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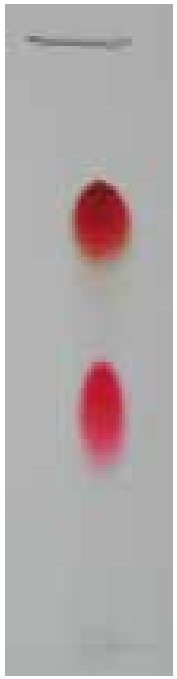
Ludwig Maximilians – Universität München

Novel Perylene and Naphthalene Fluorescent Dyestuffs by the Control with Peripheral Substituents

esthetics

functionality



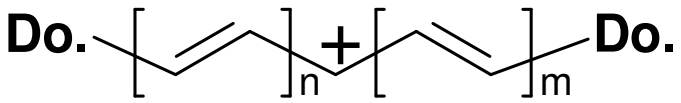
rationalization
and progress

Why dye chemistry?

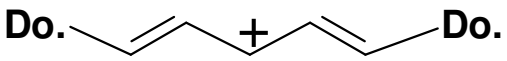
Colorants, pigments, dyes, chromophores, synthesis, analysis, photophysics, ...

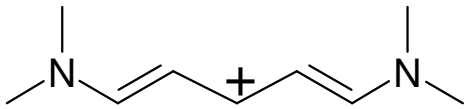
The Light of Knowledge

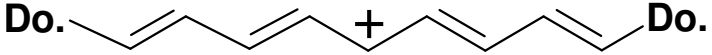
The electronen donor acceptor concept for bathochromic light absorption
(W. König and W. Ismailsky in Dresden/Germany 1913 and 1925)

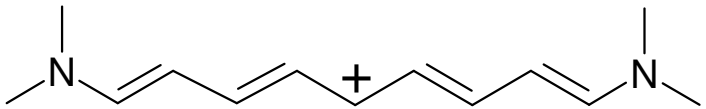


Standard arrangement







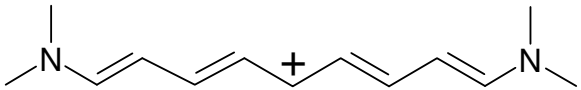


Cyanines
Problem: Stability

The Basic Therory of Dyes [1,2]

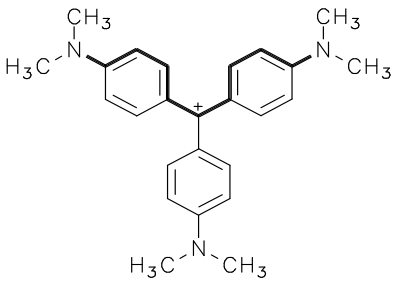
[1] W. König, *J. Prakt. Chem.* **1926**, *112*, 1-36; *Chem. Abstr.* **1926**, *20*, 8668.
[2] W. Ismailsky, *PhD Thesis*, University Dresden, **1913**.

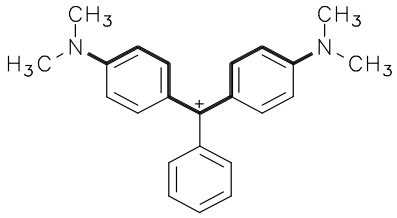
Stabilization with aromatics



Standard arrangement

Examples:





Crystal violet·(λ_{max} = 590 nm)

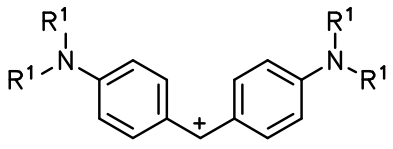
C.I. 42555

Malachite green (λ_{max} = 625 and 423 nm)

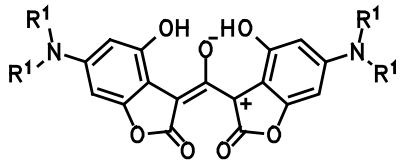
C.I. 42000

The Basic Therory of Dyes [1,2]

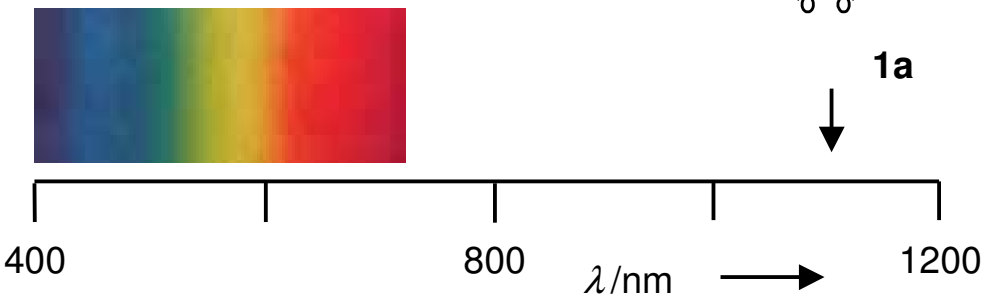
[1] W. König, *J. Prakt. Chem.* **1926**, *112*, 1-36 ; *Chem. Abstr.* **1926**, *20*, 8668.
[2] W. Ismailsky, *PhD Thesis*, University Dresden, **1913**.

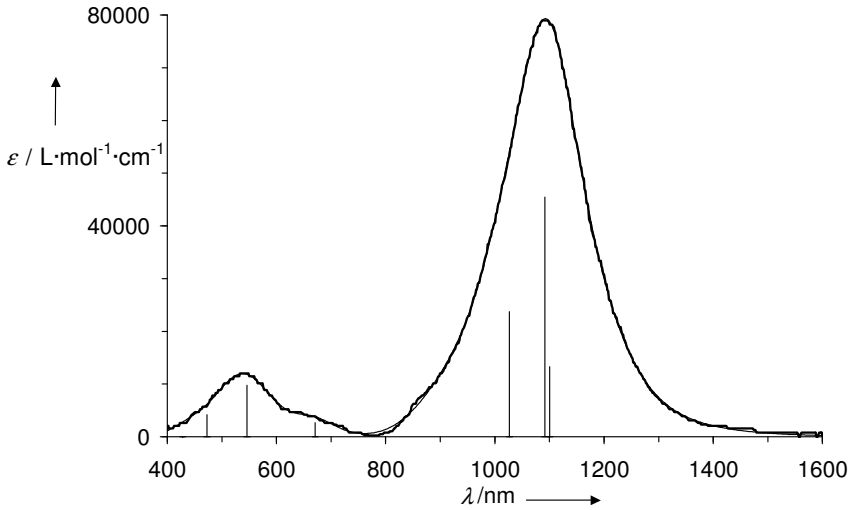


625 nm



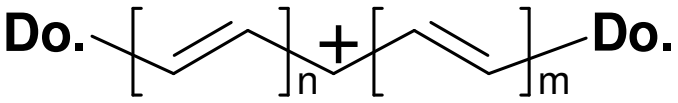
1a



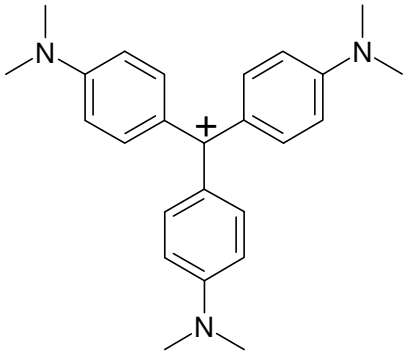


Super Acceptor Groups [1,2]

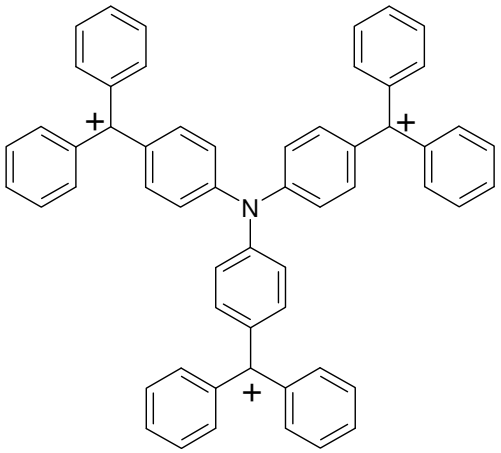
[1] M. Tian, S. Tatsuura, M. Furuki, I. Iwasa, L. S. Pu, *J. Am. Chem. Soc.* **2003**, *124*, 348-349.
[2] H. Langhals, *Angew. Chem.* **2003**, *115*, 4422-4424; *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 4286-4288.



Standard arrangement



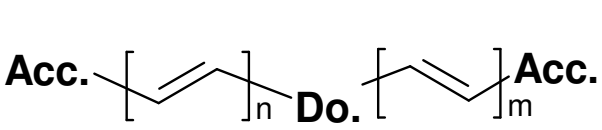
Inverse arrangement

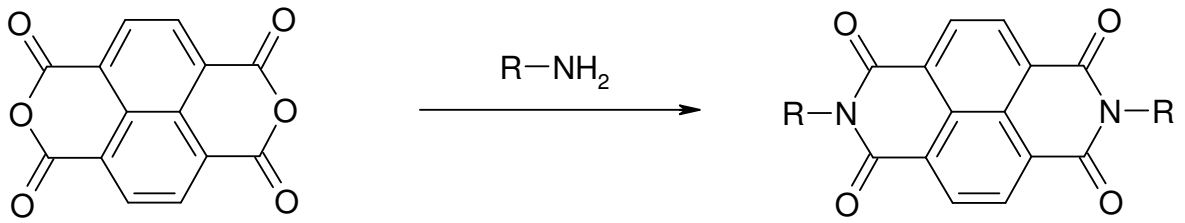


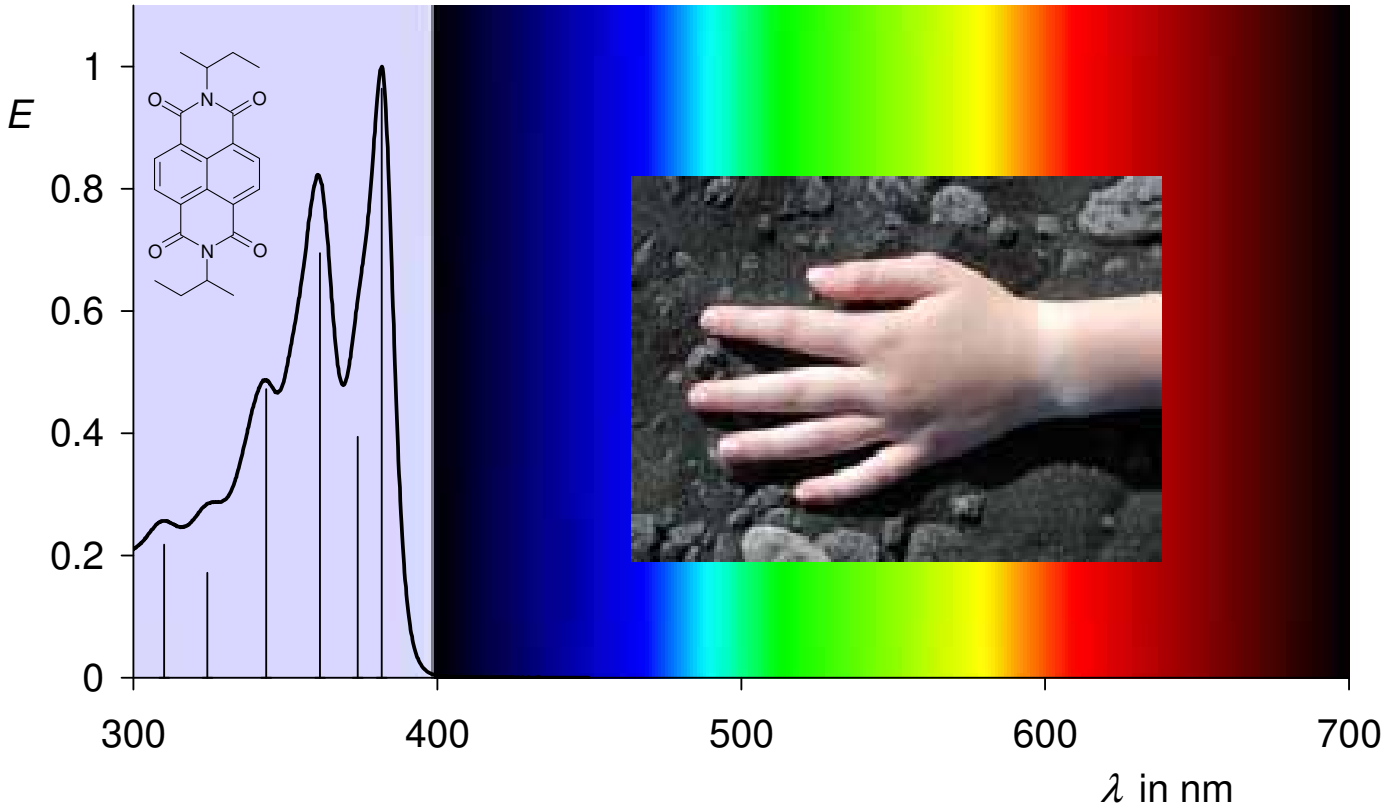
D. Hellwinkel, H. Stahl, H. G. Gaa, R. Gottfried, *Phosphorus Sulfur* **1983**, *18*, 121-124; *Chem. Abstr.* **1984**, *101*, 22633.
D. Hellwinkel, H. G. Gaa, R. Gottfried, *Zeitschr. f. Naturforsch., B* **1986**, *41B*, 1045-1060.

Inversely Arranged Dyes? [1]

[1] H. Langhals, *Angew. Chem.* **2003**, *115*, 4422-4424; *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 4286-4288.





