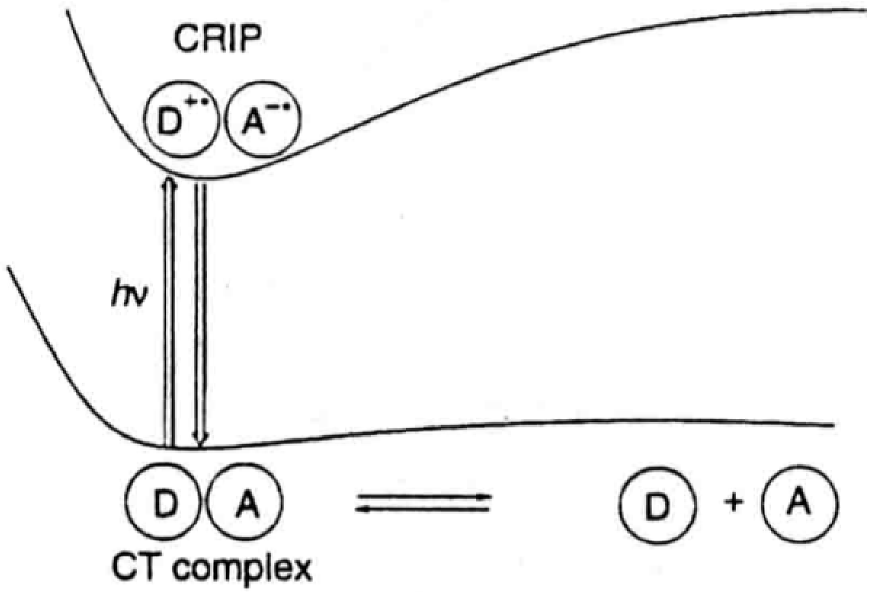
Intramolecular complexation has been referred to as exciplexes as well.

J., Waluk (**2020**). *Conformational Analysis of Molecules in Excited States*, Wiley

Exciplexes VS Excimers



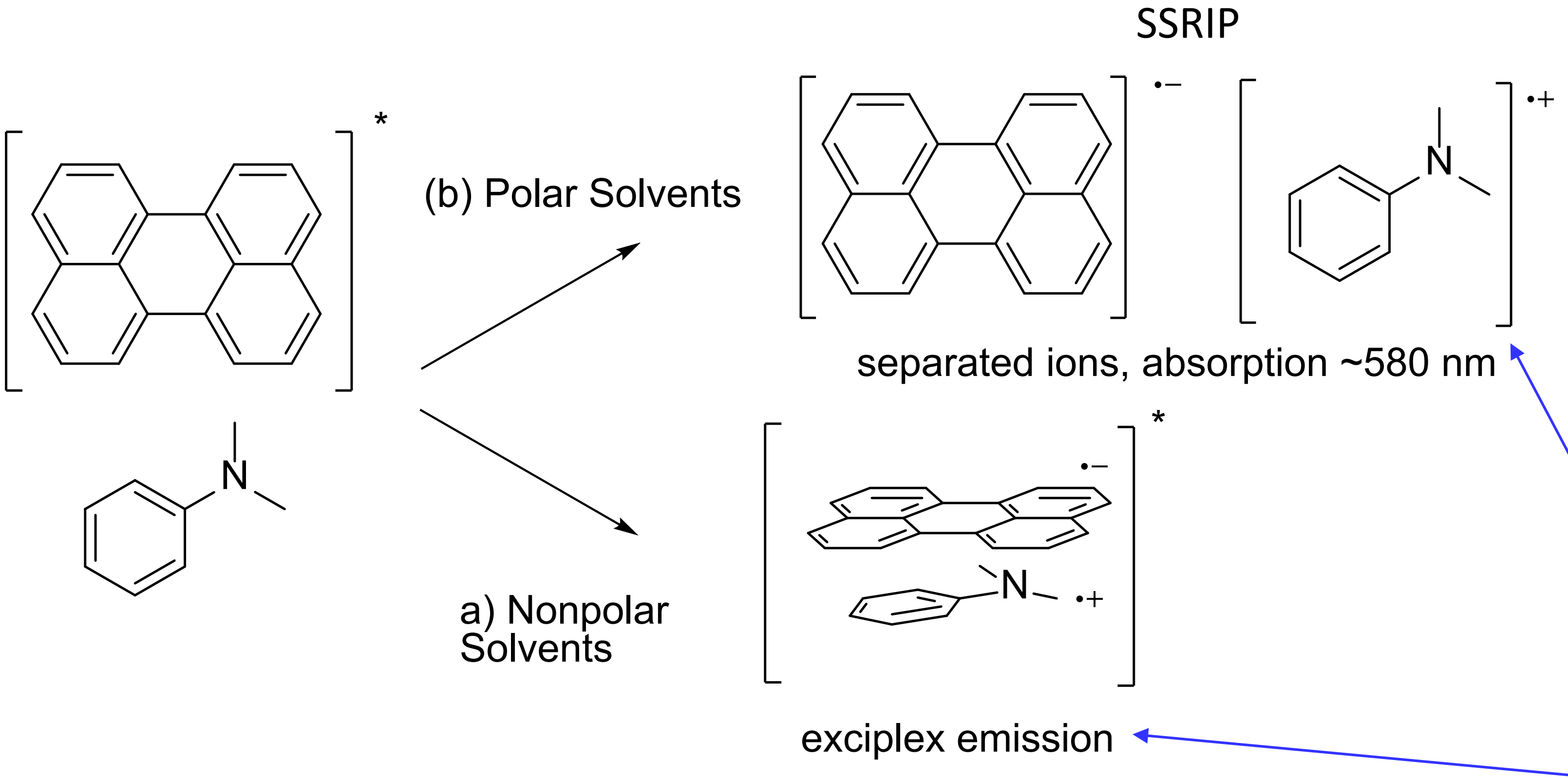
When pentamethylbenezene (donor) is added
Into tetracyanoanthracene (acceptor),
the discreet symmetry allowed transitions lowers and
CT absorptions can be observed

