

FOTOFÍSICA E FOTOQUÍMICA DAS CORES



UMA INTRODUÇÃO QUALITATIVA AOS
TIPOS DE TRANSIÇÕES ELETRÔNICAS

Marcelo H. Gehlen



TÓPICOS

- a) Aspectos históricos
- b) Mecanismos da Visão
- c) Sistemas gerando cores
- d) Combinação de Sistemas
- e) Conclusões

ASPECTOS HISTÓRICOS

CORES



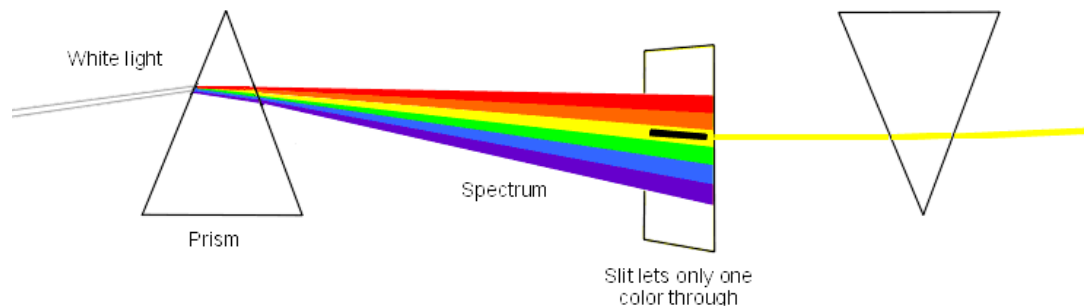
CIÊNCIAS / NATUREZA

ARTES / CULTURA

TECNOLOGIA

Estudos dos Raios de Luz

Experimento de Newton (1665)



1704 publica Opticks (teoria corpuscular da luz)

TEORIA ONDULATÓRIA

1690: Christian Huygens / Frentes de Onda

1802: Thomas Young / Interferência

1850: Foucault / velocidade da luz e polarização (meio:eter)

1860: Maxwell / Teoria eletromagnética da luz (vácuo)

1887: Michelson-Morley (inexistência do eter)

1905: Einstein / c =constante (independente do referencial)

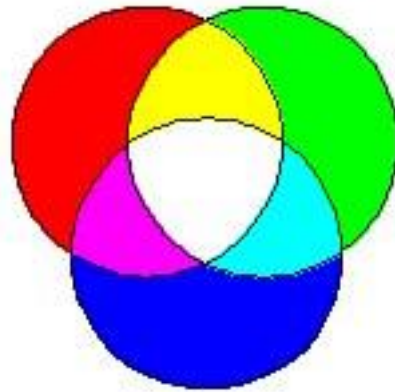
TEORIA QUANTICA

1901: Planck / Radiação de corpo negro ($E = nh\nu$)

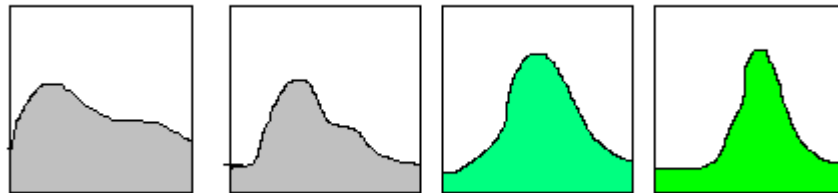
1905: Einstein / Efeito fotoelétrico ($\varepsilon = h\nu$)

MECANISMOS DA VISÃO

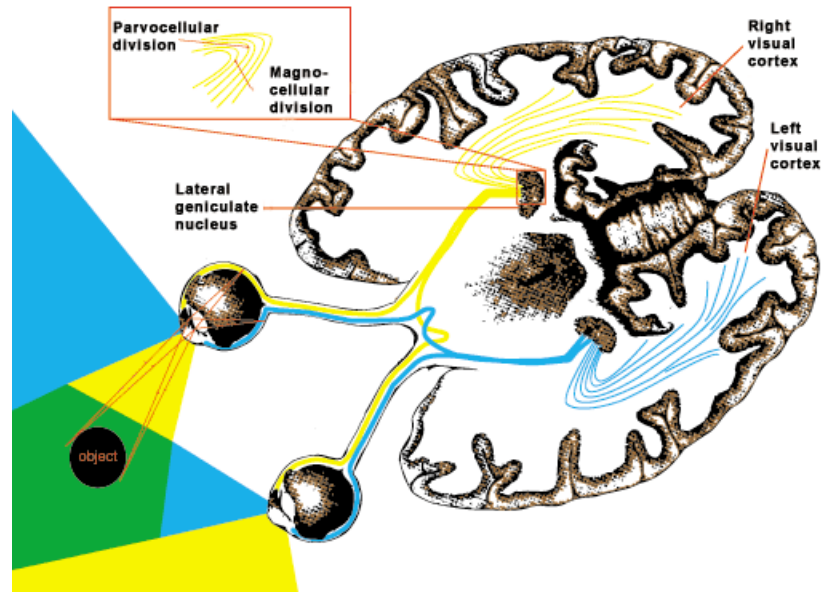
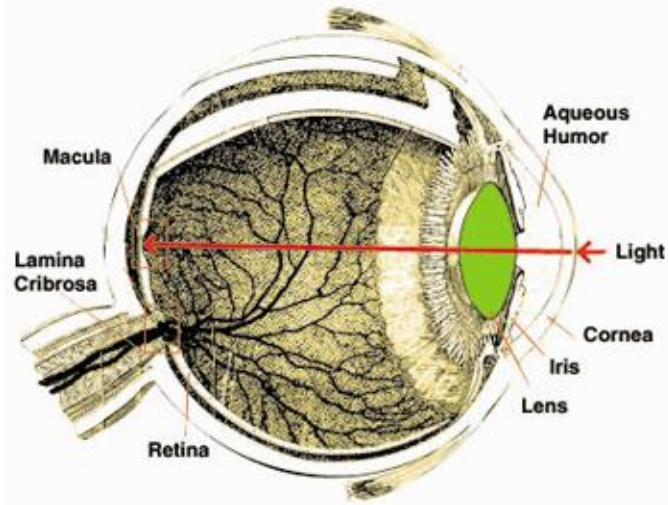
Teoria tricromática (Young-Helmholtz)