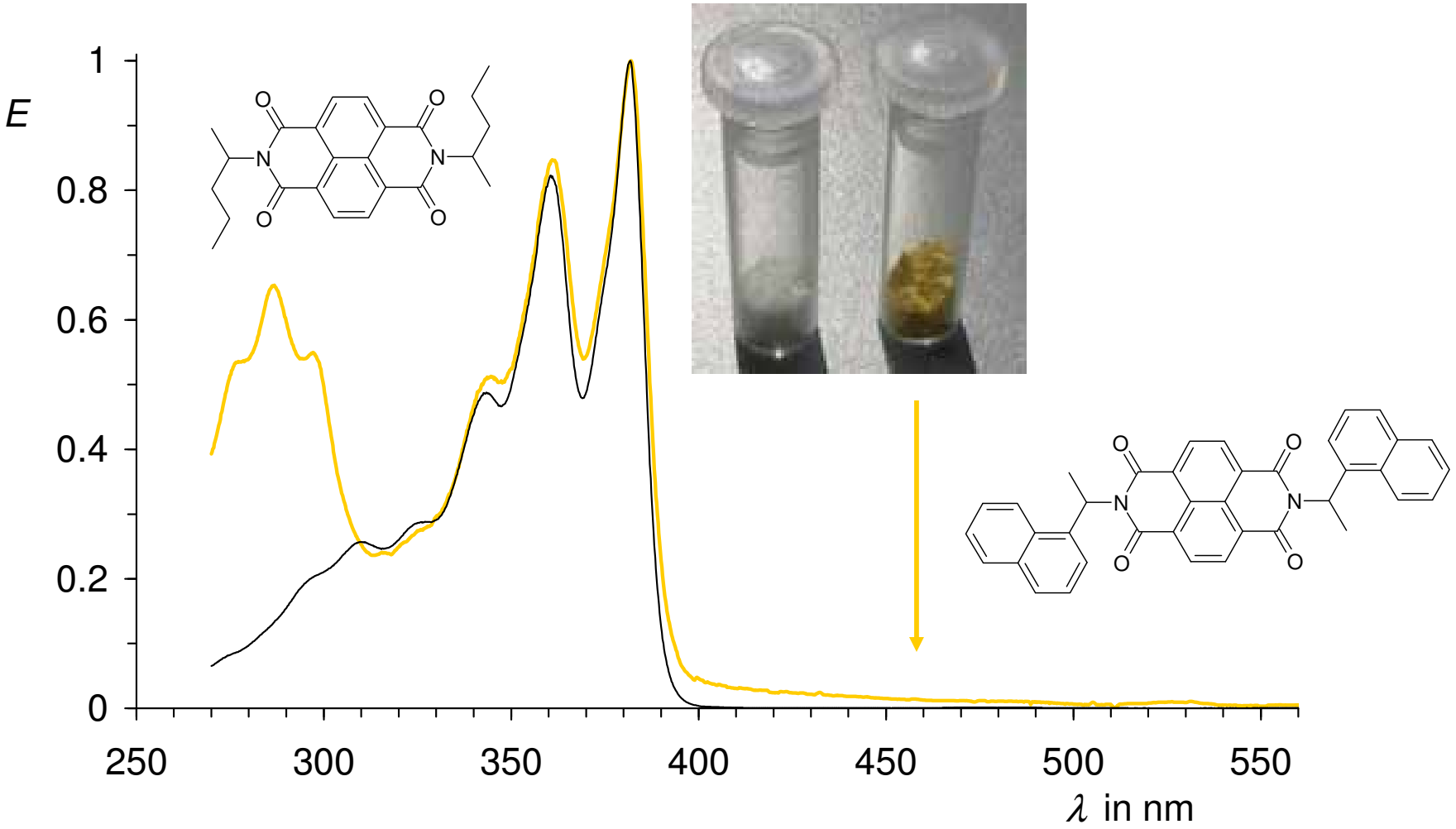


UVA protection

H. Langhals, H. Jaschke, *Ger. Offen,* DE 102005034685.5 (July 25, **2005**).

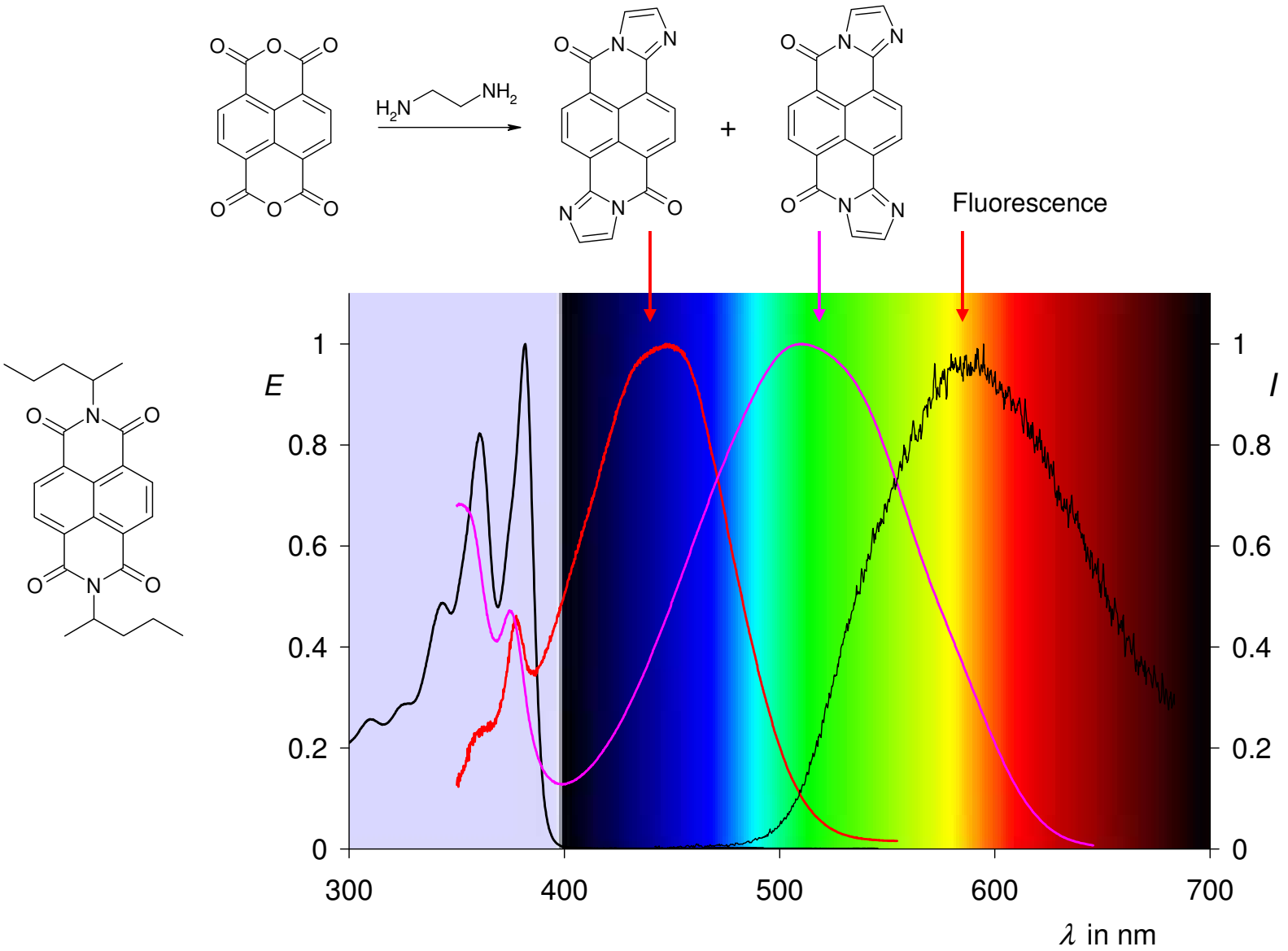
Stabilization of Inversely Arranged Dyes [1]

[1] H. Langhals, H. Jaschke, *Chem. Eur. J.* **2006**, *12*, 2815-2824.



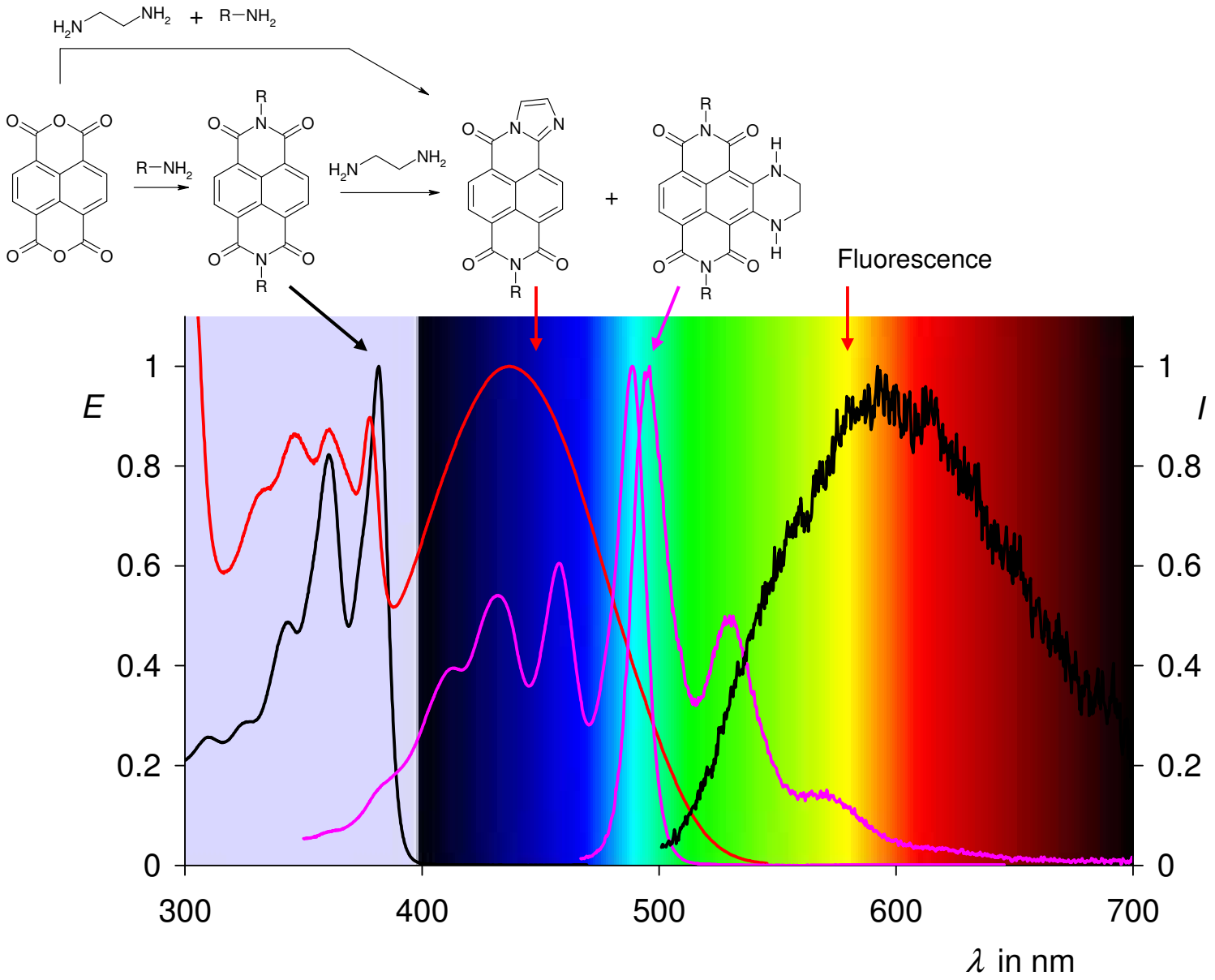
Dyes from Naphthalene Bisimides? Exciton Interactions.

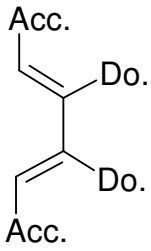
[1] H. Langhals, H. Jaschke, *Chem. Eur. J.* **2006**, *12*, 2815-2824.



Naphthalene Amidines

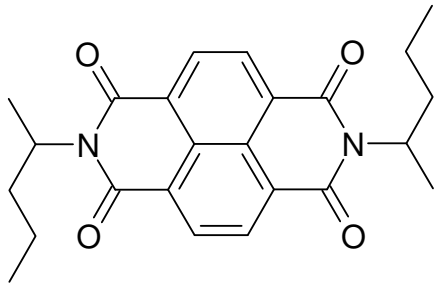
[1] H. Langhals, H. Jaschke, *Chem. Eur. J.* **2006**, *12*, 2815-2824.

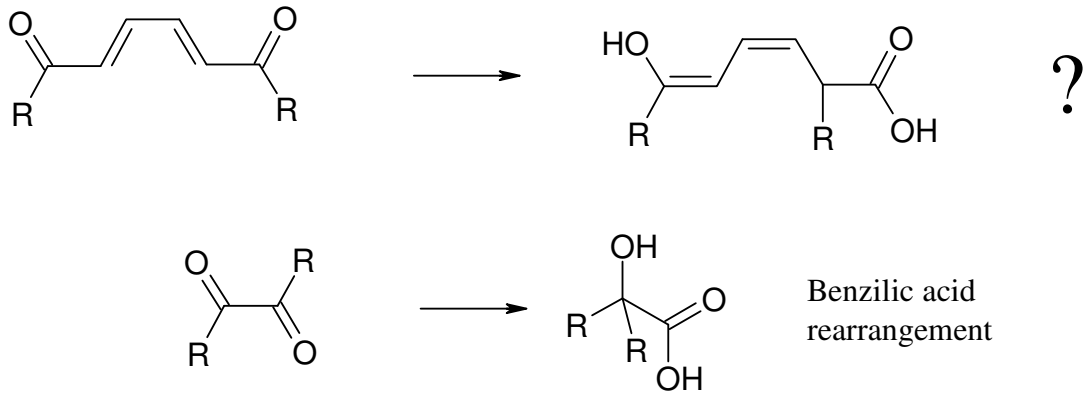




Naphthalene Bisimides with Donor Groups

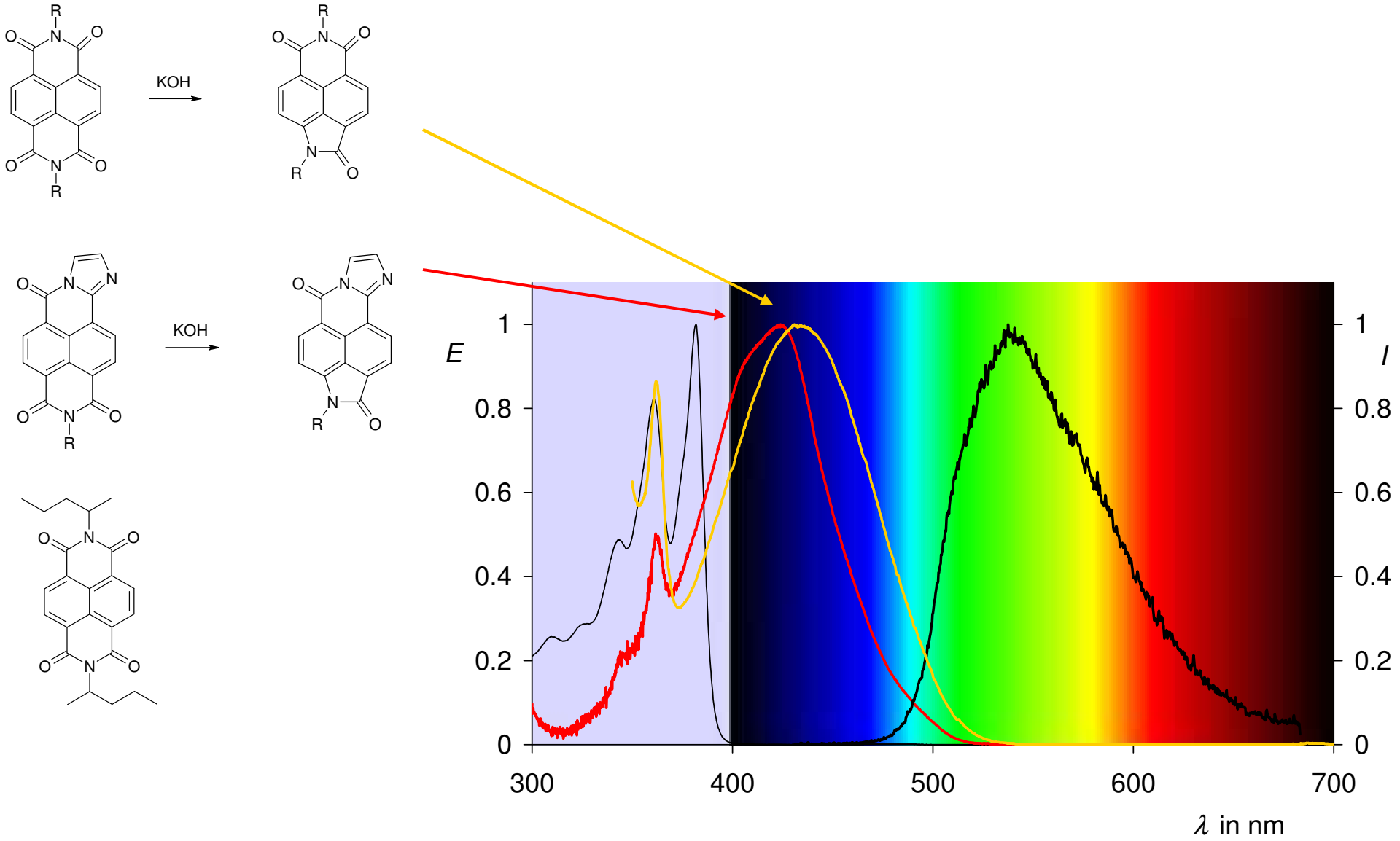
[1] H. Langhals, H. Jaschke, *Chem. Eur. J.* **2006**, *12*, 2815-2824.





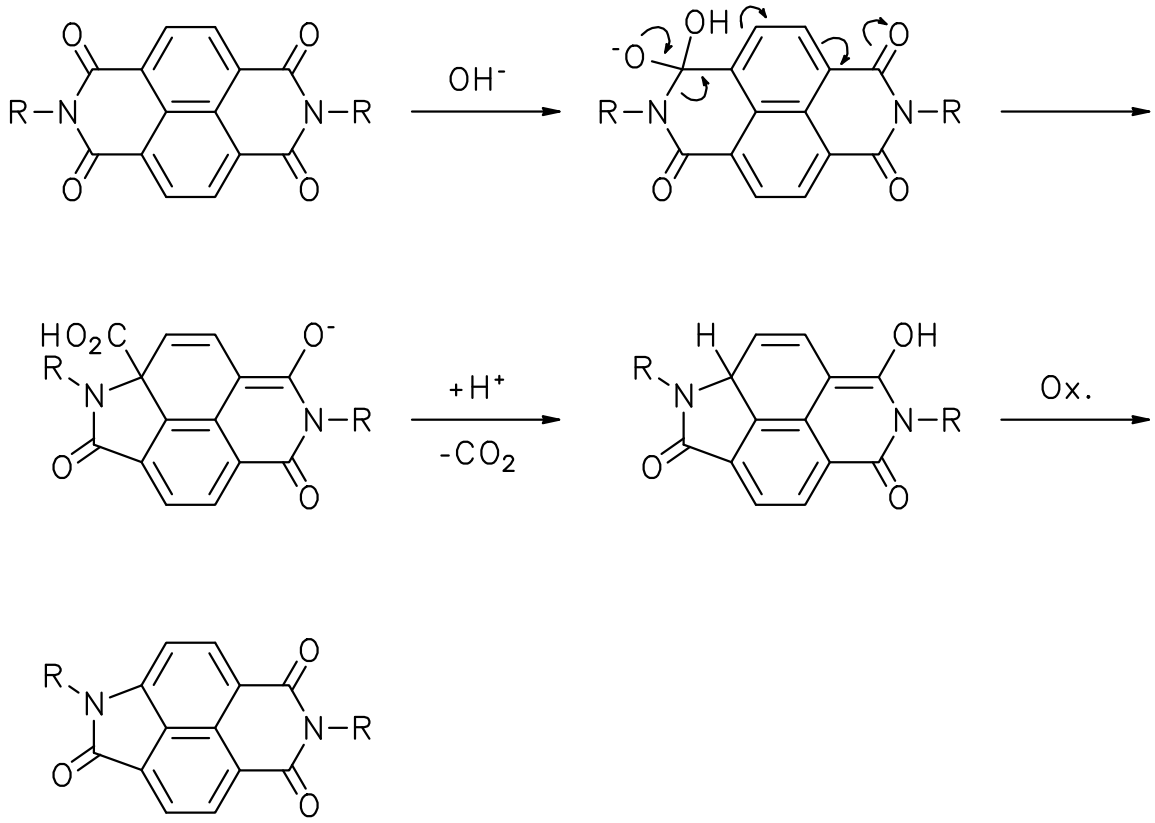
Novel Rearrangement

[1] H. Langhals, P. v. Unold,*Angew. Chem.* **1995**, *107*, 2436-2439; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2234-2236.
[2] H. Langhals, P. von Unold, *GIT Fachz. Lab.* **1997**, *41*, 974-978; *Chem. Abstr.* **1997**, *127*, 331413n.
[3] Calculations: P. Ponce, L. Fomina, S. Fomine, *J. Phys. Org. Chem.* **2001**, *14*, 657-666.