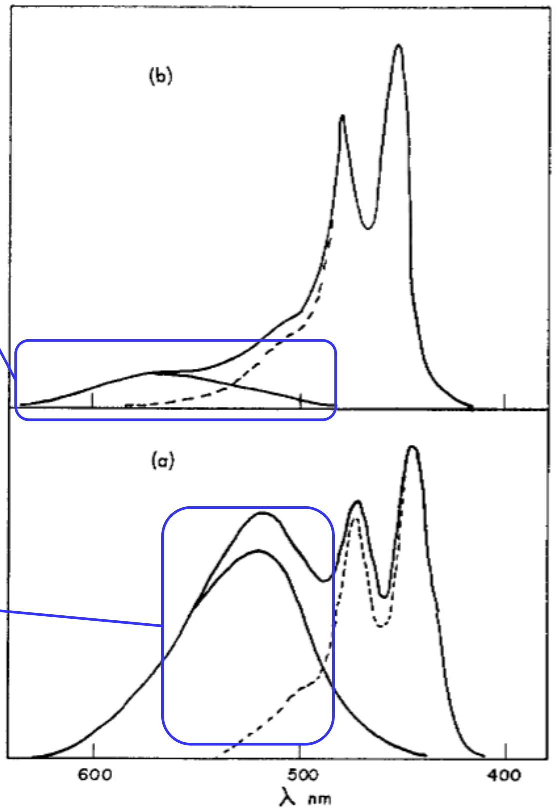


Unlike excimers, exciplexes can potentially lower energy
simply via complexation, depending on the substrate

J., Waluk (**2020**). *Conformational Analysis of Molecules in Excited States*, Wiley