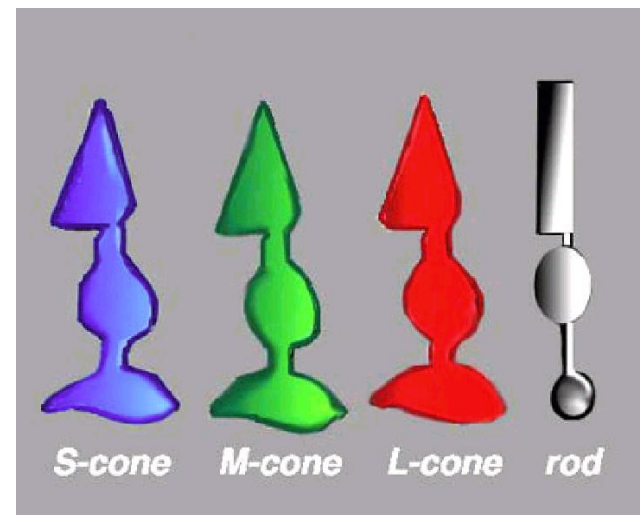
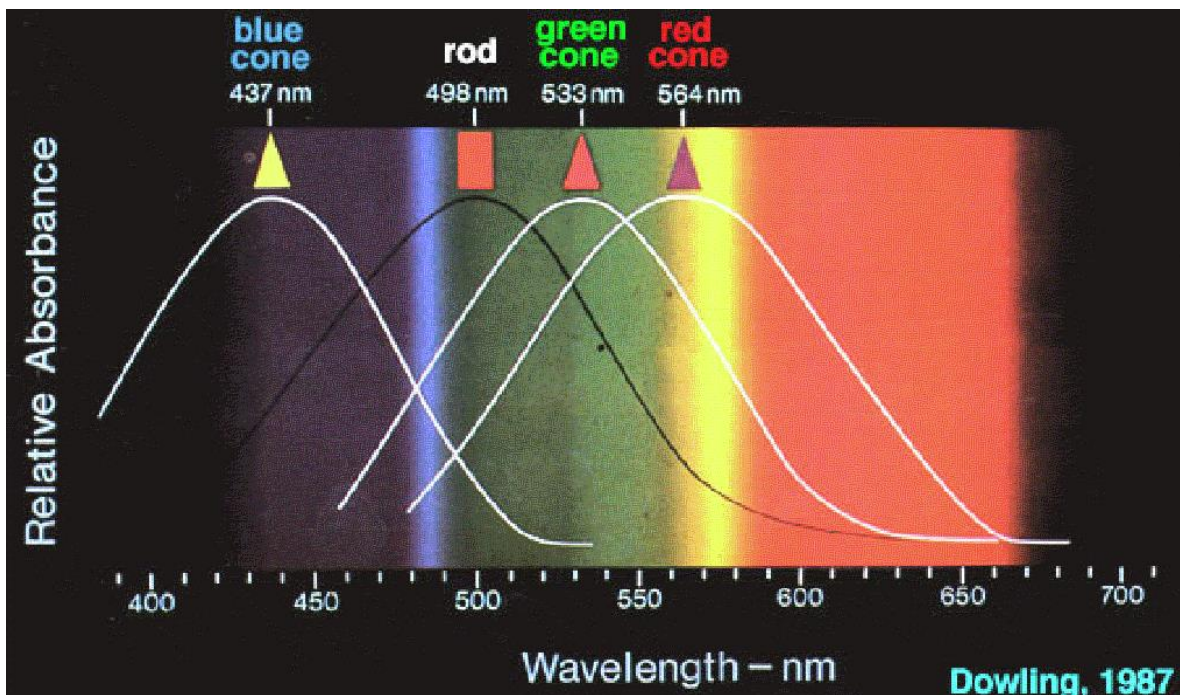
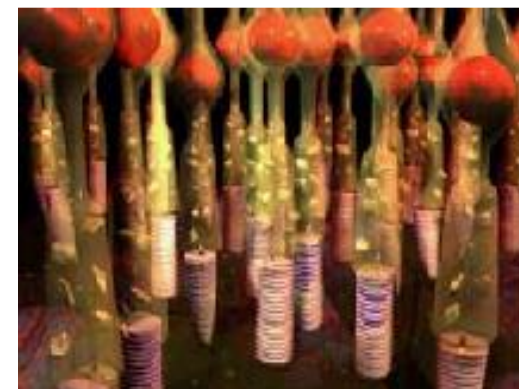
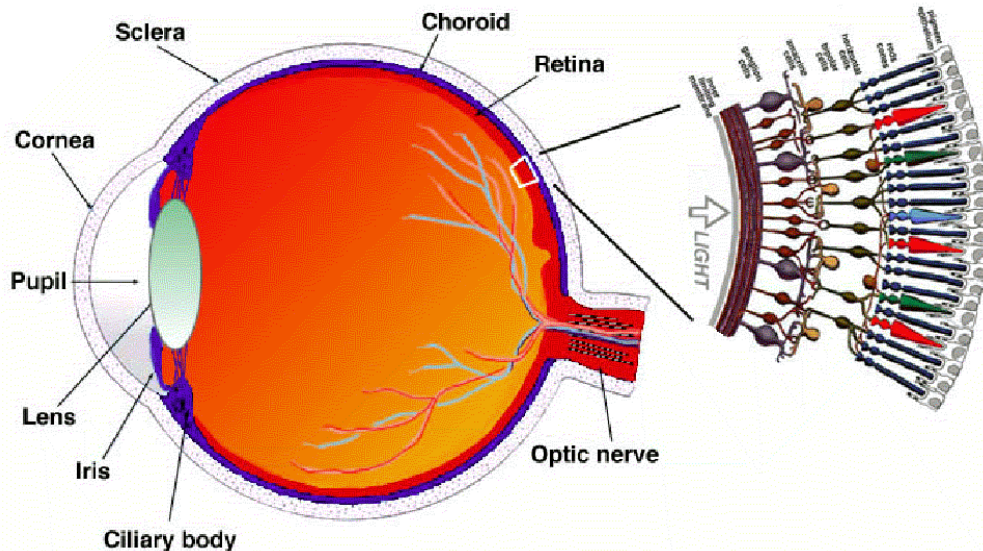
Fonte Luz → Reflectância → Resposta Espectral → Estímulo de cor