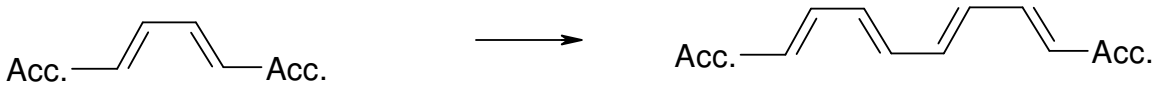
Rearranged Naphthalene Bisimides

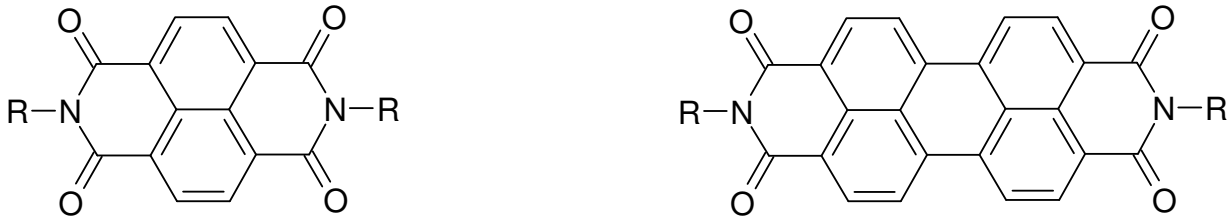
[1] H. Langhals, H. Jaschke, *Chem. Eur. J.* **2006**, *12*, 2815-2824.



Mechanism of the Novel Rearrangement [1-3]

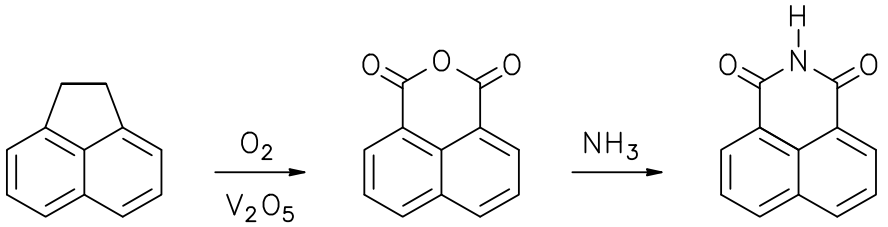
[1] H. Langhals, P. v. Unold, *Angew. Chem.* **1995**, *107*, 2436-2439; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2234-2236.
[2] H. Langhals, P. von Unold, *GIT Fachz. Lab.* **1997**, *41*, 974-978; *Chem. Abstr.* **1997**, *127*, 331413n.
[3] Calculations: P. Ponce, L. Fomina, S. Fomine, *J. Phys. Org. Chem.* **2001**, *14*, 657-666.

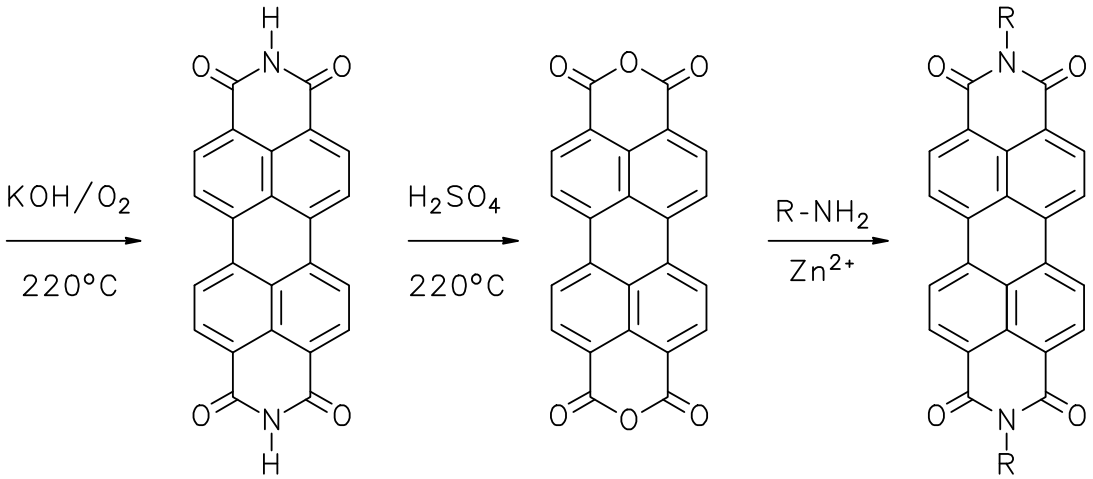




Extended Chromophore

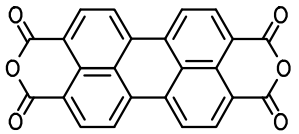
Review: H. Langhals, *Helv. Chim. Acta* **2005**, *88*, 1309-1343.



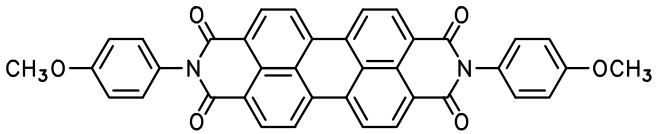


The Synthesis of Perylene Dyes [1,2]

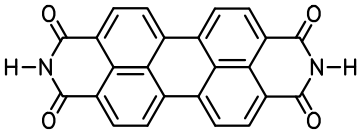
[1] Review: H. Langhals, *Heterocycles* **1995**, *40*, 477-500.
[2] Review: H. Langhals, *Helv. Chim. Acta* **2005**, *88*, 1309-1343.



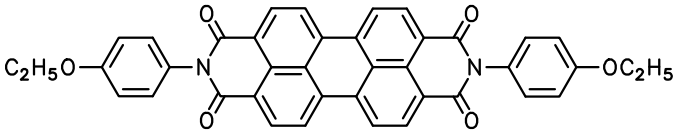
C.I. 71127
Pigment Red 224



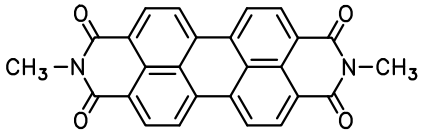
C.I. 71140
Pigment Red 190



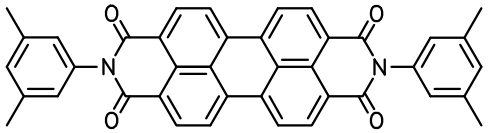
C.I. 71129
Pigment Violet 29



C.I. 71145
Pigment Red 123



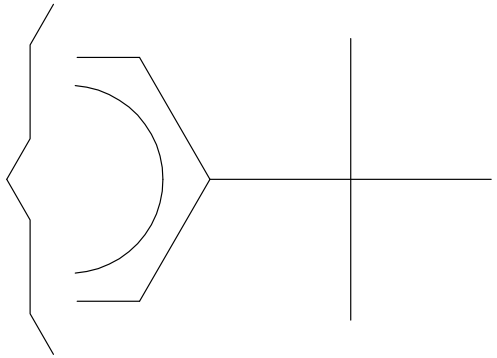
C.I. 71130
Pigment Red 179

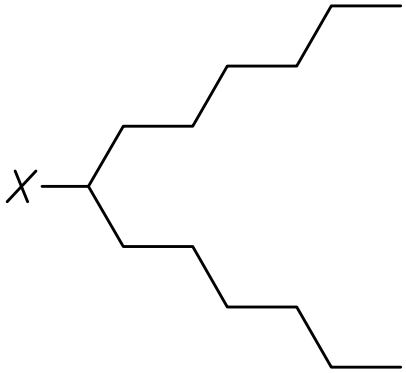


C.I. 71137
Pigment Red 149

Some Technical Perylene Pigments

Insoluble materials



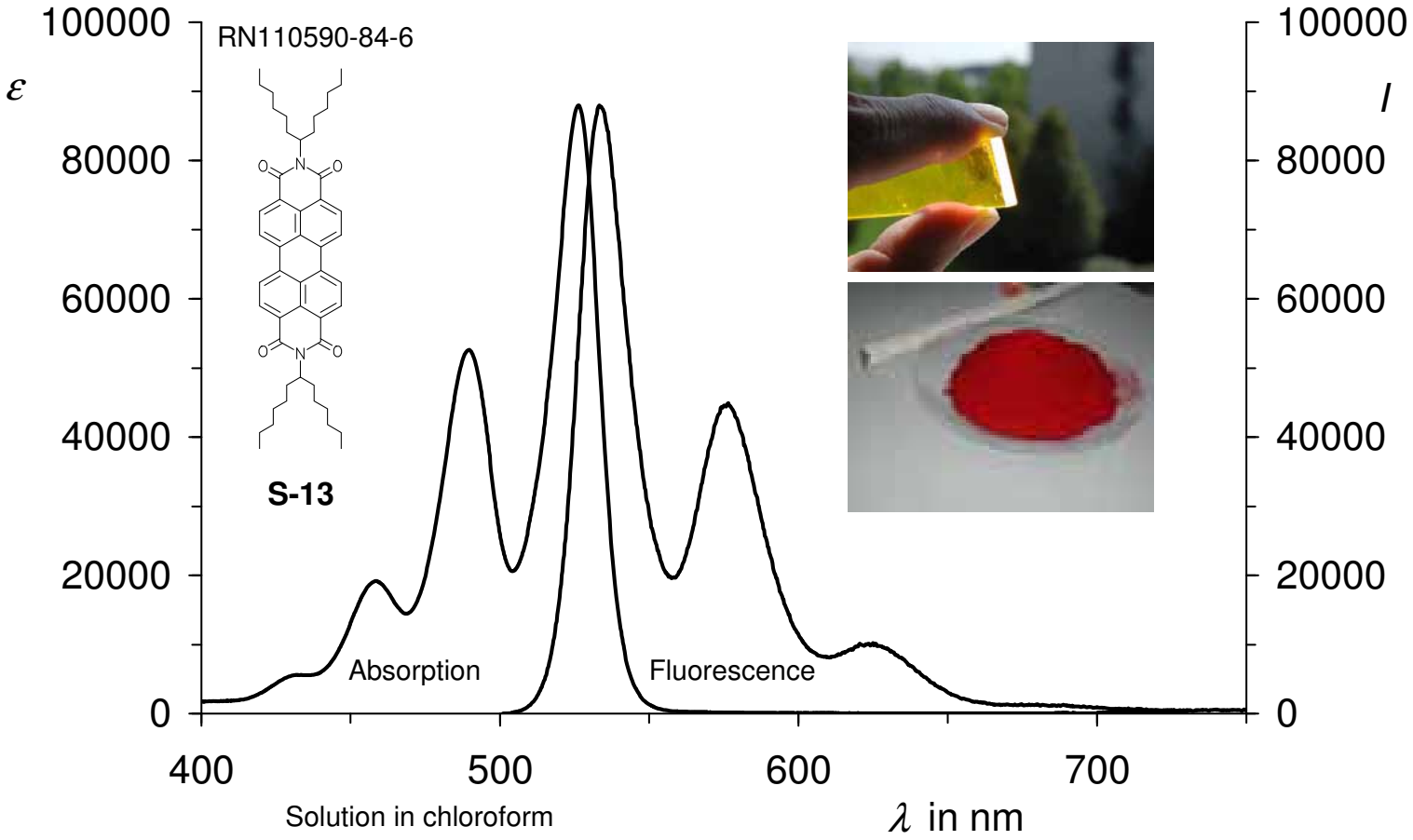


a) *tert*-butyl groups [1,2]

b) *sec*-alkyl groups [3,4]
("swallow-tail substituents")

Increasing the Solubility of Aromatic Compounds

[1] H. Langhals, 'Increasing the solubility of aromatic compounds', *Ger. Patent* 3016764 (April 30, **1980**); *Chem. Abstr.* **1982**, *96*, P70417x.
[2] H. Langhals, *Nachr. Chem. Tech. Lab.* **1980**, *28*, 716-718, *Chem.Abstr.* **1981**, *95*, R9816q.
[3] H. Langhals, 'Lightfast, readily soluble perylenetetracarboxylic (bis)imide fluorescent dyes', *Ger. Offen.* DE 3703495 (February 5, **1987**); *Chem. Abstr.* **1989**, *110*, P59524s.
[4] H. Langhals, S. Demmig, T. Potrawa, *J. Prakt. Chem.* **1991**, *333*, 733-748.



Dye **S-13** [1-3]:

Absorption:
λ_{max} = 526.3 nm
ε = 87 000 ($CHCl_3$)
Oscillator strengths:
f = 0.65

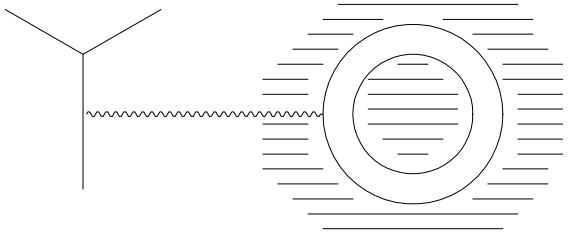
Fluorescence:
λ_{max} = 534.5 nm
Φ ~ **100%** τ = 3.95 ns

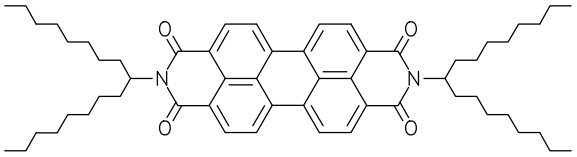
Triplet energy: 27.5 kcal/mol
(1040 nm, τ = 100 µs)

The Highly Fluorescent, Highly Soluble Perylene Dye **S-13**

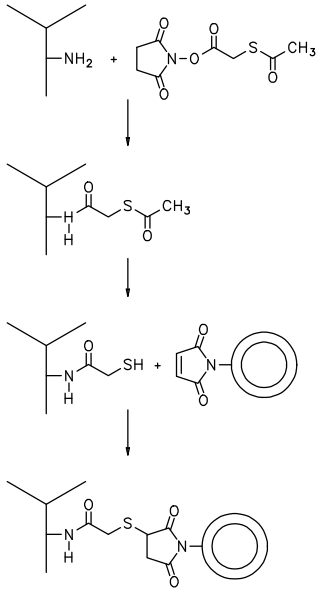
[1] S. Demmig, H. Langhals, *Chem. Ber.* **1988**, *121*, 225-230.
[2] H. Langhals, S. Demmig, T. Potrawa, *J. Prakt. Chem.* **1991**, *333*, 733-748.
[3] Review: H. Langhals, *Heterocycles* **1995**, *40*, 477-500.
[4] Review: H. Langhals, *Helv. Chim. Acta* **2005**, *88*, 1309-1343.

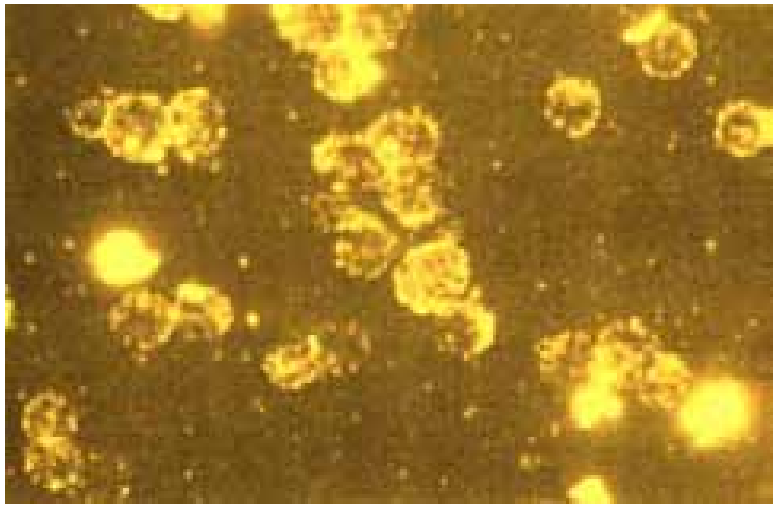
[1-4]





S-17



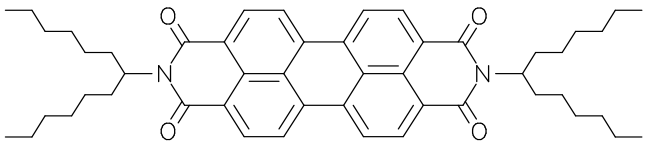


Bound fluorescent immunoliposomes at the surface of cancer cells

Fluorescent Immunoliposomes for Analytics [1-3]

[1] H. Langhals, 'Dyes for Fluorescent Immunoassays', in B. Hock, *Immunochemical Detection of Pesticides and their Metabolites in the Water Cycle*, VCH Verlagsgesellschaft, Weinheim **1995**, ISBN 3-527-27137-6; *Chem. Abstr.* **1996**, *124*, 24966z.
[2] R. A. Schwendener, T. Trüb, H. Schott, H. Langhals, R. F. Barth, P. Groscurth, H. Hengartner, *Biochim. Biophys. Acta* **1990**, *1026*, 69-79.
[3] H. Schott, D. v. Cunov, H. Langhals, *Biochim. Biophys. Acta* **1992**, *1110*, 151-157.