Perylene and Dimethylaniline Exciplex

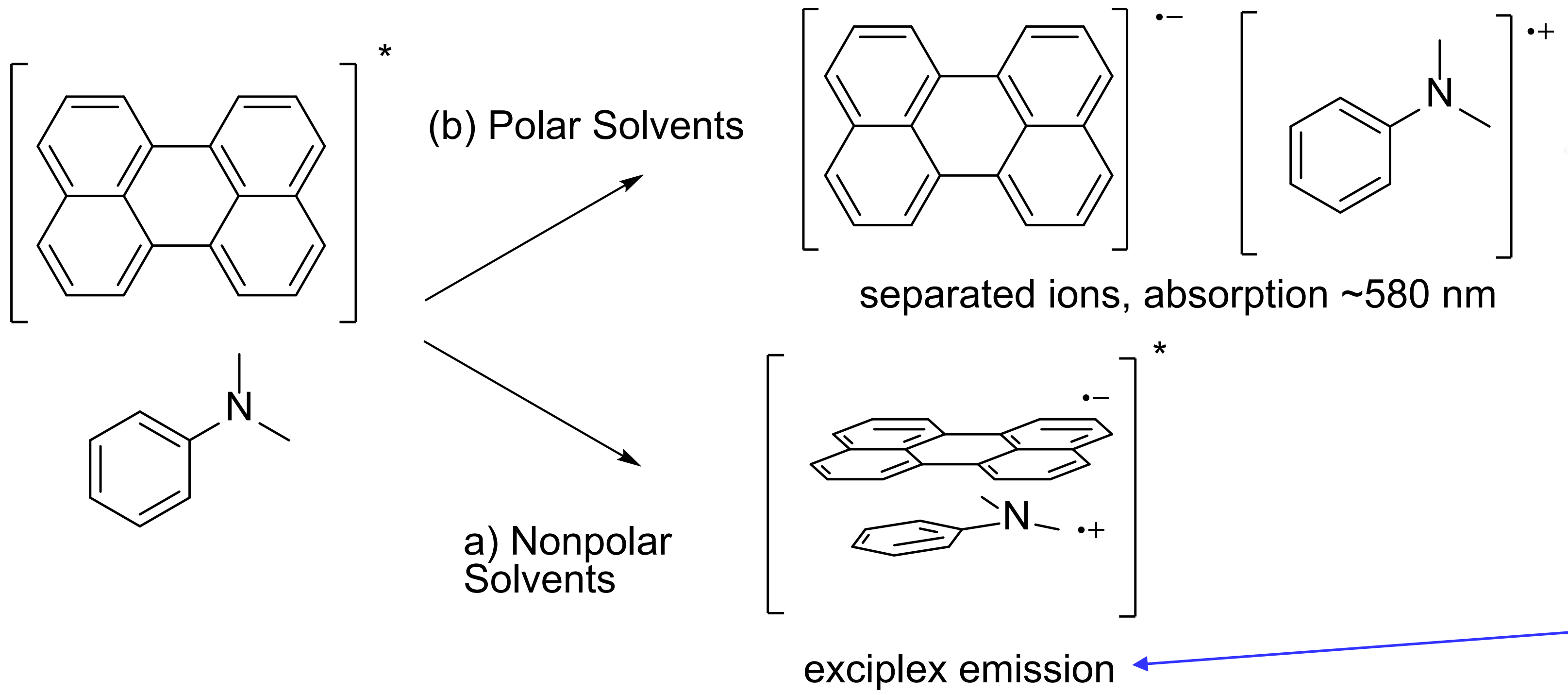


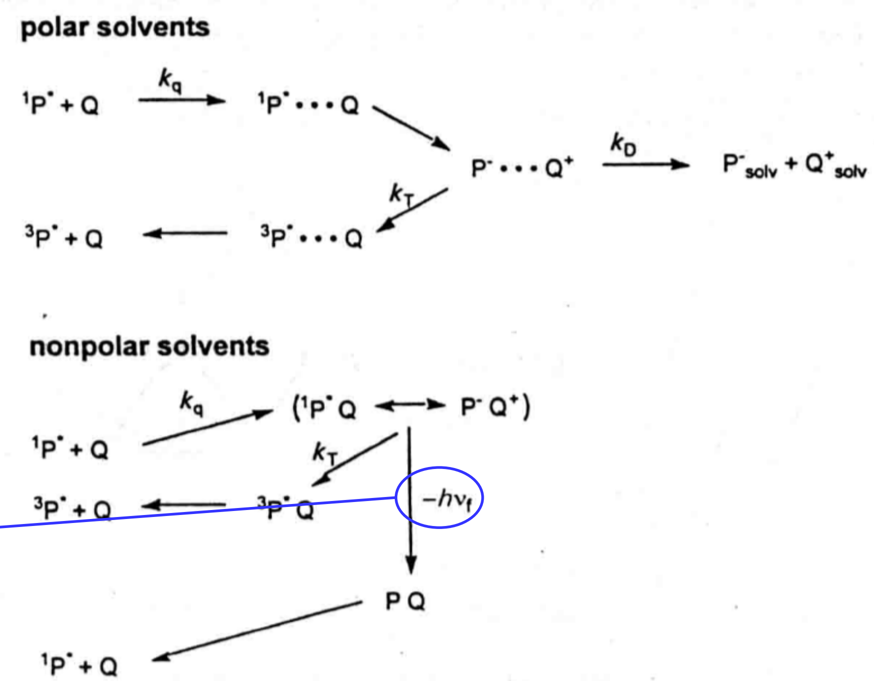


In polar solvents, the charged complexes can be separated and CT emission is greatly reduced

J., Waluk (**2020**). *Conformational Analysis of Molecules in Excited States*, Wiley
K. Yoshihara; K. Futamura; S. Nagakura *Chemistry Letters*, **1972**, 1243–1247
W. R. Ware; H. P. Richter *J. Chem. Phys*. 48, 1595–1601 (**1968**)