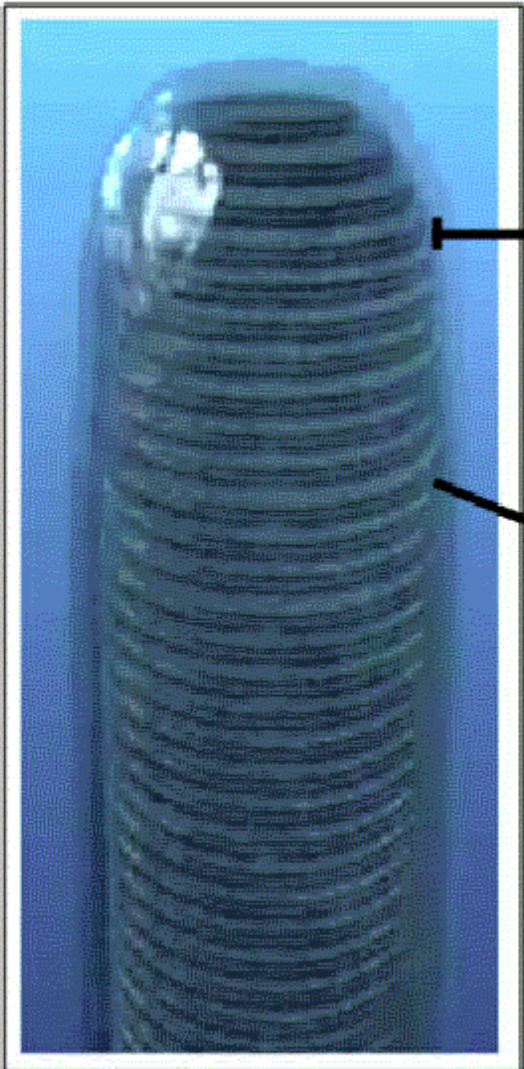
FISIOLOGIA DA VISÃO



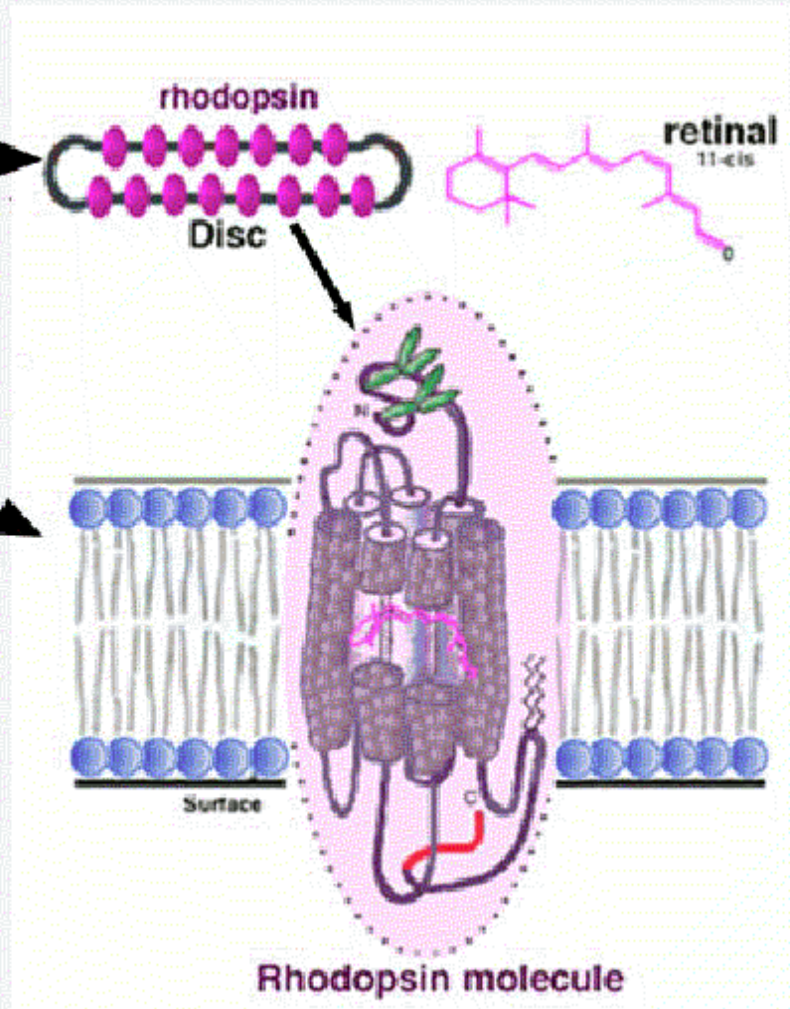
FOTORECEPTORES



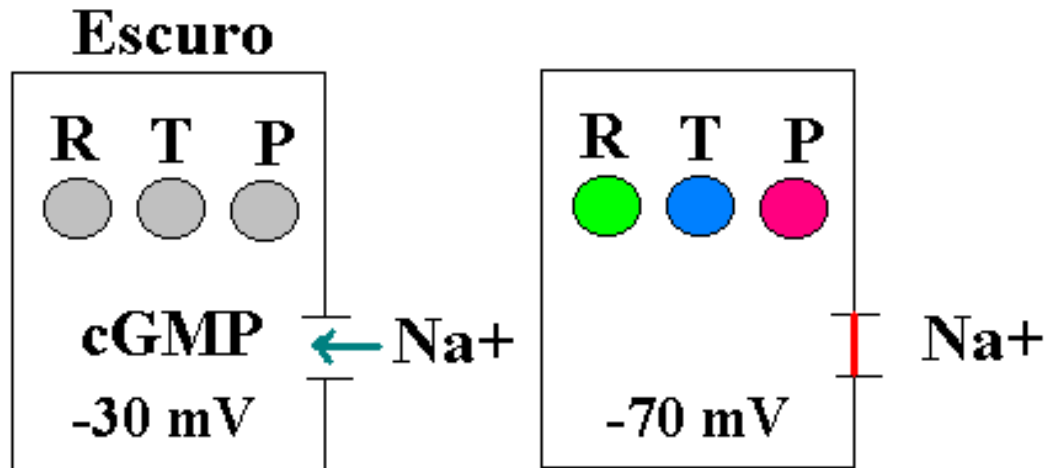
BASTONETES - RODOPSINA



outer segment



GERAÇÃO DO IMPULSO NERVOSO