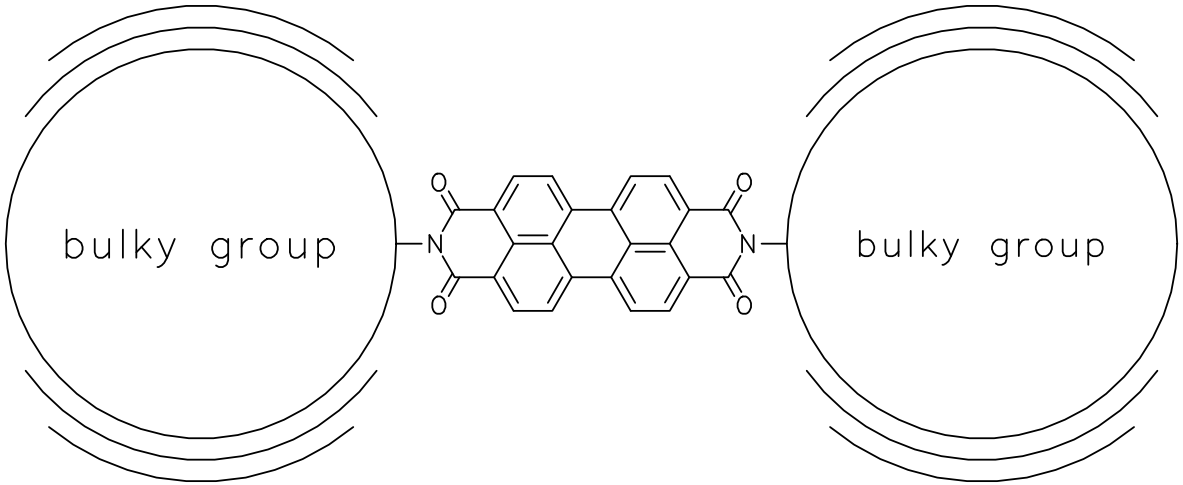
Perylene fluorescent dyes off limits?



Limitation:
quenching of fluorescence by
high concentration

The Inhibition of the Concentration Quenching of Fluorescence

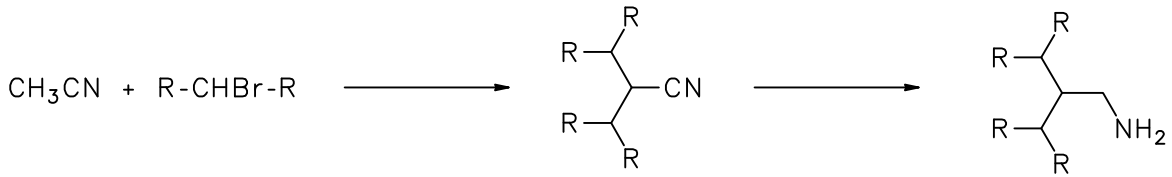
Aggregation is the most important process for the quenching of fluorescence

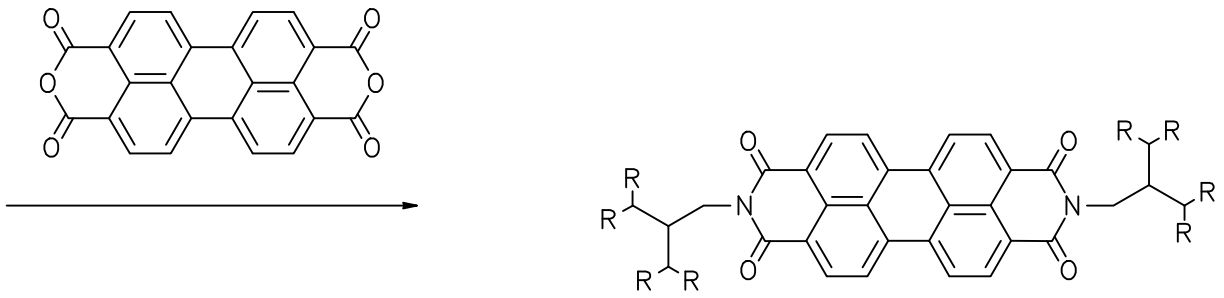


Steric Inhibition of Aggregation

[1] H. Langhals, R. Ismael, O. Yürük, *Tetrahedron* **2000**, *56*, 5435-5441.

Synthesis of perylene dyes with highly branched aliphatic substituents

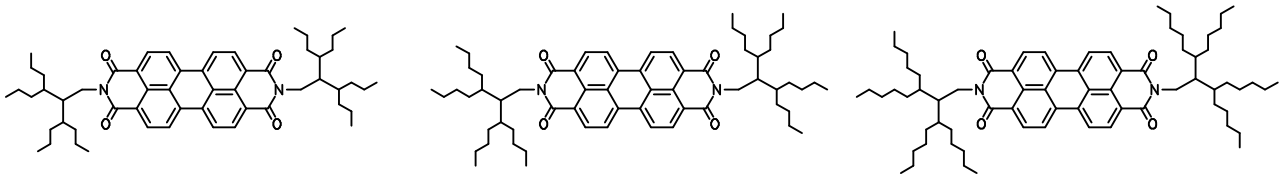




Persistent Fluorescence by Steric Inhibition of Aggregation [1]

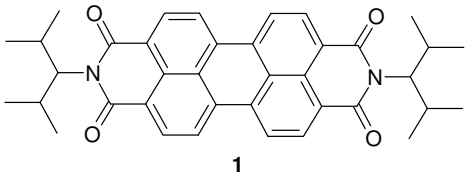
[1] H. Langhals, R. Ismael, O. Yürük, *Tetrahedron* **2000**, *56*, 5435-5441.

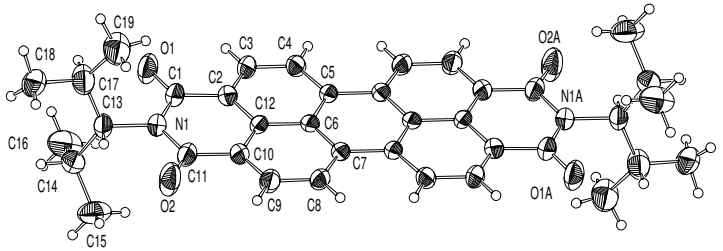
Highly branched aliphatic substituents

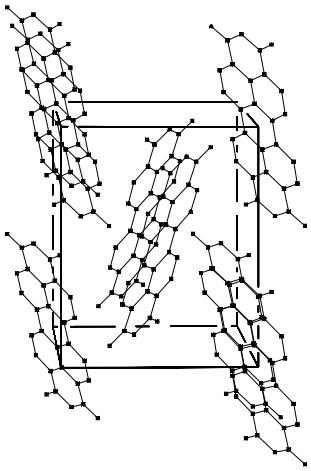


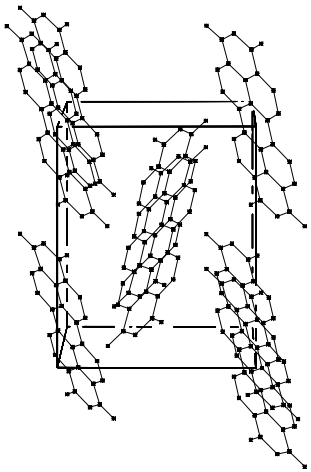
Persistent Fluorescence by Steric Inhibition of Aggregation [1]

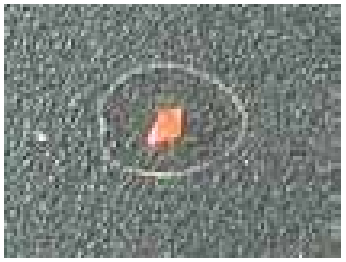
[1] H. Langhals, R. Ismael, O. Yürük, *Tetrahedron* **2000**, *56*, 5435-5441.

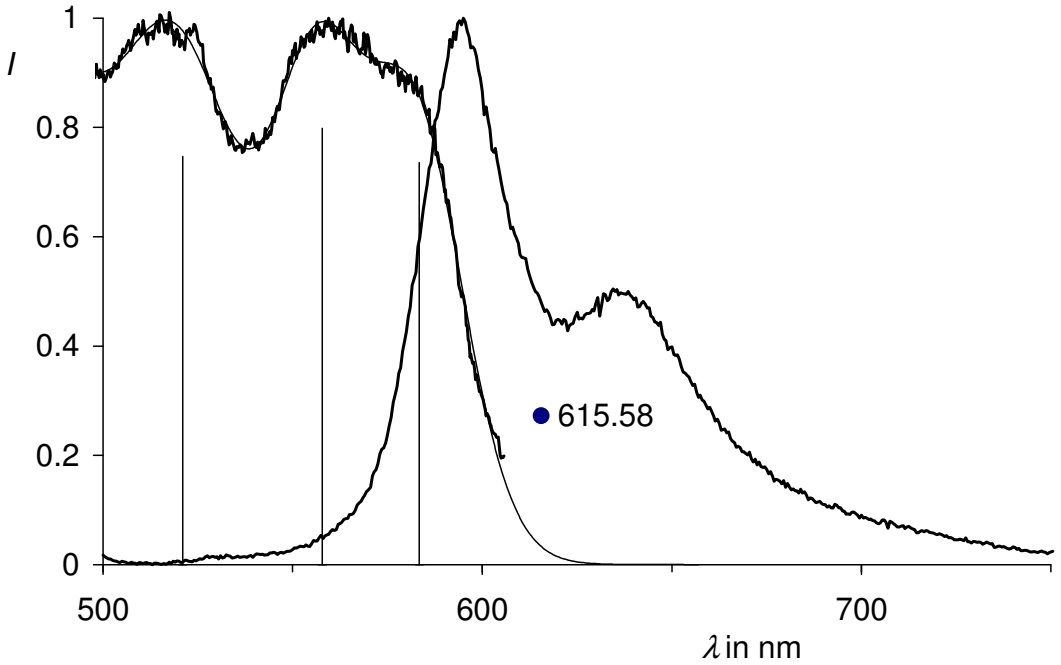






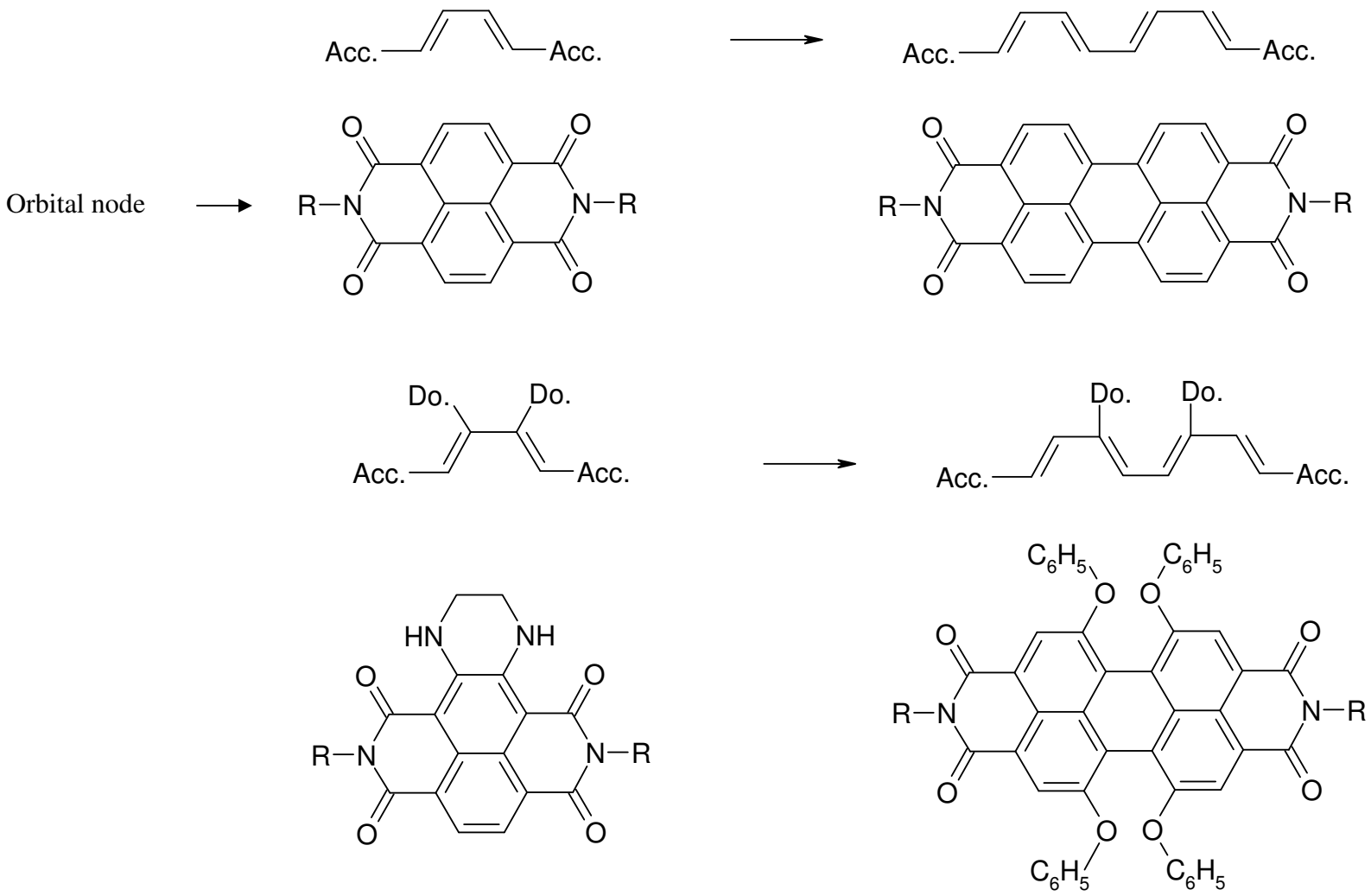




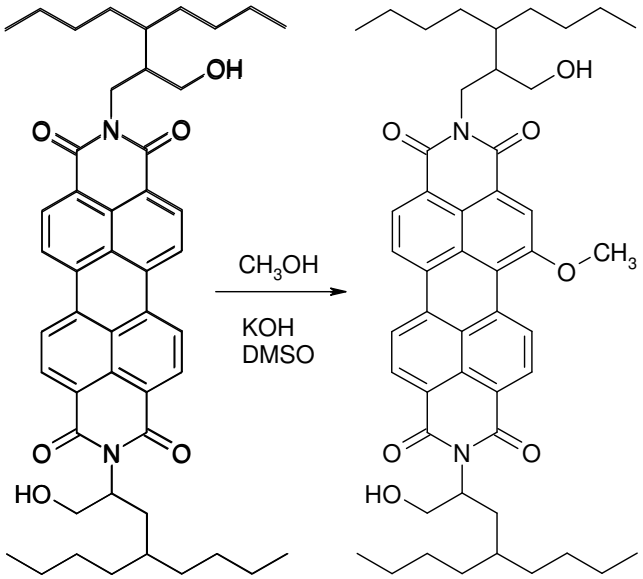


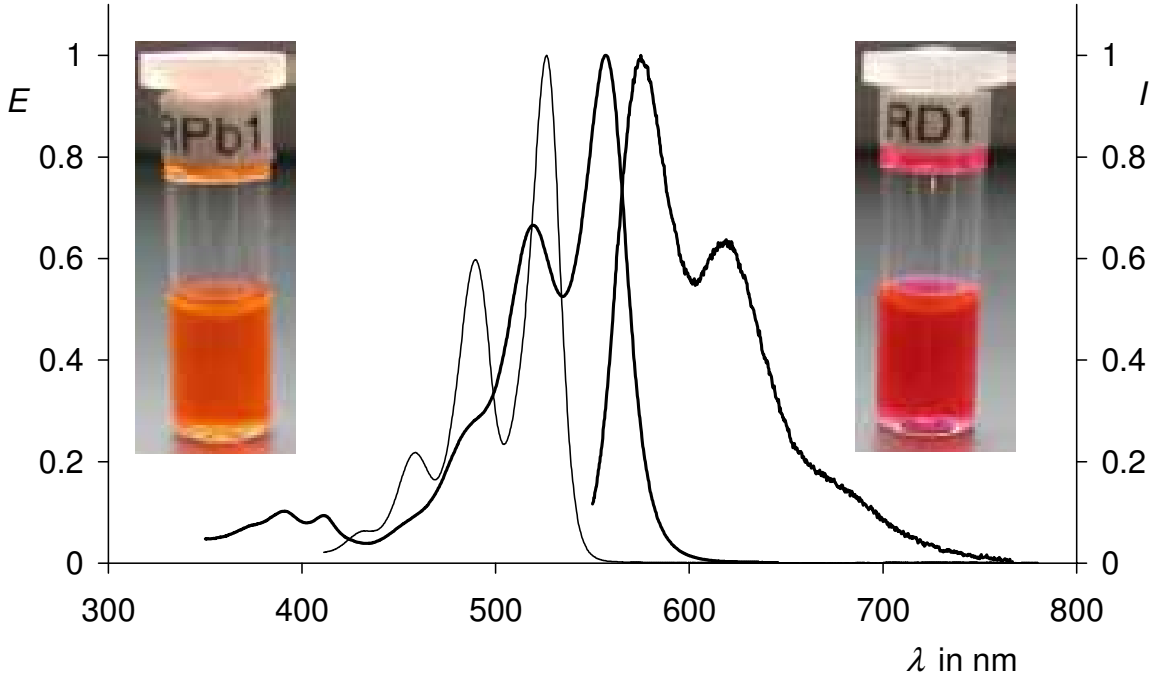
Cooling with Light [1]

[1] H. Langhals, O. Krotz, K. Polborn, P. Mayer, *Angew. Chem* **2005**, *117*, 2479-2480; *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 2427-2428.