Perylene and Dimethylaniline Exciplex





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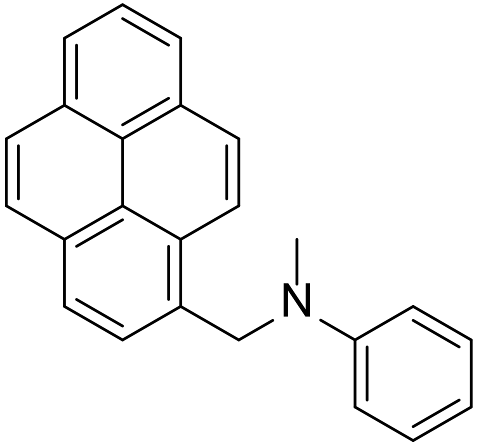
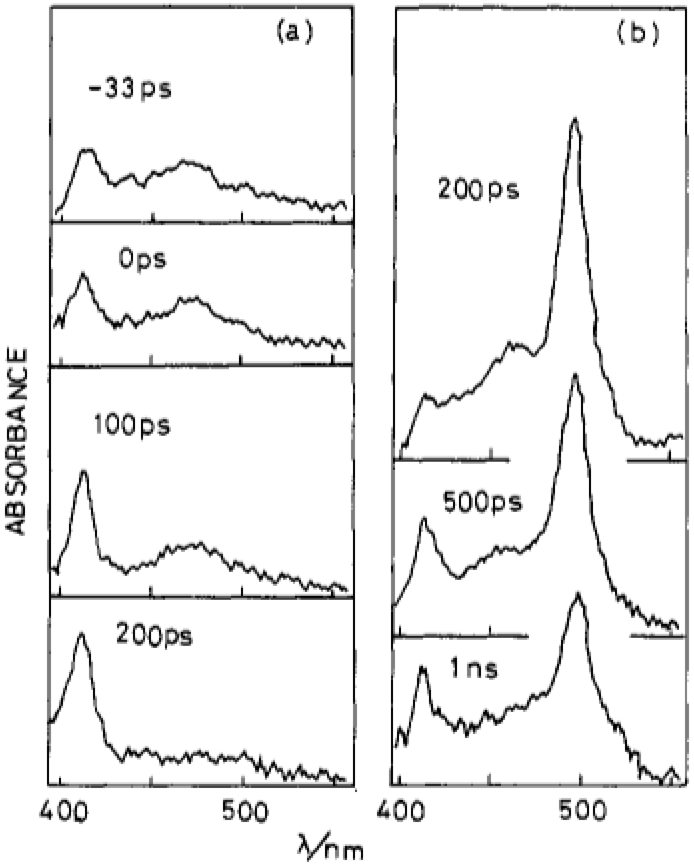
Connected Exciplexes





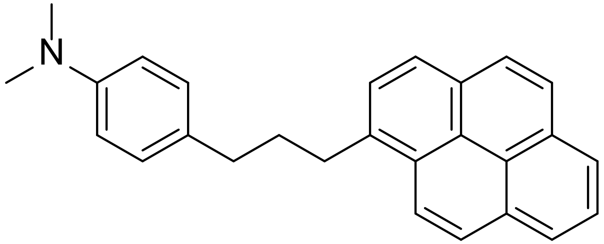
a) Hex　　b) ACN

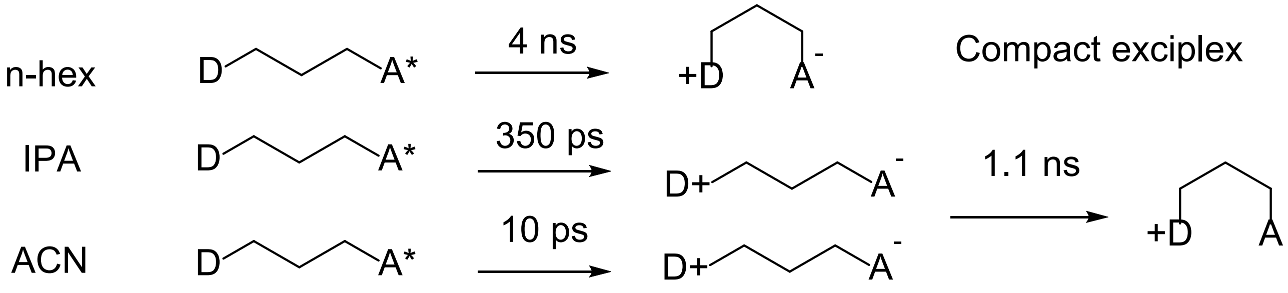
Triplet: 415 nm

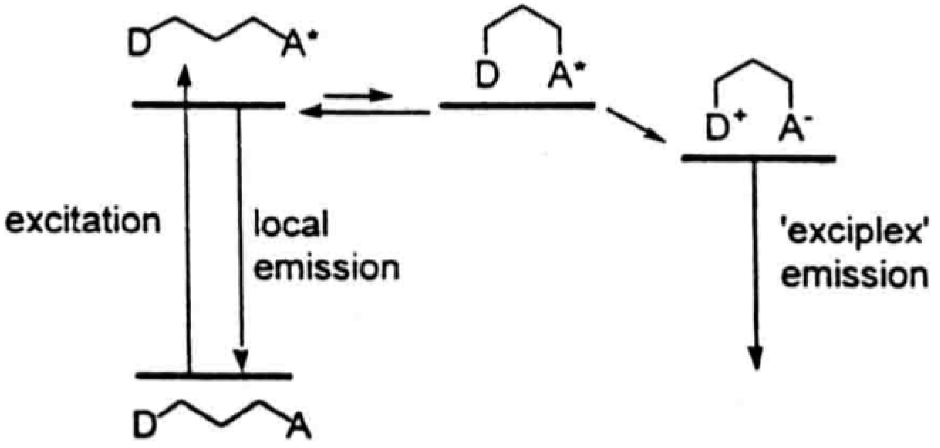
Exciplex emission: 500 nm

T., Okada; I., Karaki; E., Matsuzawa; N., Malaga; Y., Sakata; S., Misumi. *The Journal of Physical Chemistry*, Vol. 85, No. 26, **1981**