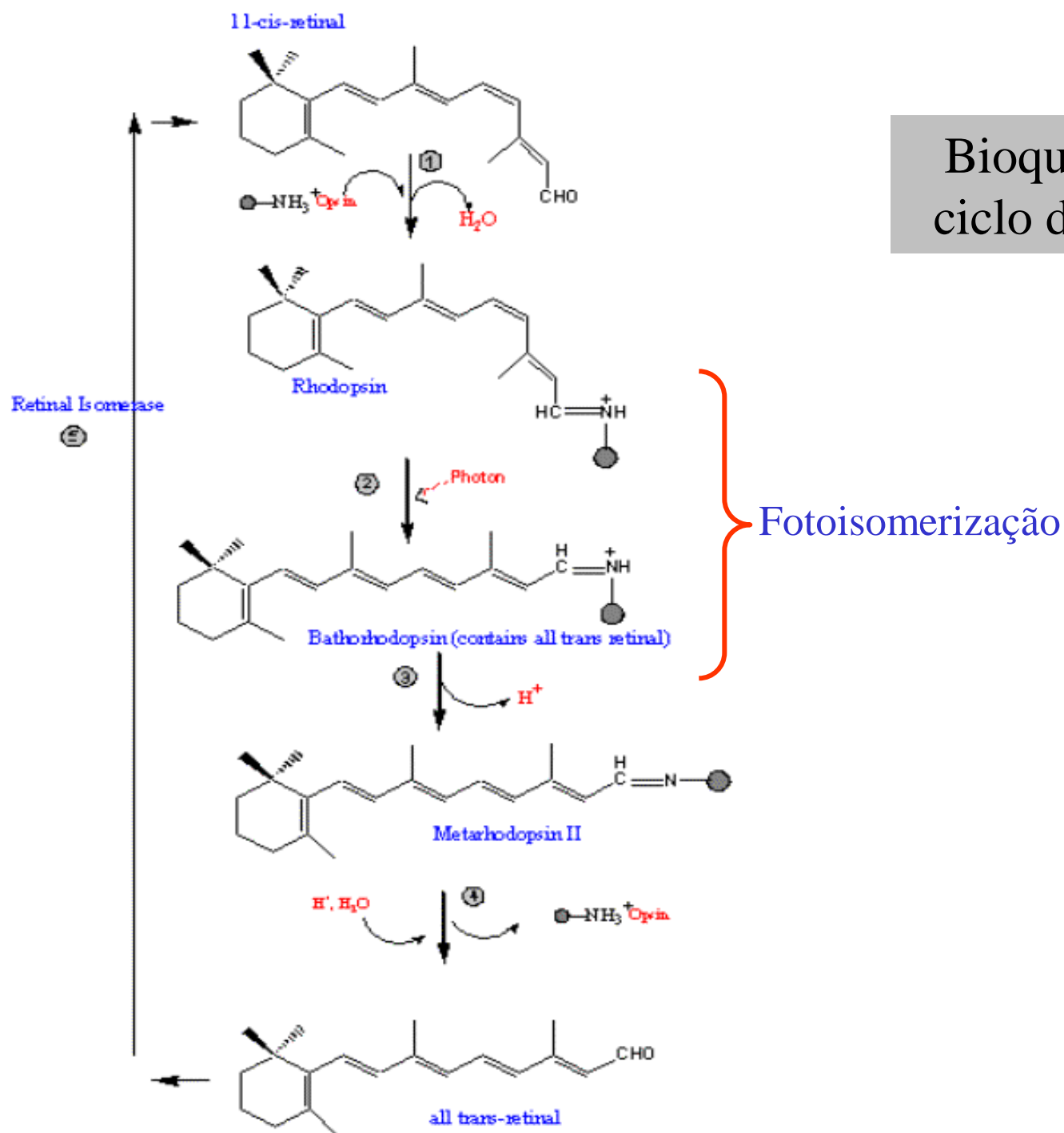


R = rodopsina

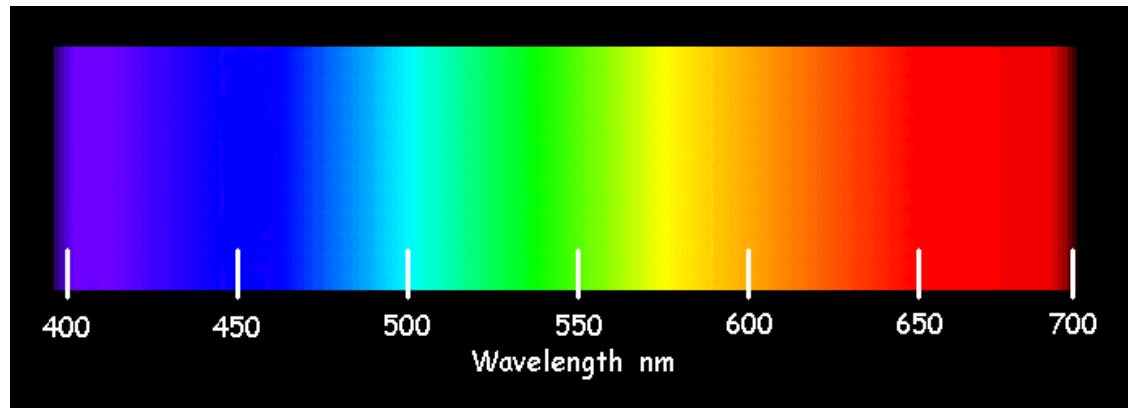
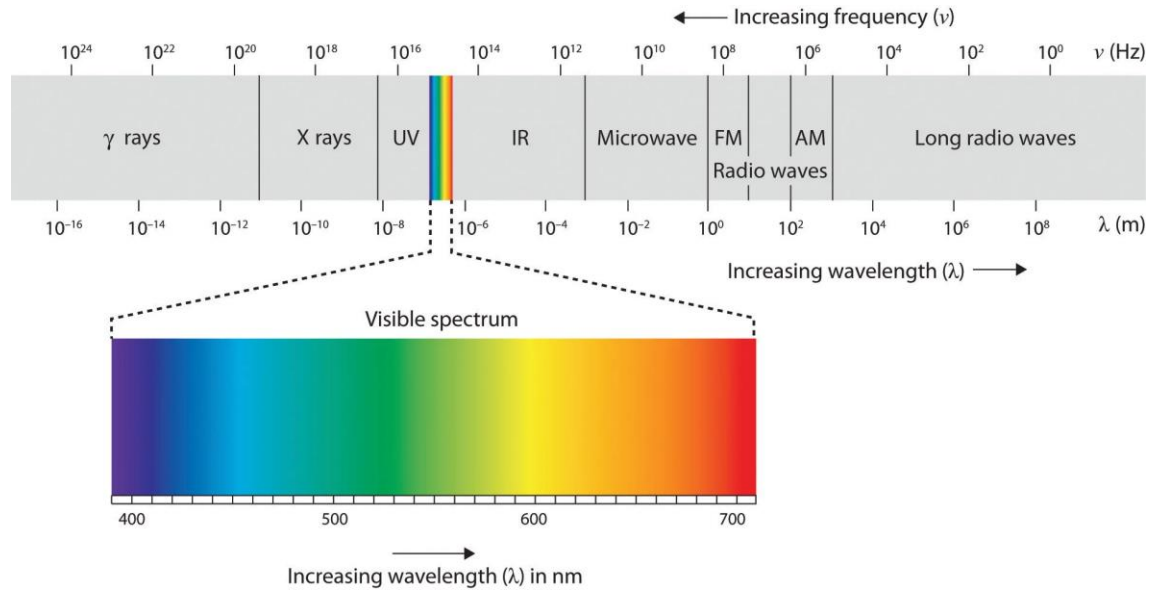
T = transducina

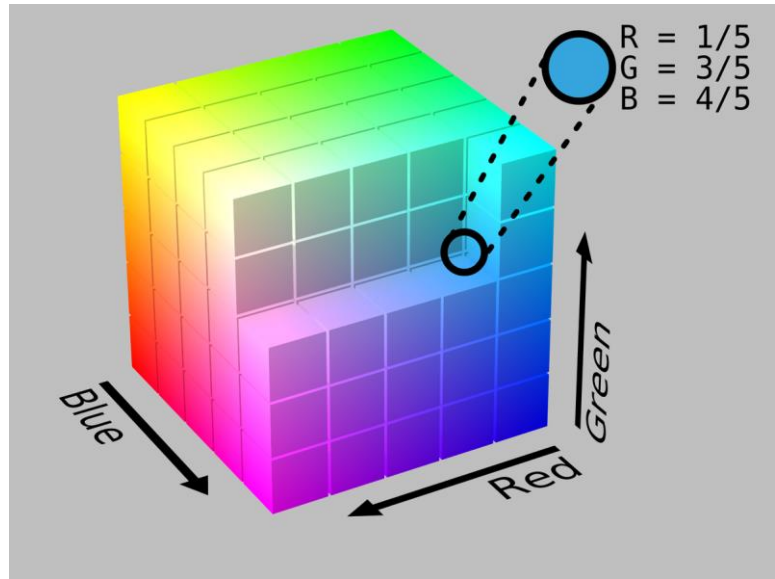
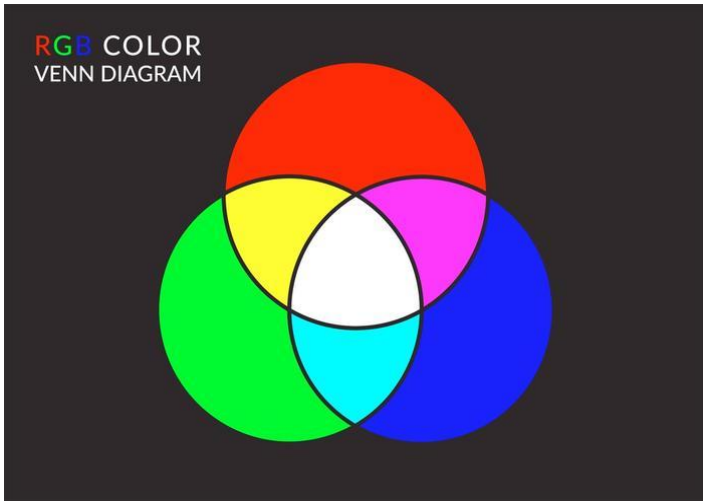
P = fosfodiesterase