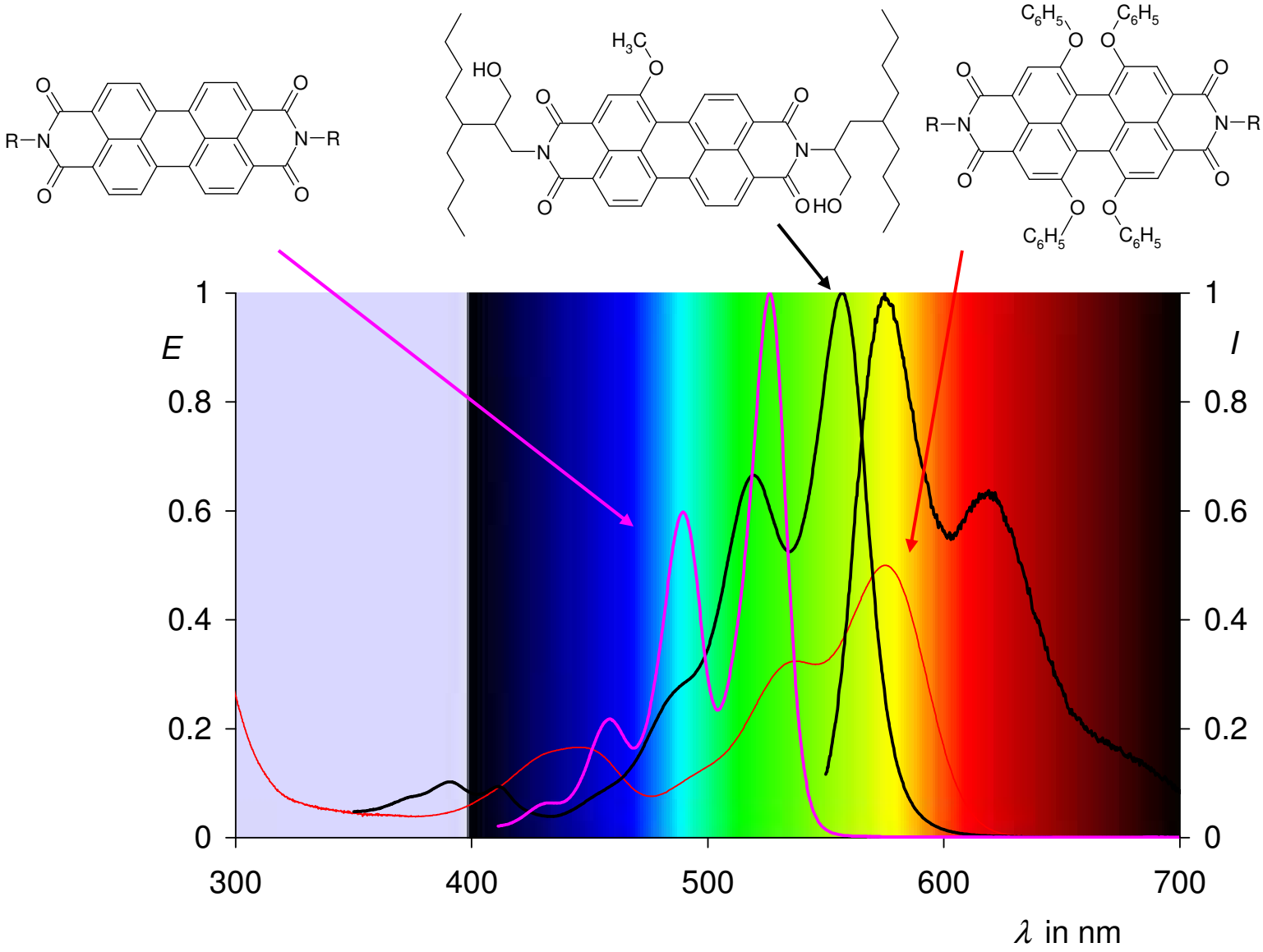
Donor Groups in Perylene Dyes



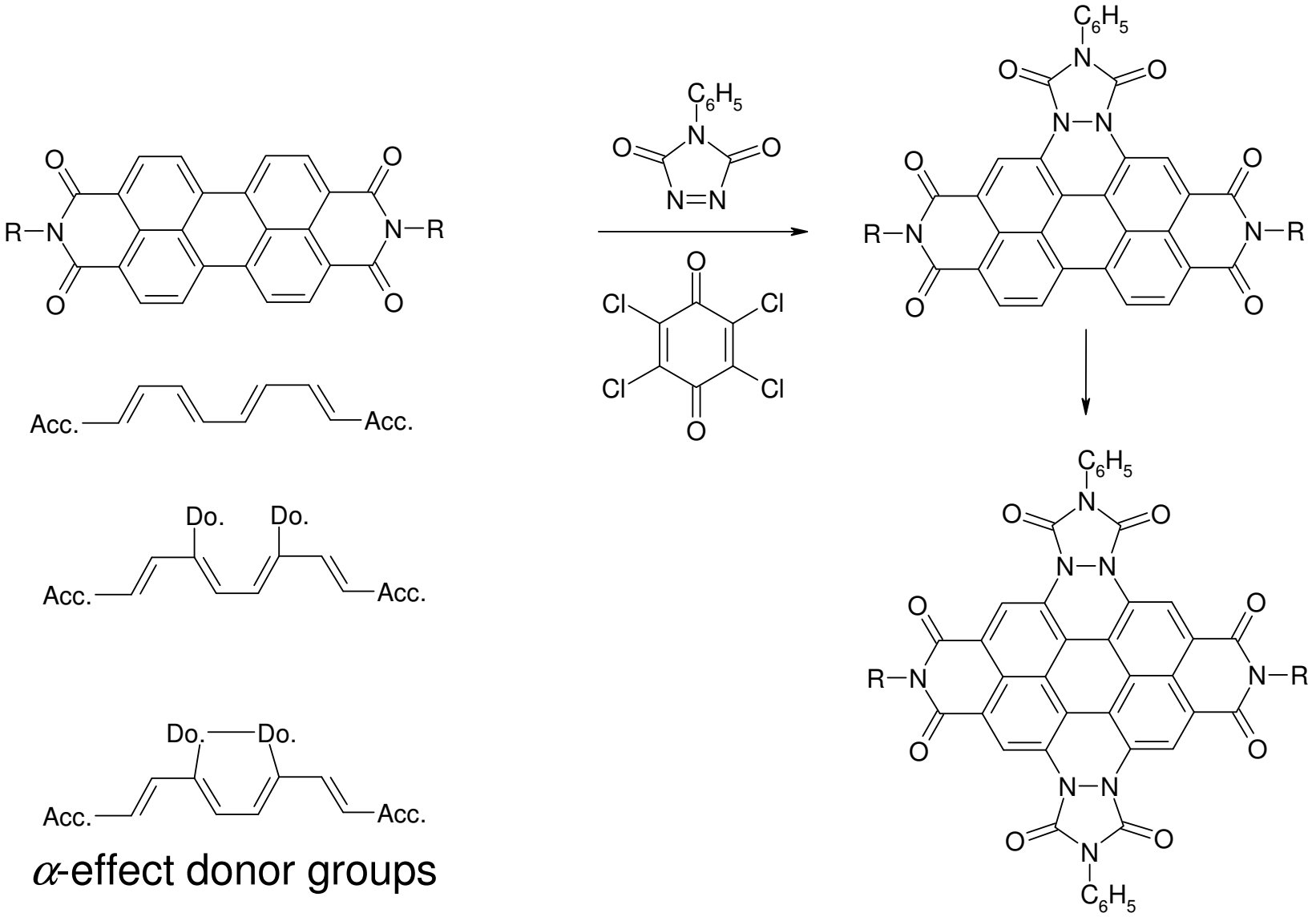


Alkaliresistant Perylenes [1] – Methoxyperylenes [2]

[1] H. Langhals, H. Jaschke, H. Bastani-Oskoui, M. Speckbacher, *Eur. J. Org. Chem.* **2005**, 4313-4321.
[2] H. Langhals, R. El-Shishtawy, P. von Unold, M. Rauscher, *Chem. Eur. J.* **2006**, *12*, 4642-4645.

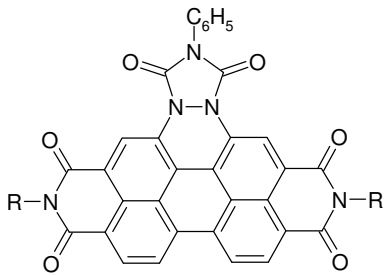


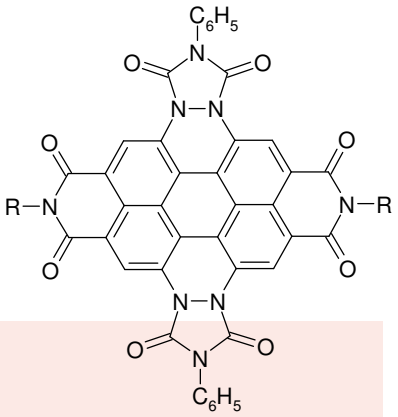
Donor Substututed Perylene Dyes

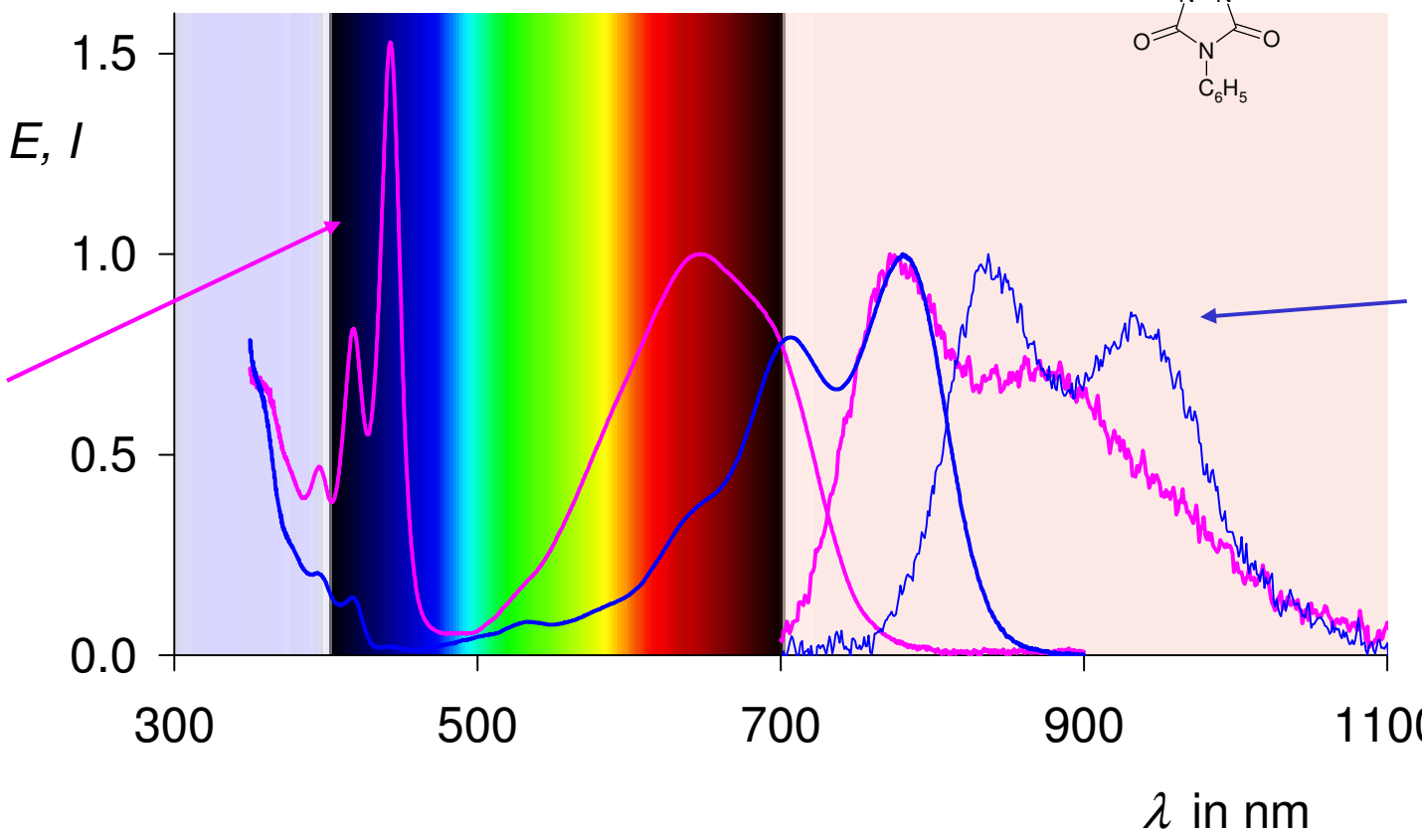


Super Donor Groups in Dyes?

[1] H. Langhals, P. Blanke, *Dyes Pigm.* **2003**, *59*, 109-116.
[2] H. Langhals, P. Blanke, *Ger. Offen.* DE 10132116.3 (July 3, **2001**).