Connected Exciplexes







In close proximities, exciplex state decays to triplet states and is observed by emission spec (~300 ps)

In longer chains, the 2 sites need to fold to a specific geometry just to interact and emit

Polar solvents can directly access loose ion pairs and

J., Waluk (**2020**). *Conformational Analysis of Molecules in Excited States*, Wiley

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- Synthesis Usages

- Perspective

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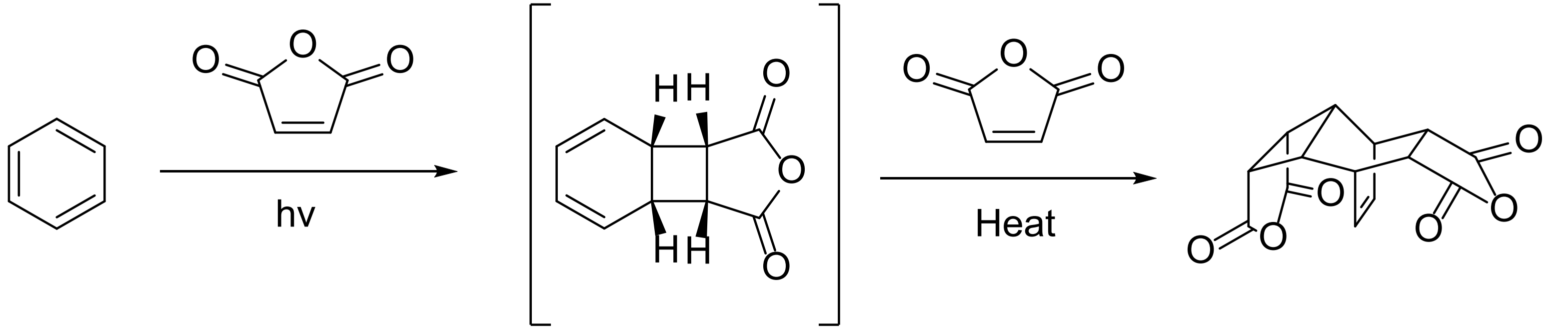
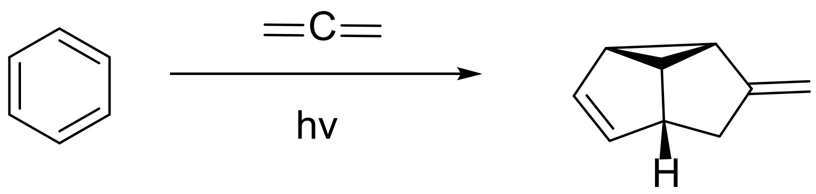
- Synthesis Usages