Bioquímica do ciclo do Retinal

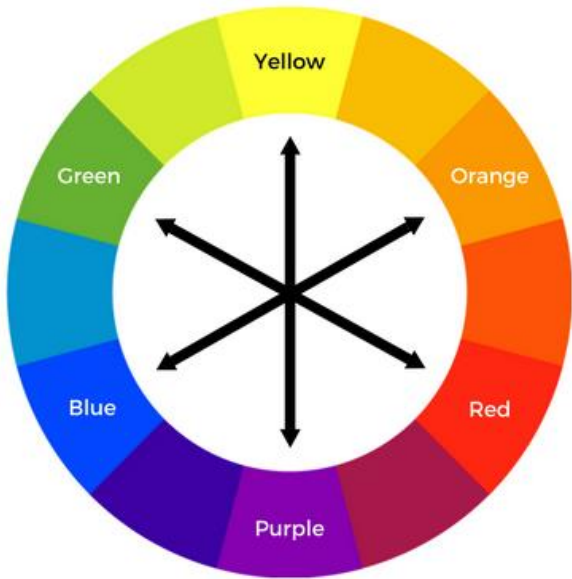


RADIAÇÃO ELETROMAGNÉTICA E LUZ VISÍVEL

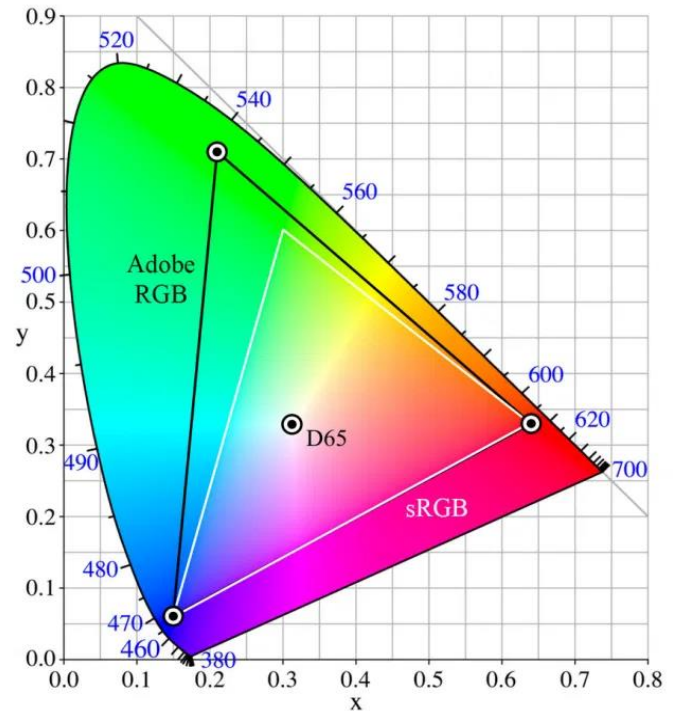




Complementary



COR COMPLEMENTAR



SISTEMAS GERANDO CORES

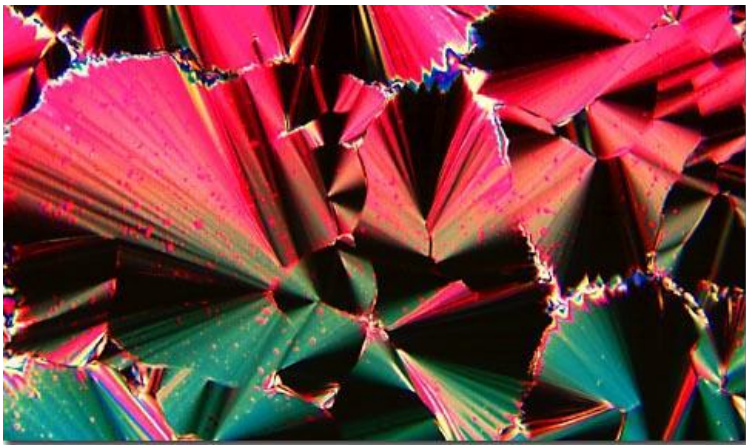
PURAMENTE
FÍSICO

Dispersão

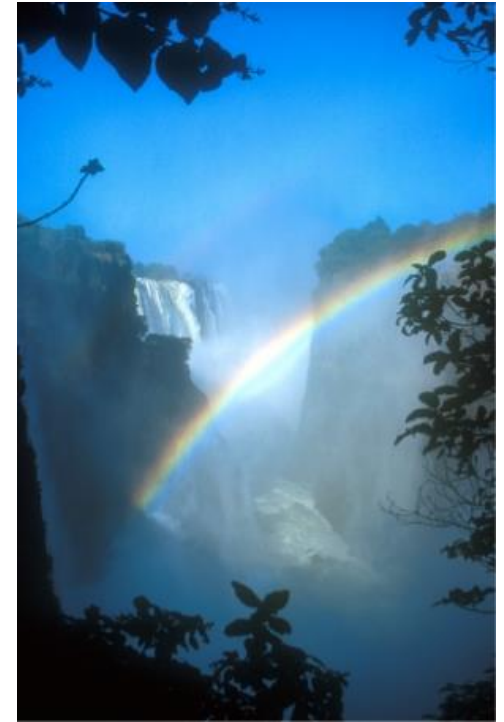
Espalhamento

Interferência

Difração



Birrefringência de cristal líquido de DNA



Arco íris

CORES ENVOLVENDO PROCESSOS FOTOFÍSICOS E FOTOQUÍMICOS

- 1) Incandescência
- 2) Excitação de gases e vapores

3) Cores em metais e ligas

4) Cores em semicondutores

5) Centros de cor

Teoria de bandas

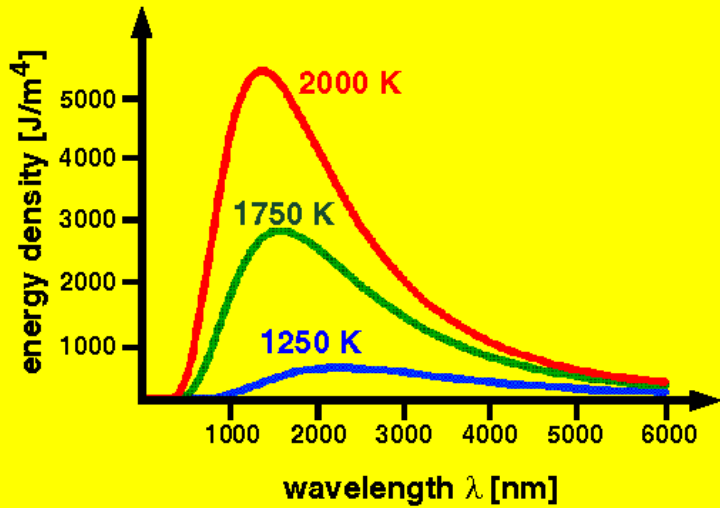
6) Cores em complexos inorgânicos

7) Cores em compostos orgânicos

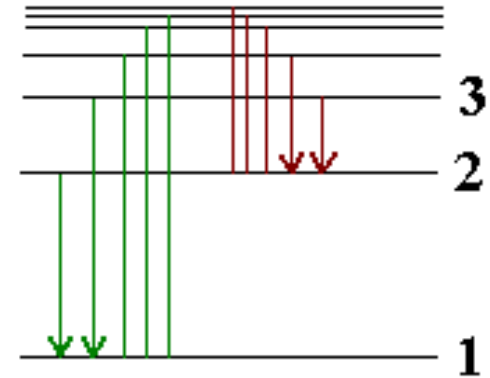
Teoria de orbital
molecular

2 – 7 : ENVOLVEM TRANSIÇÕES ELETRÔNICAS

Incandescência

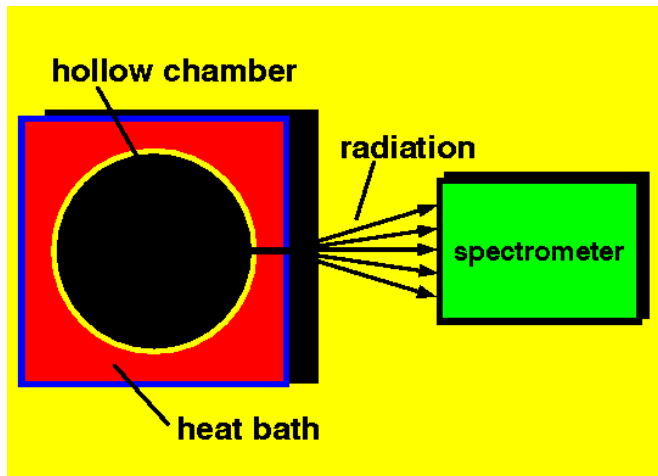


Excitação de gases e vapores (metais)



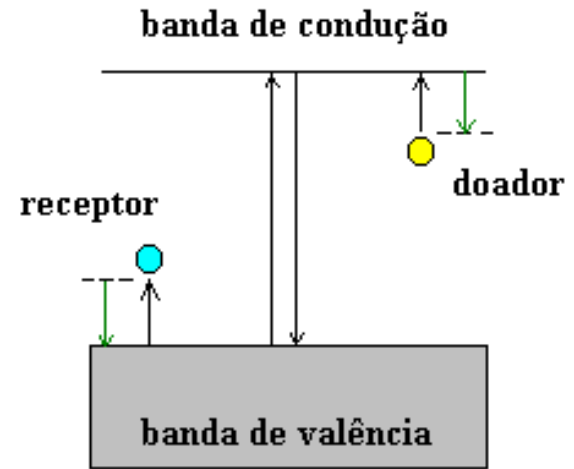
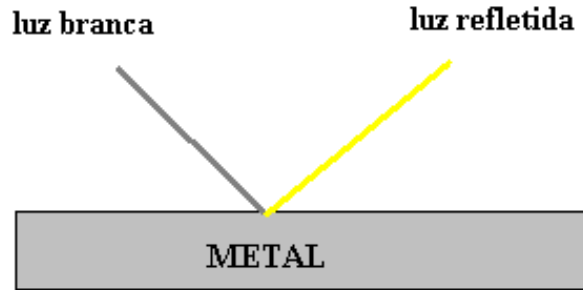
Espectro do hidrogênio

Series de Lyman, Balmer, Paschen



Cores em metais, semicondutores e centros de cor

Teoria de bandas



- 1) eficiência de absorção e re-emissão independente de λ (formam espelhos): Prata, Cromo, e Alumínio
- 2) Reflectividade depende de λ (metais com cor): Ouro, Cobre ...