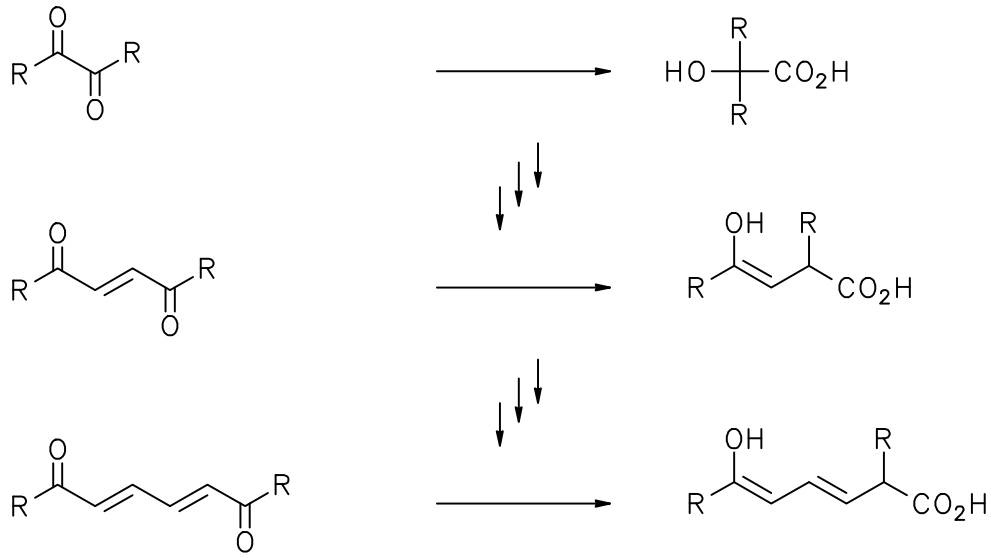


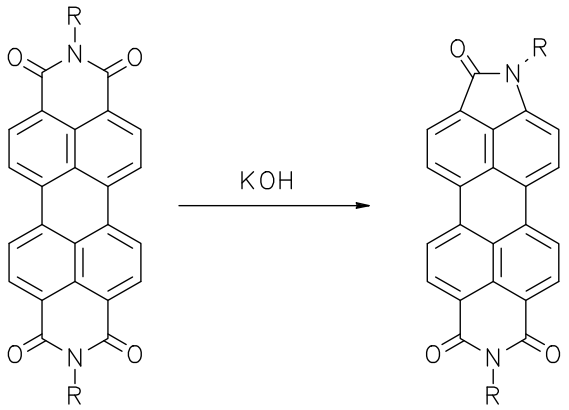




Novel NIR Dyes by α-effect Donor Groups [1,2]

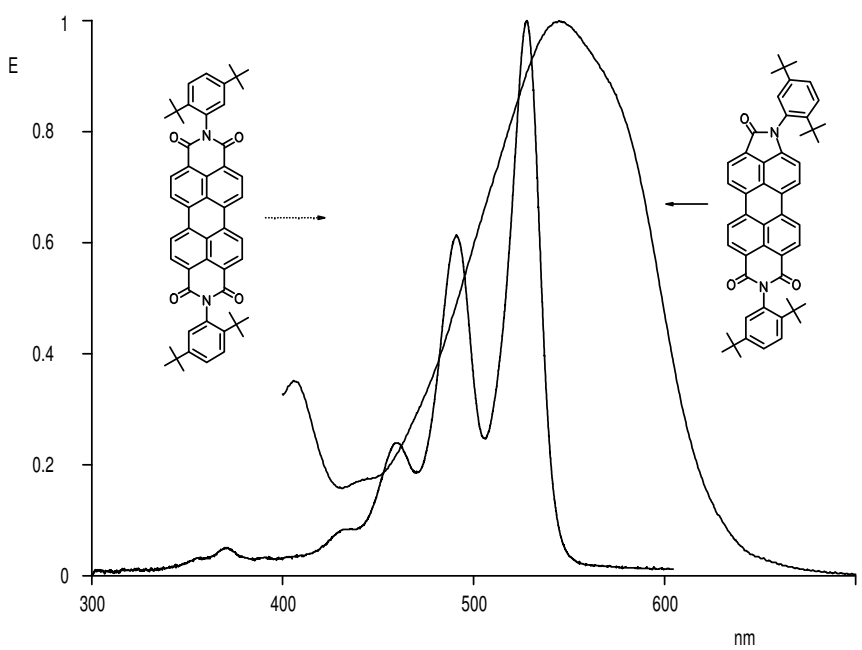
[1] H. Langhals, P. Blanke, *Dyes Pigm.* **2003**, *59*, 109-116.
[2] H. Langhals, P. Blanke, *Ger. Offen.* DE 10132116.3 (July 3, **2001**).

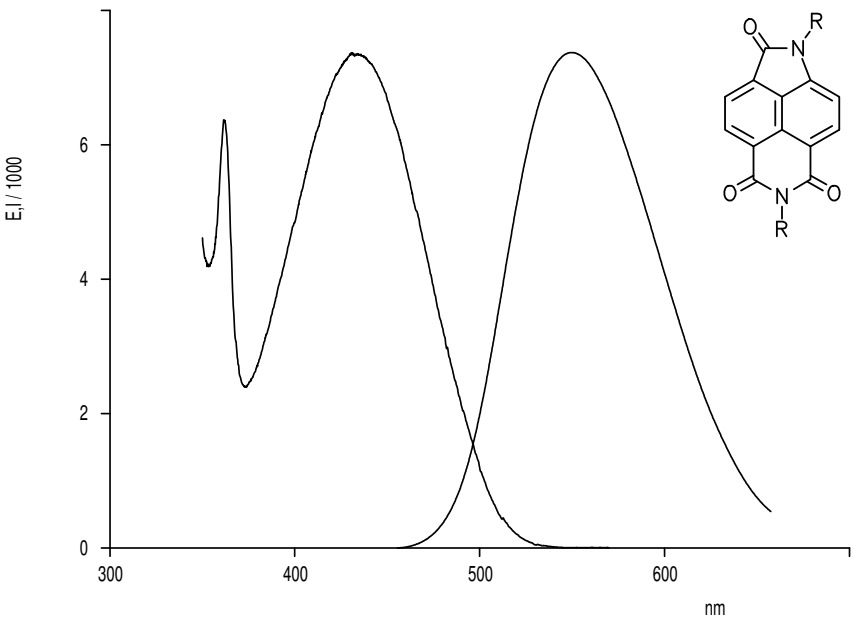




1 2

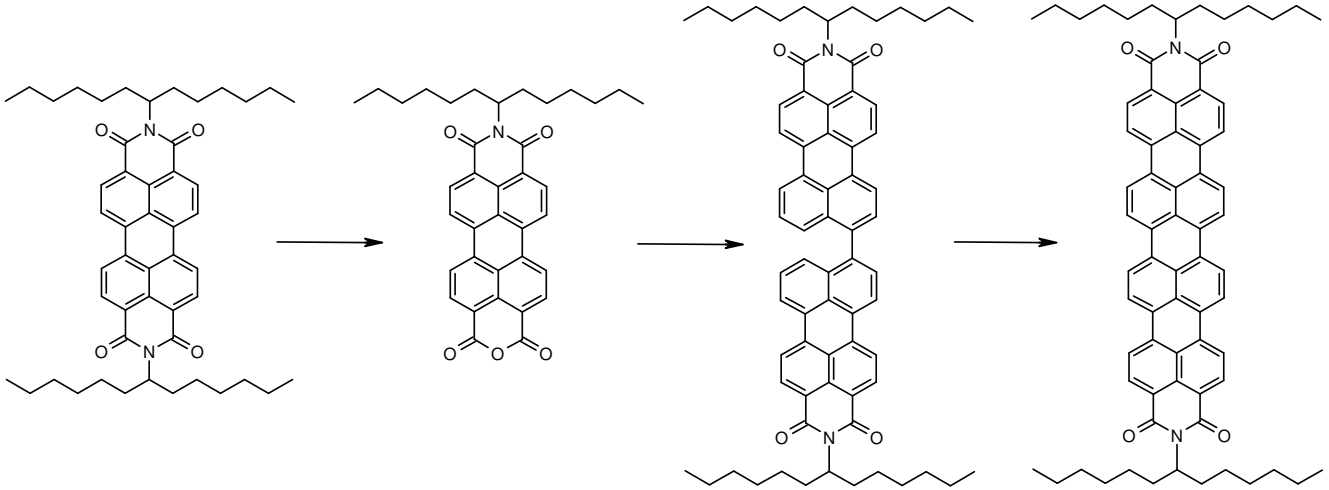
Mechanism of the Novel Rearrangement



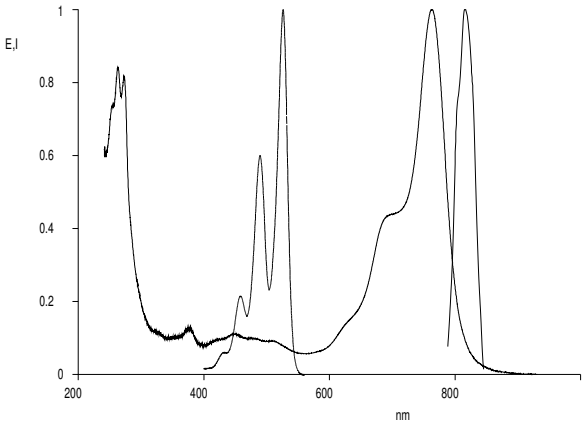


UV/Vis Spectra of Novel Lactameimides

NIR



1 **2** **3** **4**

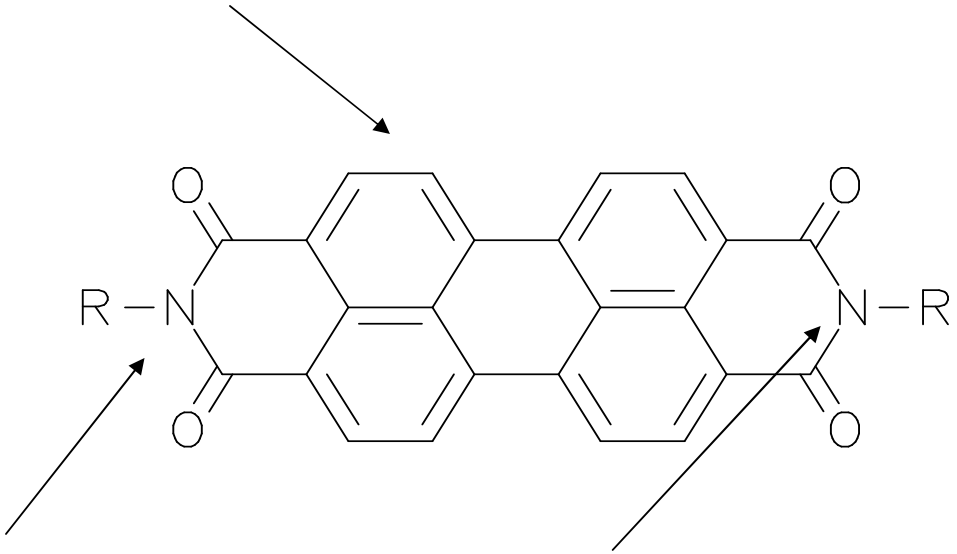


UV/Vis spectra in chloroform.

Synthesis of Quaterrylene Bisimides [1]

[1] H. Langhals, J. Büttner, P. Blanke, *Synthesis* **2005**, 364-366.

Substituents at the core can control UV/Vis spectra



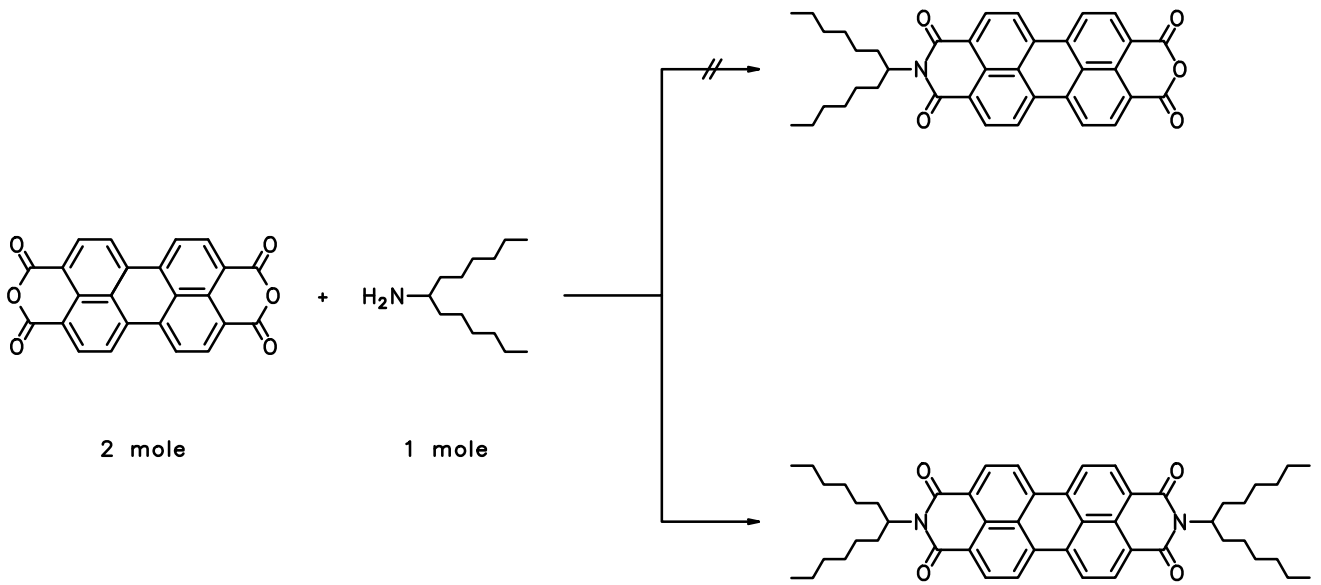
Nodes in the orbitals HOMO and LUMO

Perylene bisimides are suitable building blocks for larger assemblies

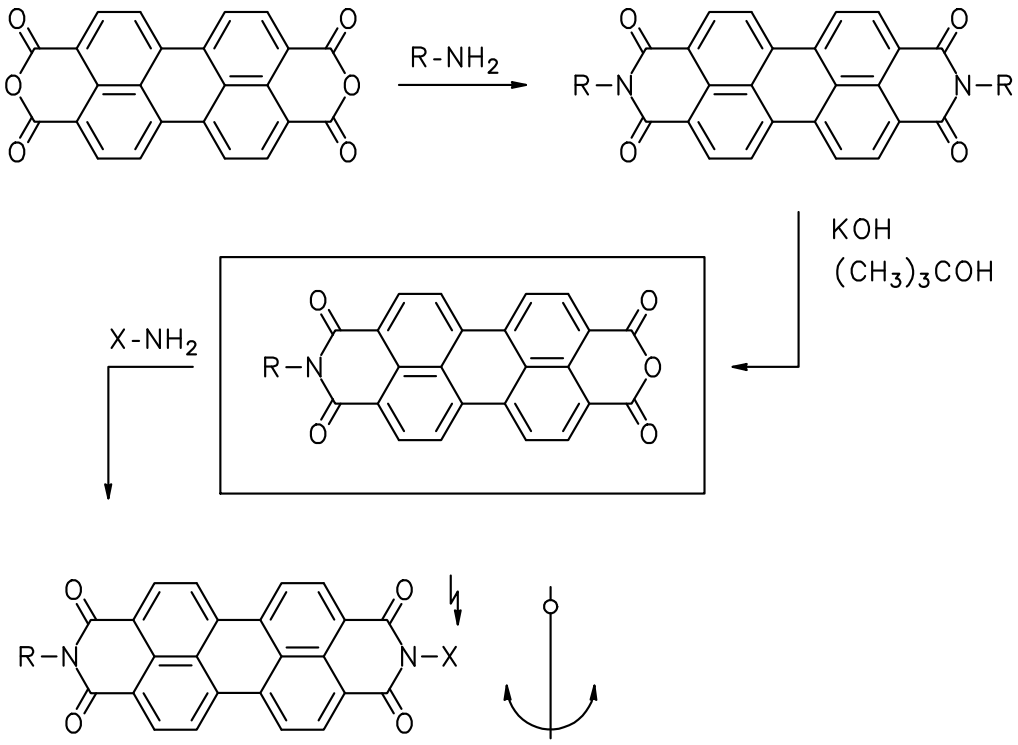
Perylene dyes represent "*The Electron in a Box*" [1]

The perylene bisimide is a module with a "*Closed chromophore*"

[1] Compare: H. Langhals, S. Demmig, H. Huber, *Spectrochim. Acta* **1988**, *44A*, 1189-1193.