Photochemistry of Benzene

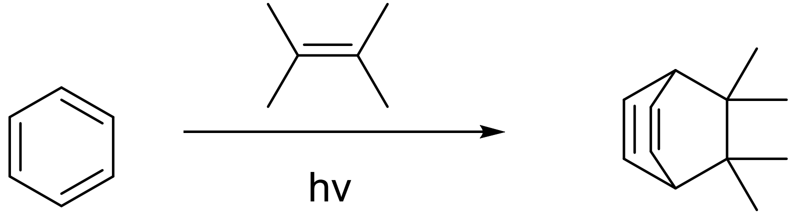
1959: Ortho [2+2] cycloaddition



1966: Meta [2+3] cycloaddition

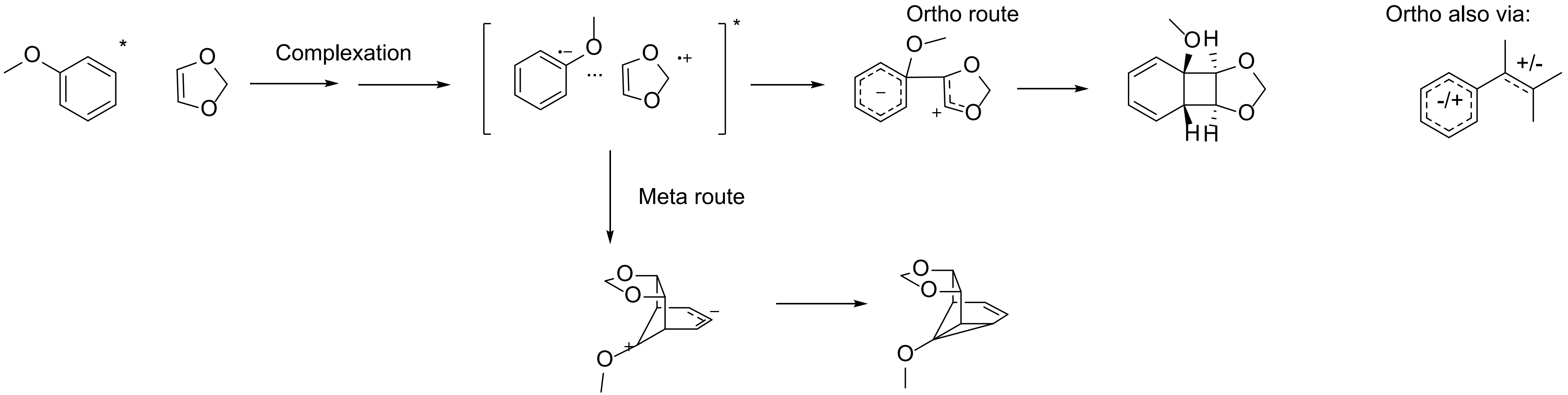


1971: Para [2+4] cycloaddition

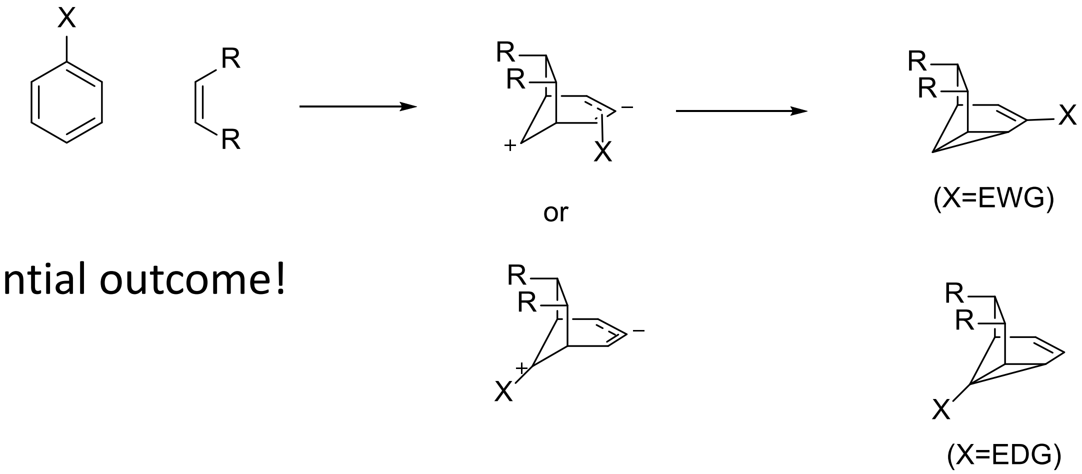


Angus, H. J. F.; Bryce-Smith, D. *Proc. Chem. Soc. London* **1959**, 326–327
D. Bryce-Smith, A. Gilbert, B. H. Orger, *Chem. Commun*. **1966**, 512 - 514
K. E. Wilzbach, L. Kaplan, *J. Am. Chem. Soc*. **1971**, 93, 2073 - 2074

Mechanism



Anecdotal evidence:

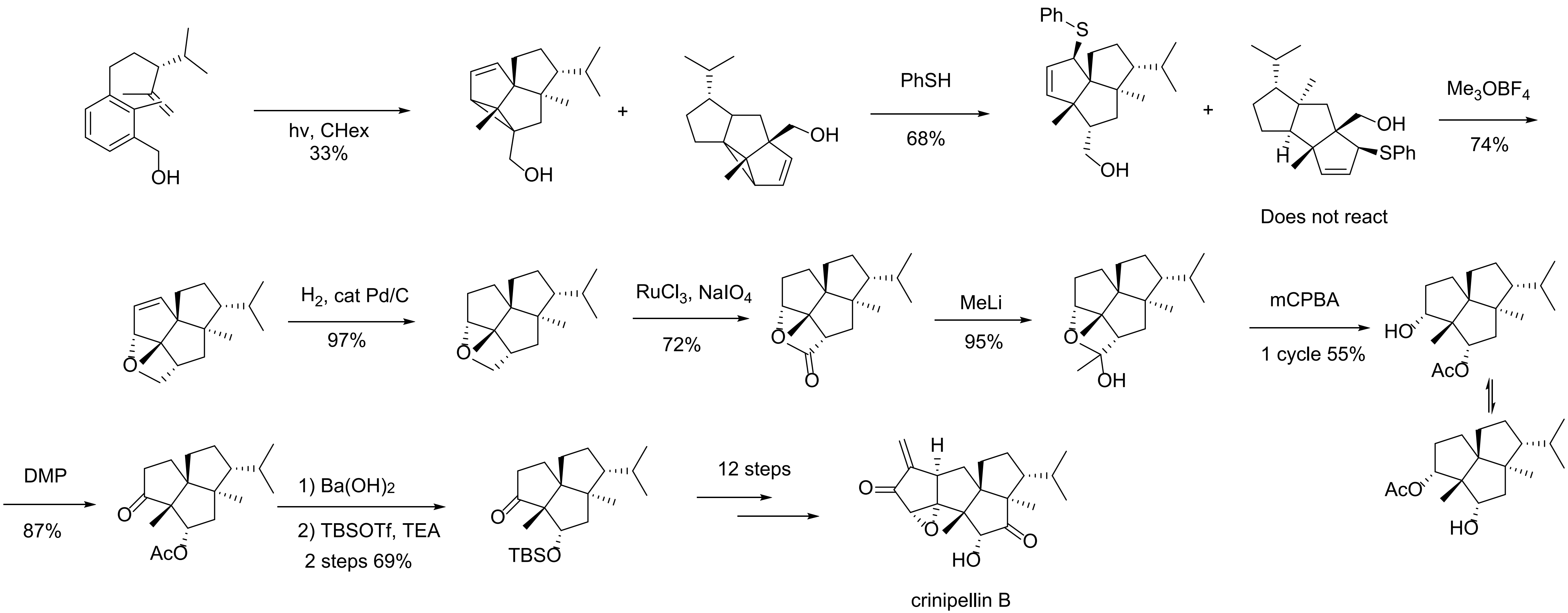


EDG and EWG drastically changes the potential outcome!