Diamante: puro incolor (gap 5.4 eV)

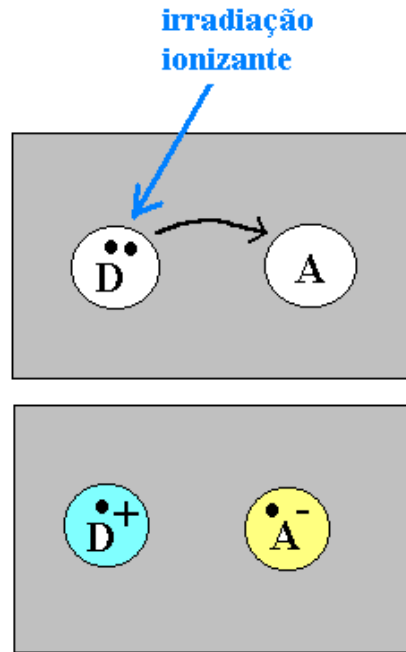
Dopado/impuro

- Nitrogênio / doador (gap 2.2 eV) / Amarelo

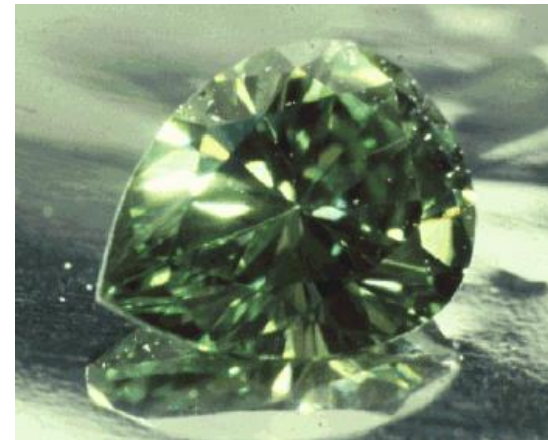
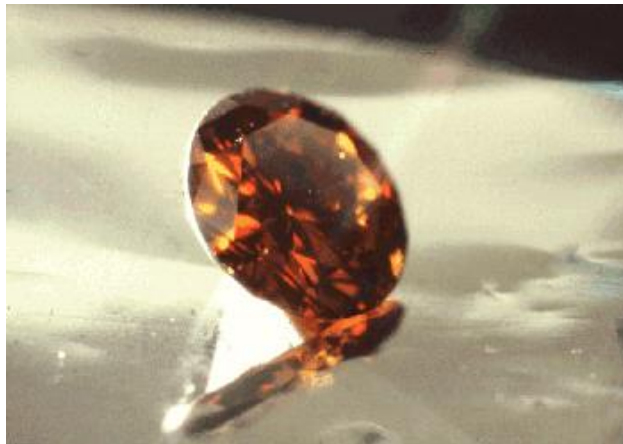
- Boro / Receptor (gap 0.5 eV) / Azul



Centros de Cor



Topázio: Natural / γ irradiado / tratamento térmico



Diamantes irradiados

ORBITAL MOLECULAR E TRANSIÇÕES ELETRÔNICAS

$$H\psi_n = E_n\psi_n$$

$$E_n = \langle \psi_n | H | \psi_n \rangle$$

$$\Delta E = E_2 - E_1 = h\nu$$

Aproximação de Born-Oppenheimer $\psi = \phi_e \phi_N$

Integral de momento de transição dipolar

$$\mu_{2,1} = \langle \psi_2 | \mu | \psi_1 \rangle = \langle \phi_2 | \mu | \phi_1 \rangle \langle \phi_{v'} / \phi_{v''} \rangle$$

Probabilidade de transição é proporcional a: $|\mu_{2,1}|^2 \langle \phi_{v'} / \phi_{v''} \rangle^2$

Transições permitidas p/ simetria e spin → Fortes

Fator de Franck-Condon

Transições proibidas p/ simetria ou spin → Muito Fracas

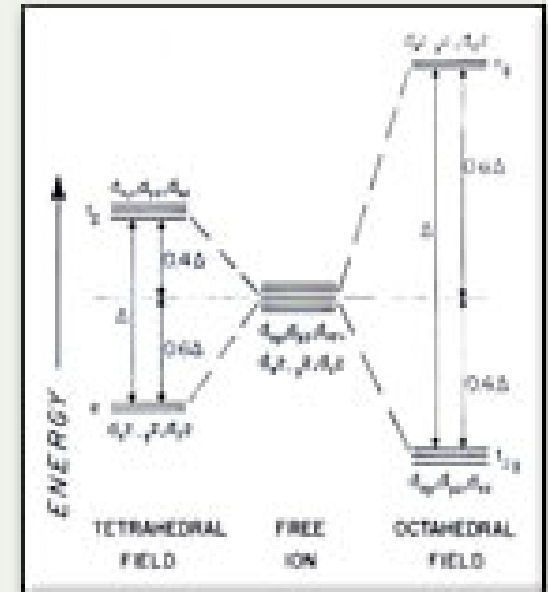
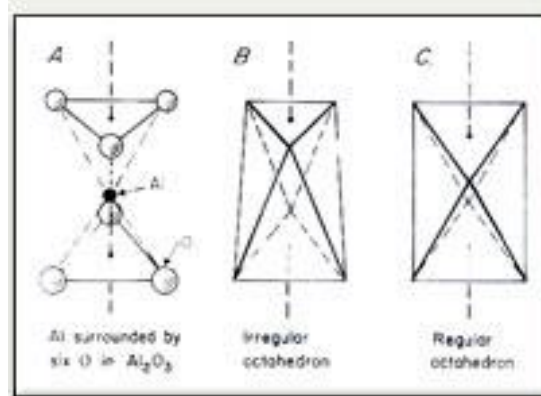
Quebra de Regra:

Simetria → Acoplamento Vibrônico

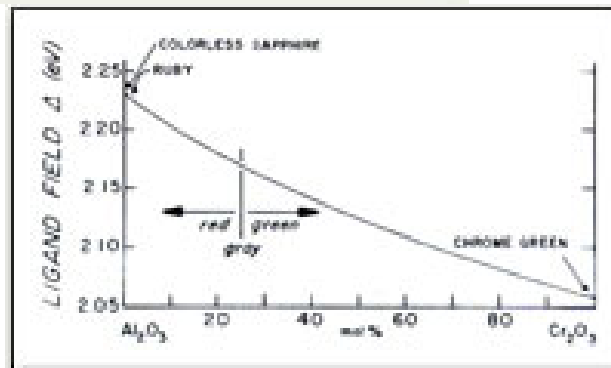
Spin → Acoplamento Spin-Orbita

Cores em Compostos e Complexos Inorgânicos

- a) Efeito de Campo Ligante (LF , d→d)
- b) Transferência de Carga (CT)
- c) Centrada no Ligante (LC)