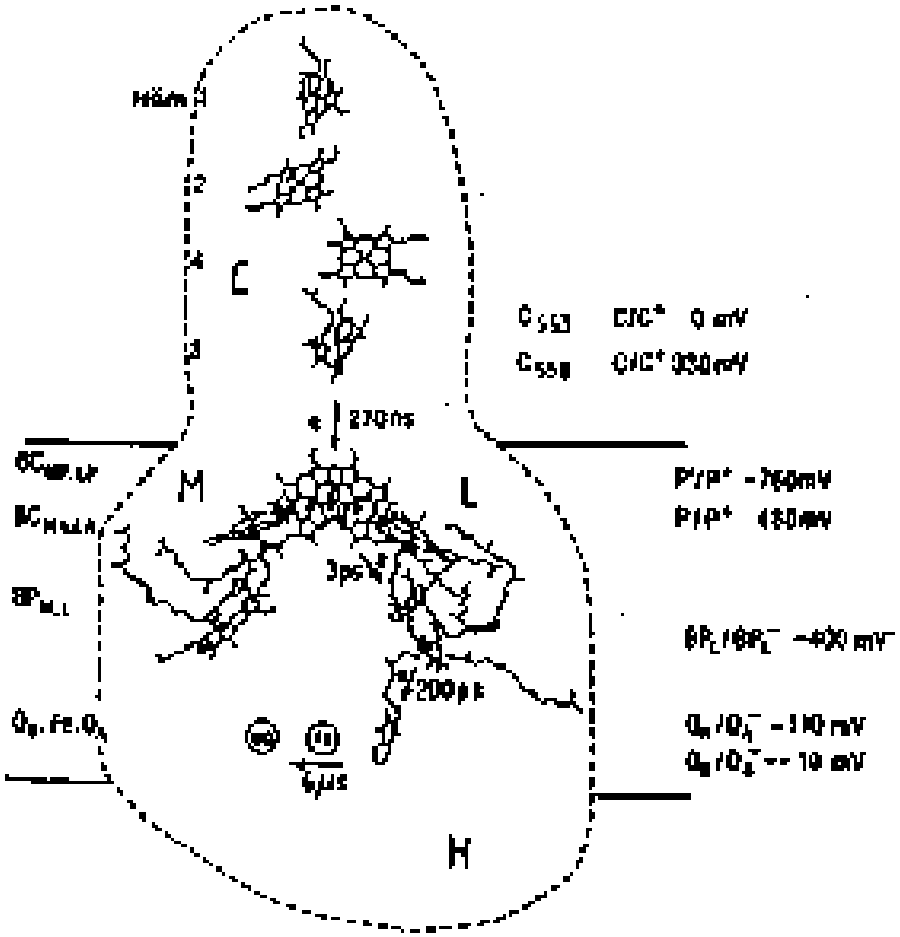


Fluorescent Labels: Monofunctionalized Perylene Dyes



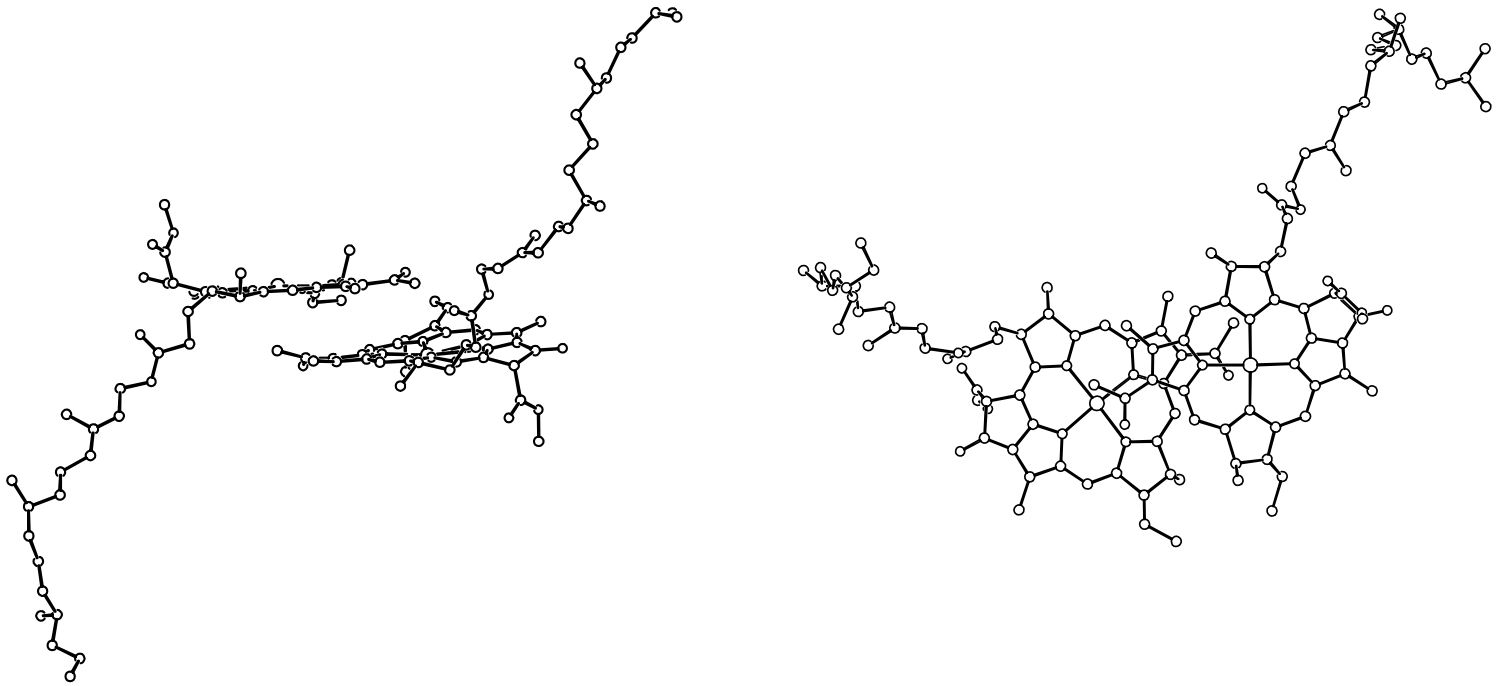
Fluorescent Labels: Synthesis of Monofunctionalized Perylene Dyes [1]

[1] H. Kaiser, J. Lindner, H. Langhals, *Chem.Ber.* **1991**, *124*, 529-535.

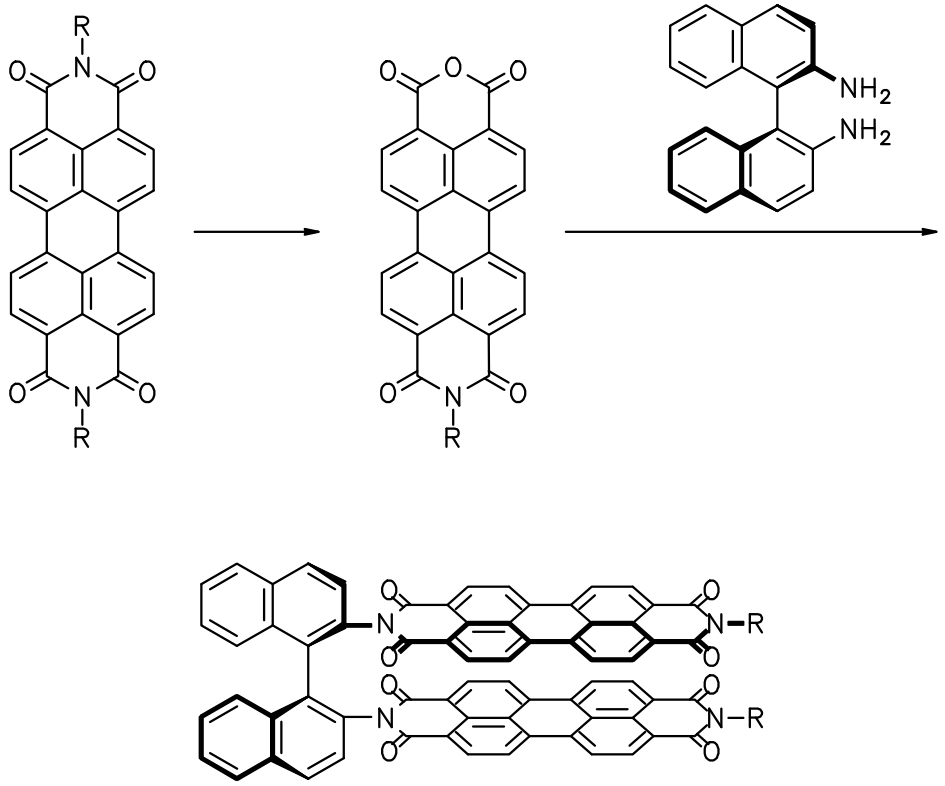


The Structure of the Reaction Center of Photosynthesis [1]

[1] *Rp. Viridis*: J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, *J. Mol. Biol.* **1984**, *180*, 385.

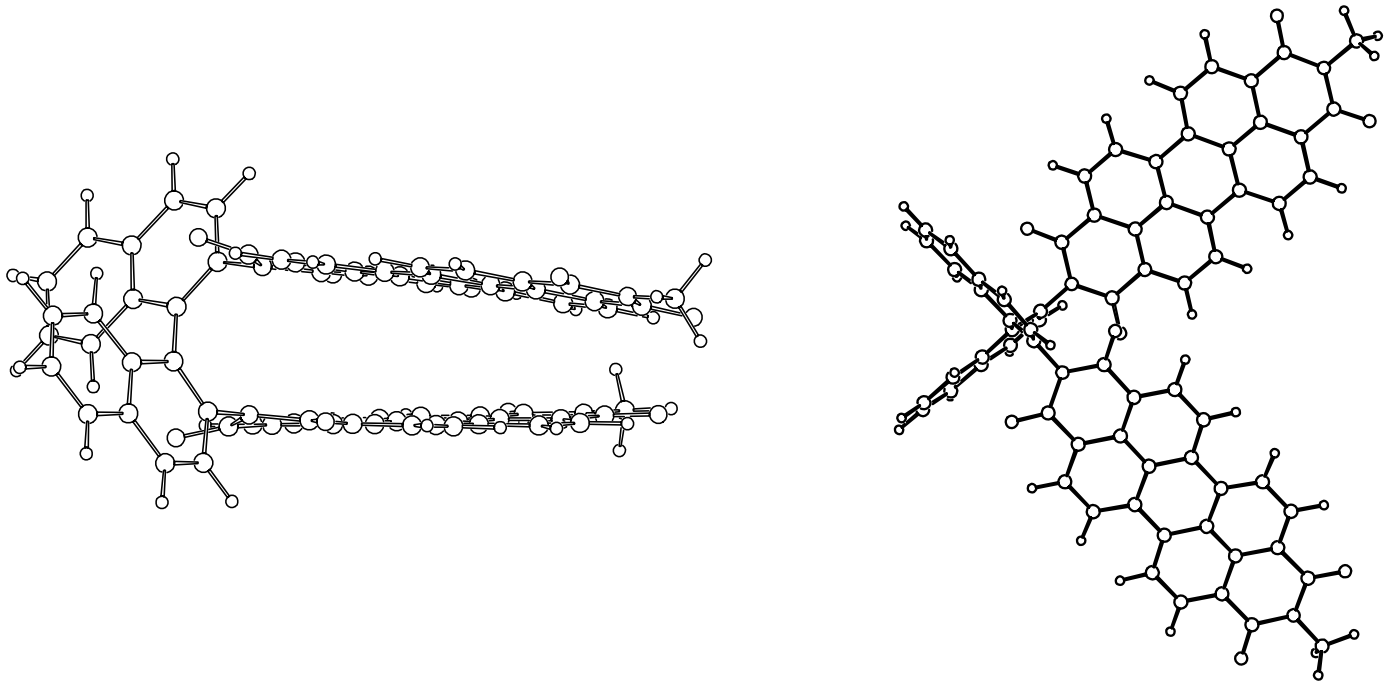


The "*special pair*" of the Reaction Centre of Photosynthesis

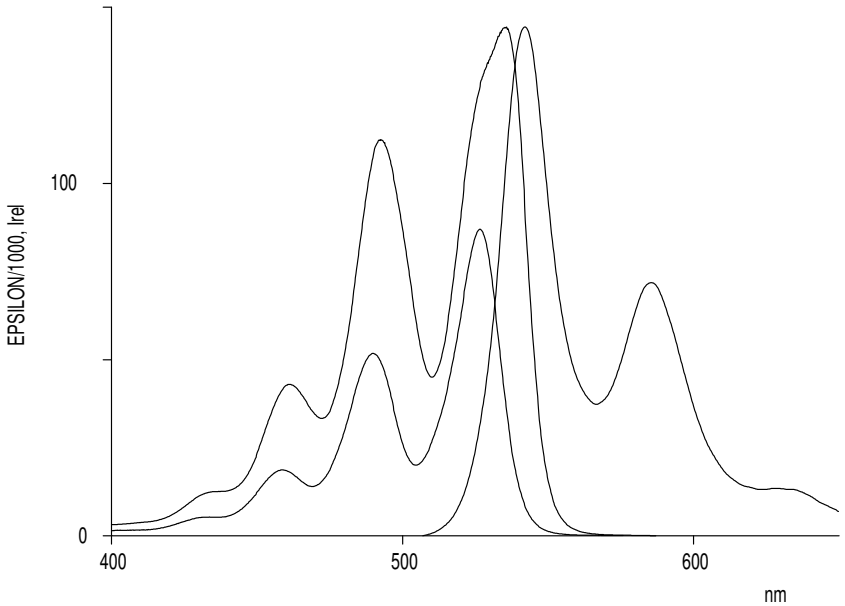


Chiral Bifluorophoric Perylene Dyes with Unusually High CD Effects - a Simple Model for the Photosynthesis Reaction Center [1]

[1] H. Langhals, J. Gold, *Liebigs Ann./Recueil* **1997**, 1151-1153.



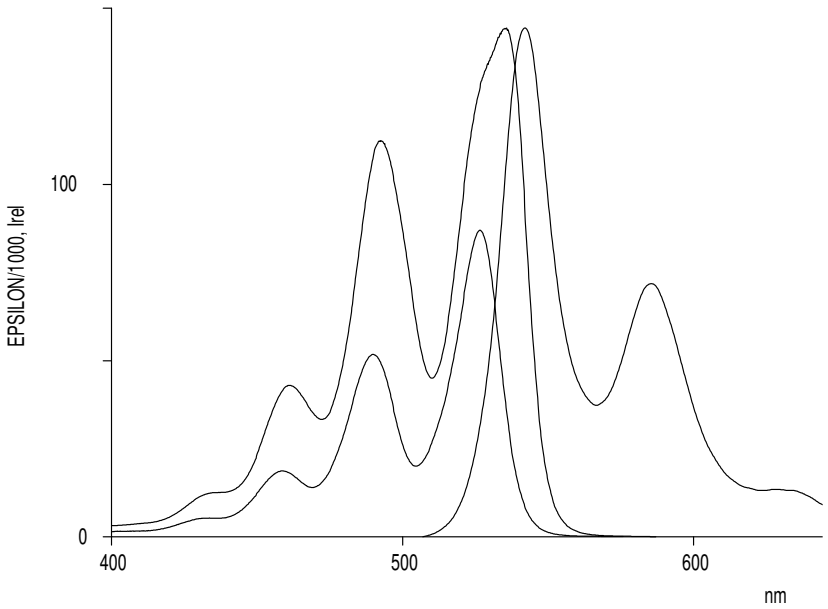
An Artificial Photosynthesis Reaction Centre

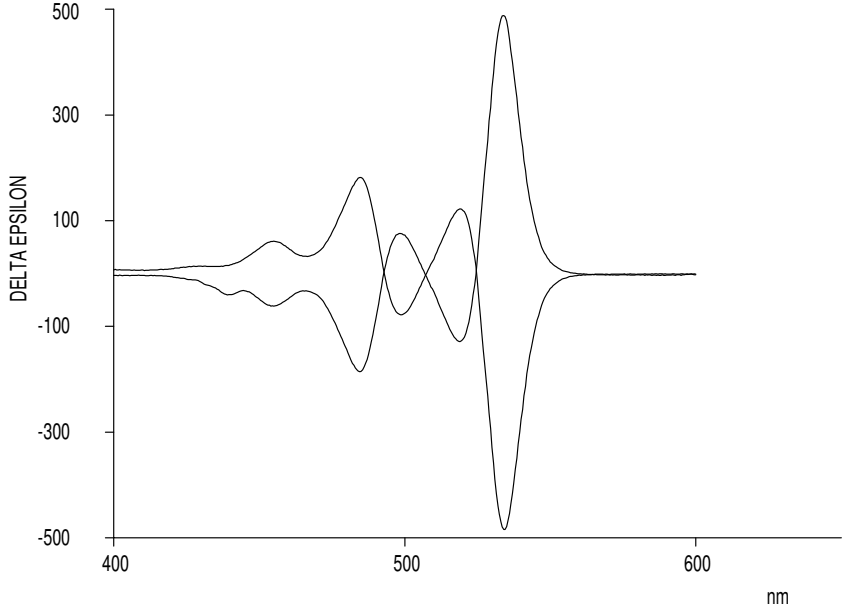


Absorption (upper left) and fluorescence spectra (right) of the (*P*)-bichromophore in chloroform (oscillator strength: f = 1.35) compared to the absorption spectrum of the monochromophore **S-13** (lower left) (oscillator strength: f = 0.65).

UV/Vis-spectra of a Chiral Perylene Bichromophore

[1] H. Langhals, J. Gold, *Liebigs Ann./Recueil* **1997**, 1151-1153.