Mattay, J. *J. Photochem*. **1987**, 37, 167

Mattay, J. *Angew. Chem. Int. Ed*. **2007**, 46, 663 – 665

Arene-Alkene Meta addition to Access Crinipellin B



Crinipellin antibiotics, which are active against gram-positive bacteria, yeasts, filamentous fungi, and Ehrlich carcinoma ascites cells

P., A., Wender; T., M., Dore. *Tet Let* 39 (**1998**) 8589-8592

P., E.; Renaud, J. *J. Org. Chem*. **1993**, 58, 11-13

Summary

Photochemical methods can be used to access exotic chemical reactivities

By leveraging the elusive reactivity of excited state species, one can

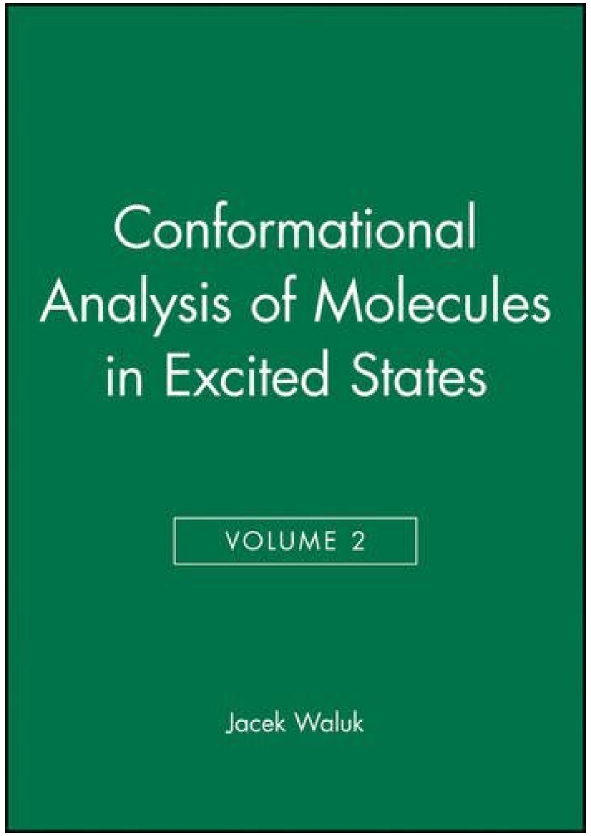
Even without activation, a simple mixture of compounds in solvents allow for interesting spectroscopic results