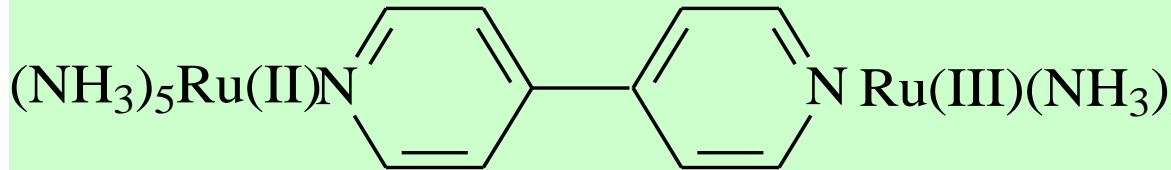
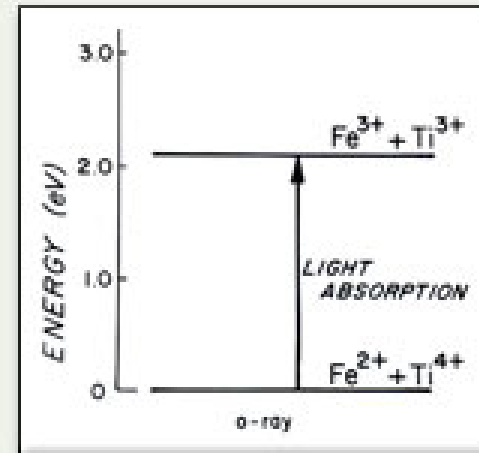
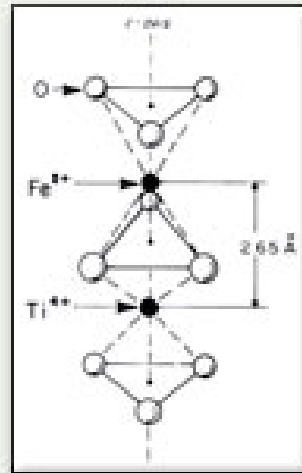


Al₂O₃ / Cr³⁺ (Rubi)

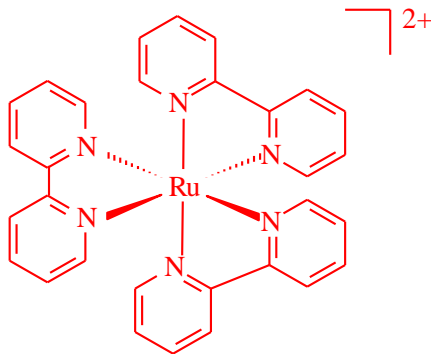


Transferência de Carga (IT e MLCT)

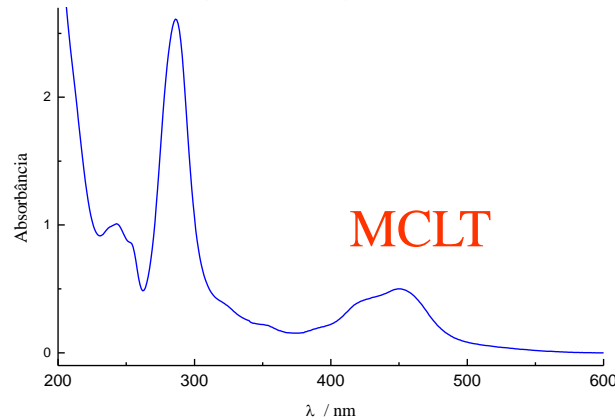
$\text{Al}_2\text{O}_3 / \text{Fe}^{2+} : \text{Ti}^{4+}$
(Safira)



IT = INTERVALÊNCIA

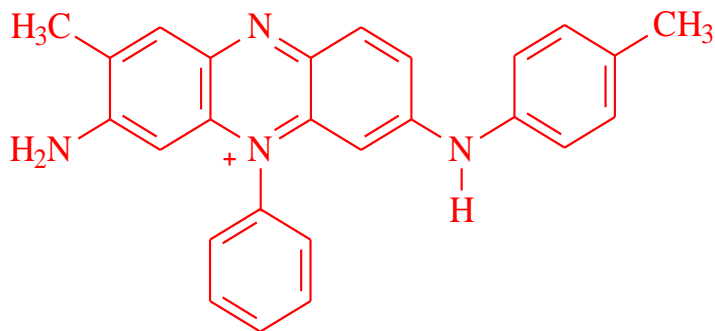


LC ($\pi \rightarrow \pi^*$)

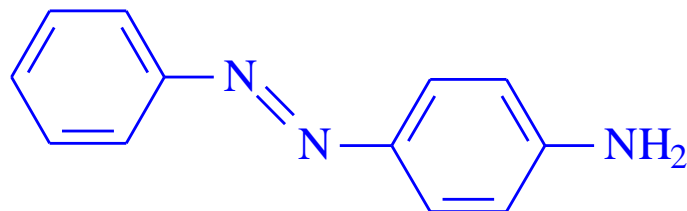


Cores em Compostos Orgânicos - Corantes

1856: Síntese da Mauveína (Willian Perkin)

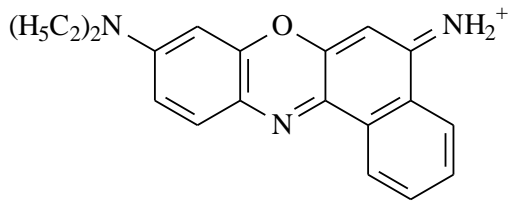


1858: Síntese de Azocorantes (Peter Griess)

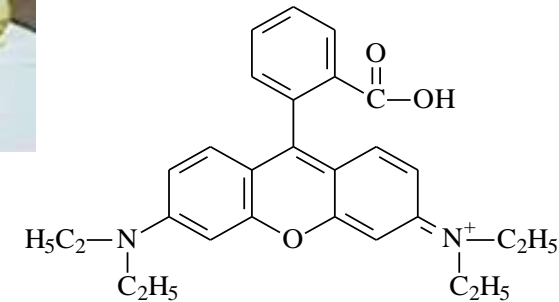
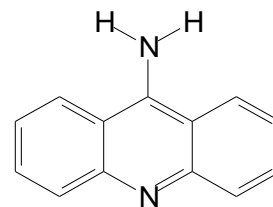
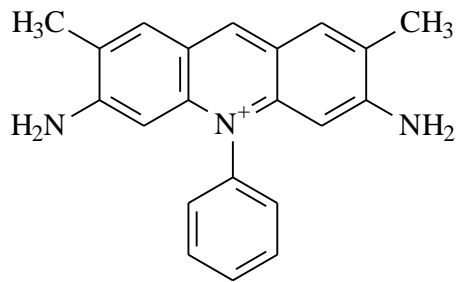
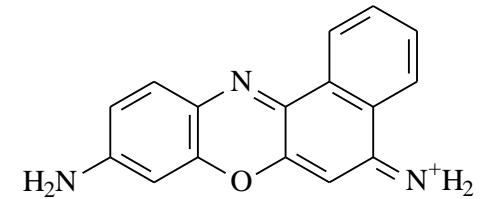


Corantes Orgânicos

Azul do Nilo



Violeta de cresila



Safranina

9-amino acridina

Rodamina B

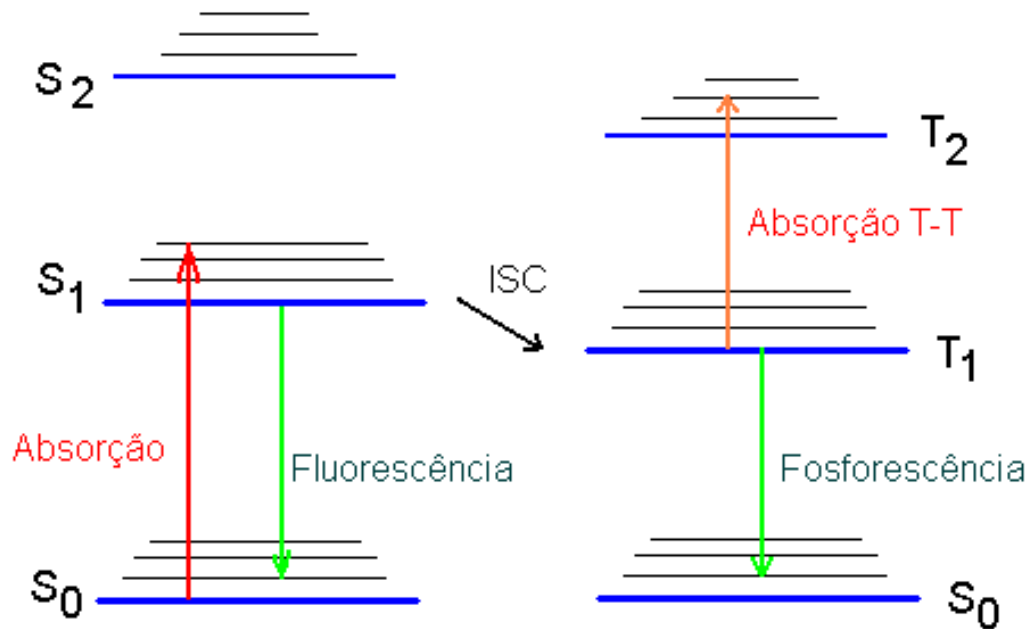
Transições $\pi \rightarrow \pi^*$ c/ alta absorvidade molar