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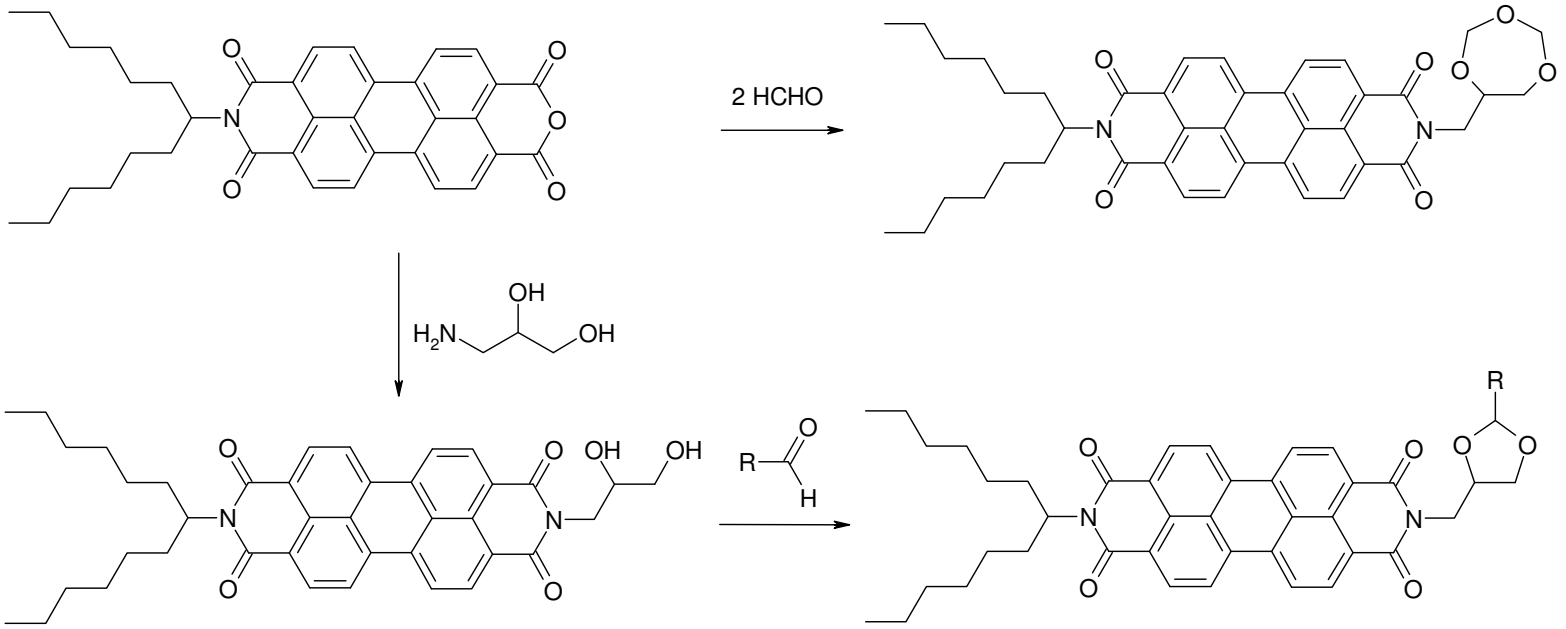
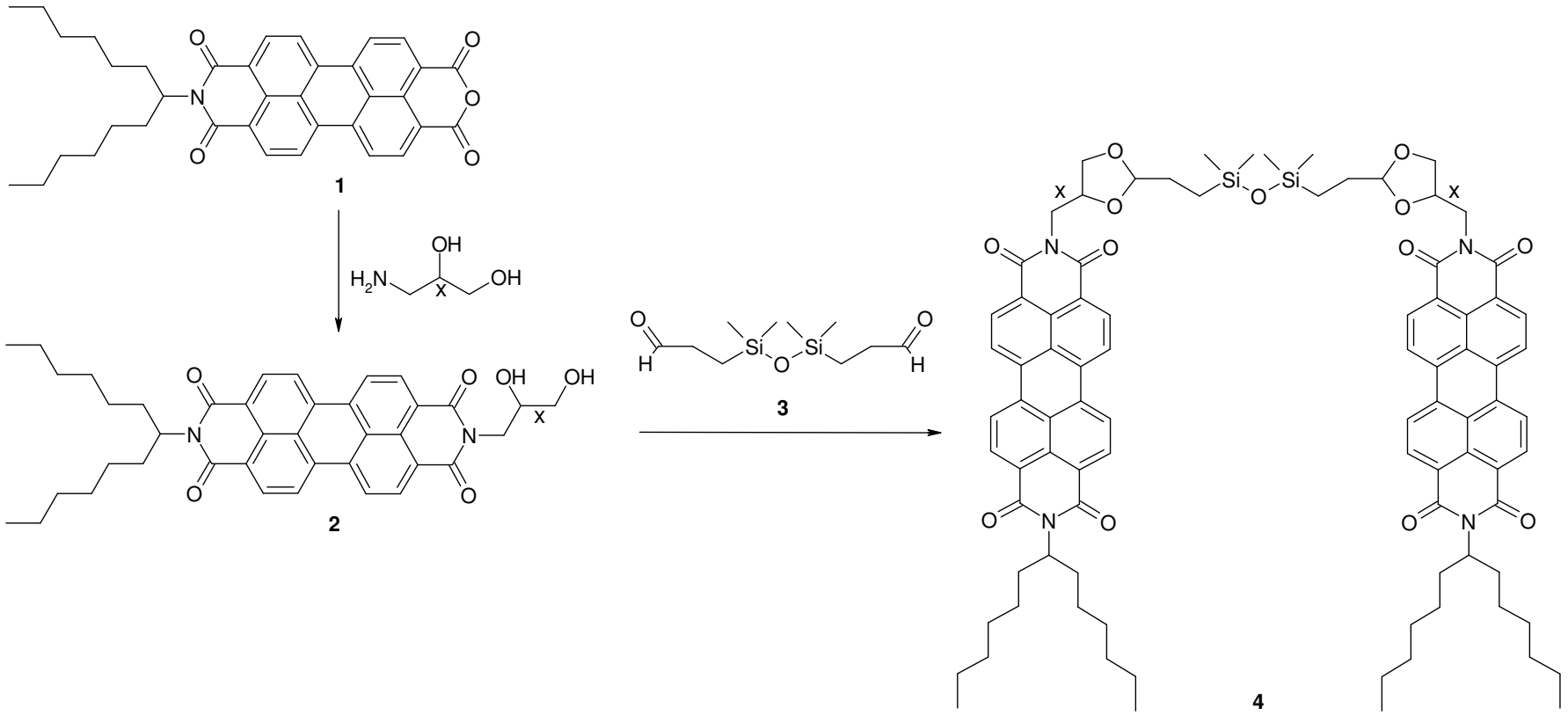
CD-spectrum of the (*P*)- bichromophore (___) and the (*M*)- bichromophore (---) in chloroform.

UV/Vis-spectra of Chiral Perylene Bichromophores with Unusually High CD Effects



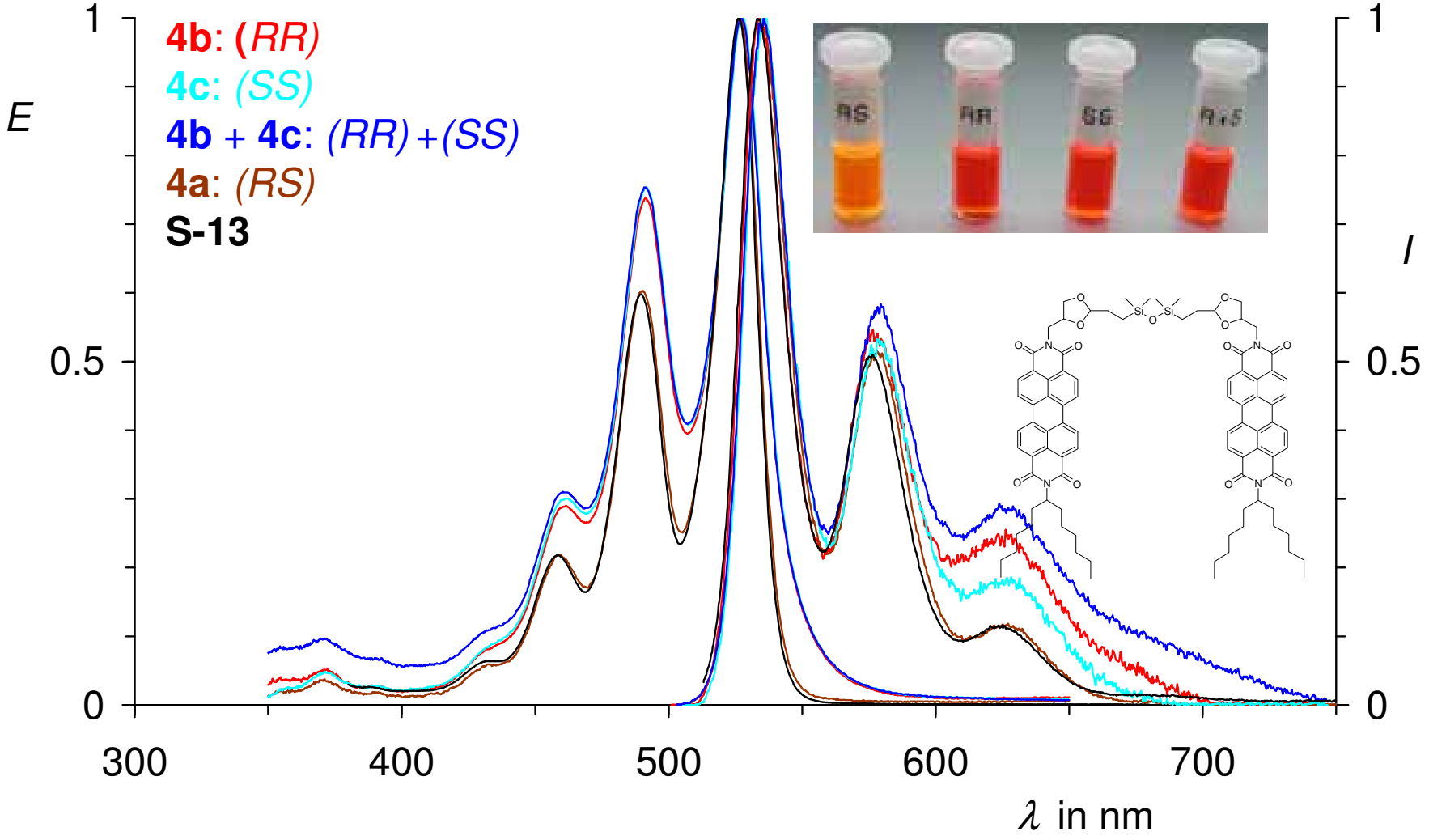
Fluorescent Labels for Aldehydes [1]

[1] H. Langhals, K. Fuchs, *Coll. Czech. Chem. Commun.* **2006**, *71*, 625-634.

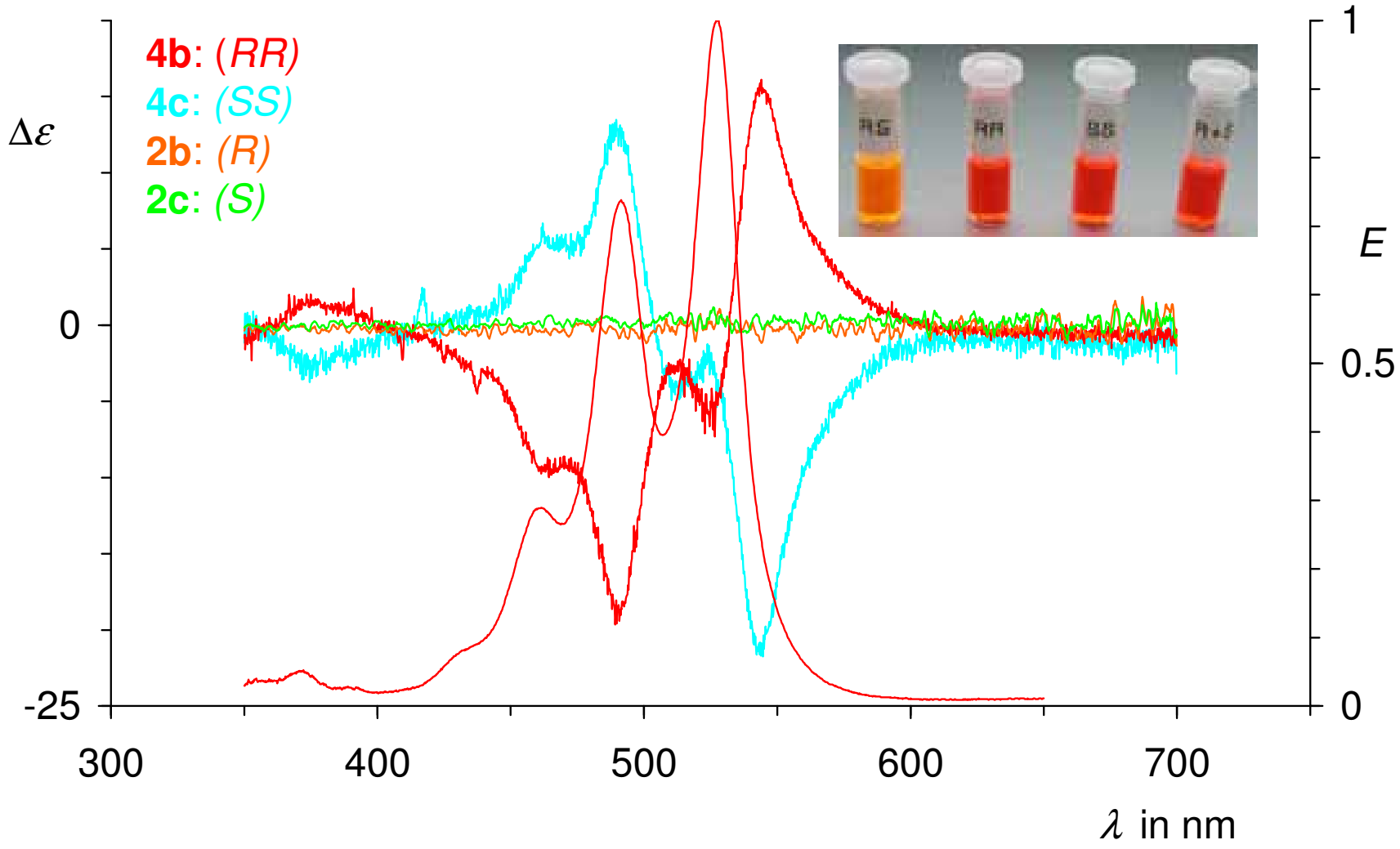


Chiral, Bichromophoric Silicones: Ordering Principles [1]

[1] H. Langhals, O. Krotz, *Angew. Chem.* **2006**, *118*, 4555-4561; *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 4444-4447.



Chiral, Bichromophoric Silicones: Ordering Principles



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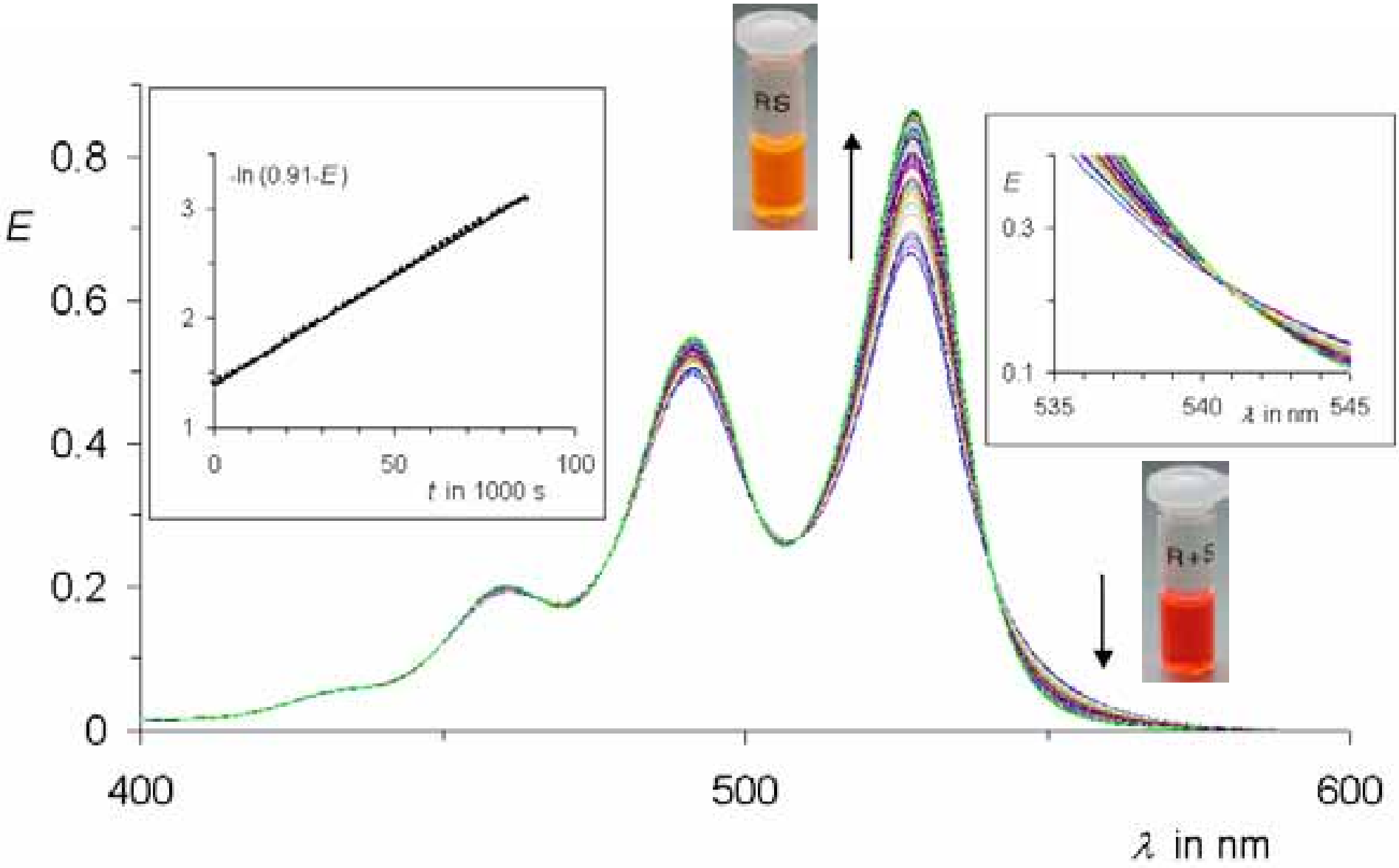

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Conclusion

COC 2005

COC 2007

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Nature knows how to handle colorants perfectly.
Man has to learn...