Thank You

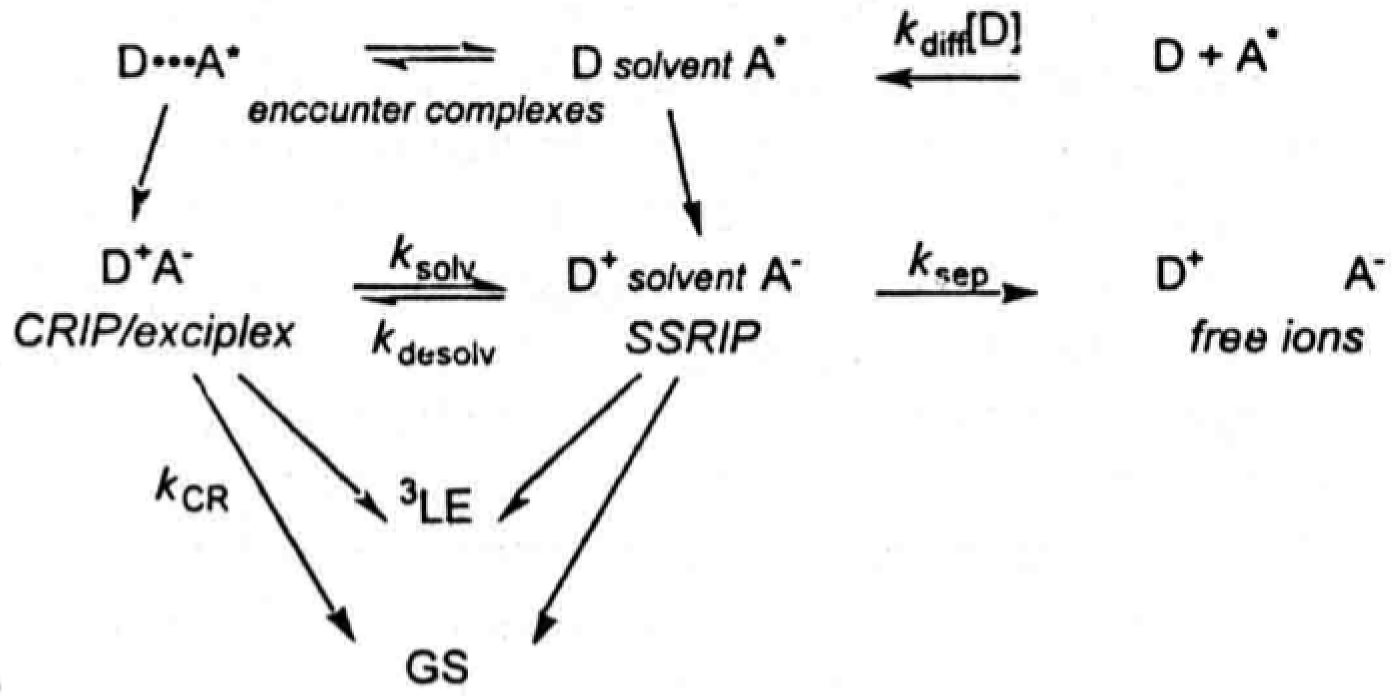
Further Reading

Thorsten Bach’s Review, informative on physical organic principles of exciplexes:
Chem. Rev. 2022, 122, 1626−1653

Chapter 4 was the main reference for this presentation, heavy on physical chemistry:



Backup slides



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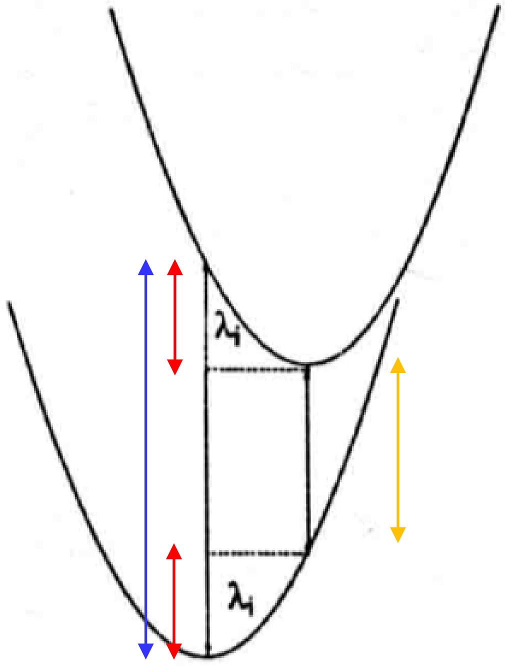

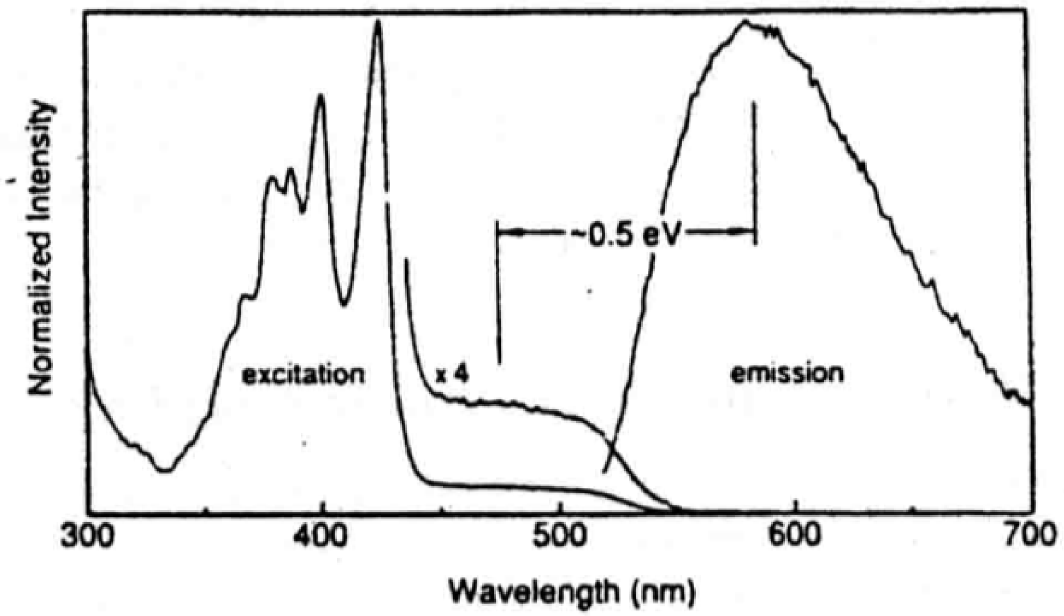

Between the excited and ground state, the energy difference between absorption and emission is twice that of the reorganization energy.
In nonpolar solvents, it's contribution to the reorganization energy is negligible, so it can be simply measured using emission spec