CORES DE SISTEMAS NATURAIS: ESPONJAS



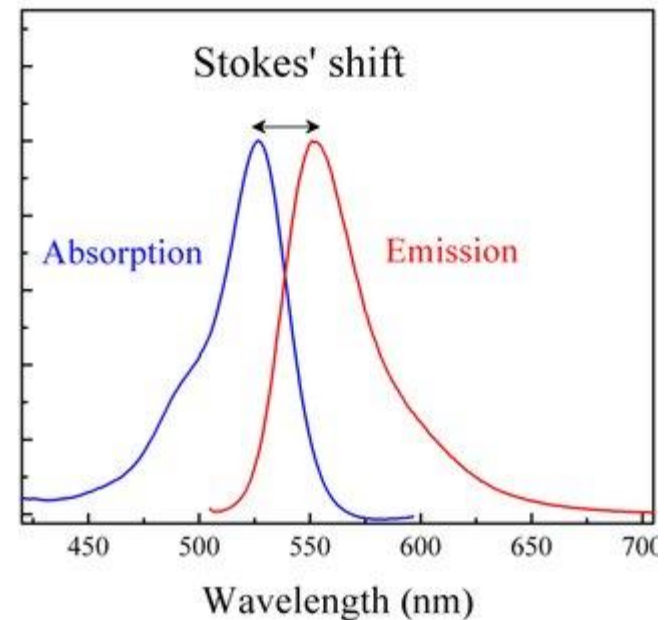
TRANSIÇÕES ELETRÔNICAS

DIAGRAMA DE JABLONSKI

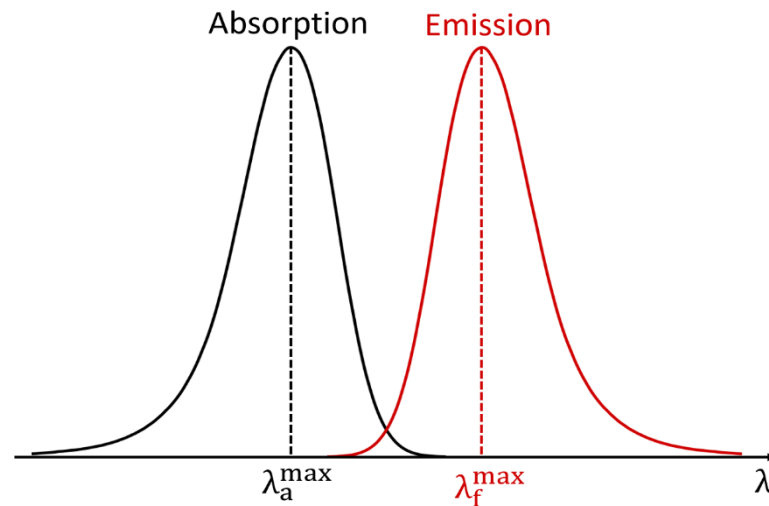


1) Absorção de fótons

2) Emissão de fótons

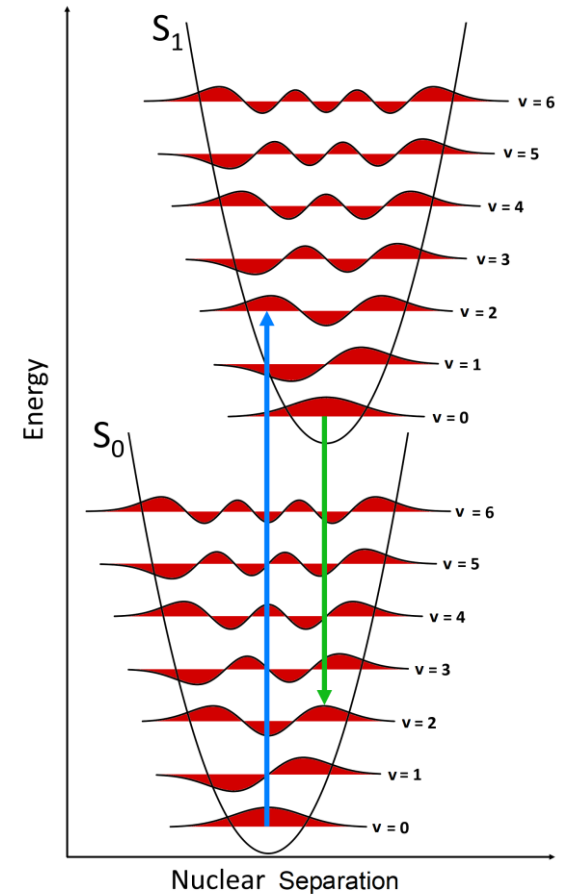


Deslocamento de Stokes entre absorção e emissão



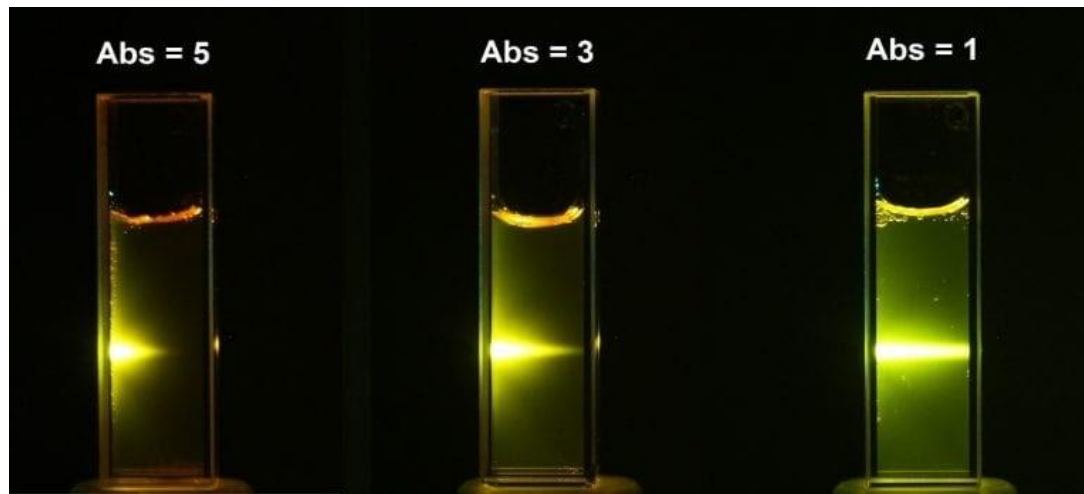
Stokes Shift (Wavelength) $\Delta\lambda = \lambda_f^{\max} - \lambda_a^{\max}$

Stokes Shift (Wavenumber) $\Delta\bar{\nu} = \bar{\nu}_a^{\max} - \bar{\nu}_f^{\max} = \frac{1}{\lambda_a^{\max}} - \frac{1}{\lambda_f^{\max}}$



ABSORÇÃO DE LUZ

Lei de Lambert - Beer



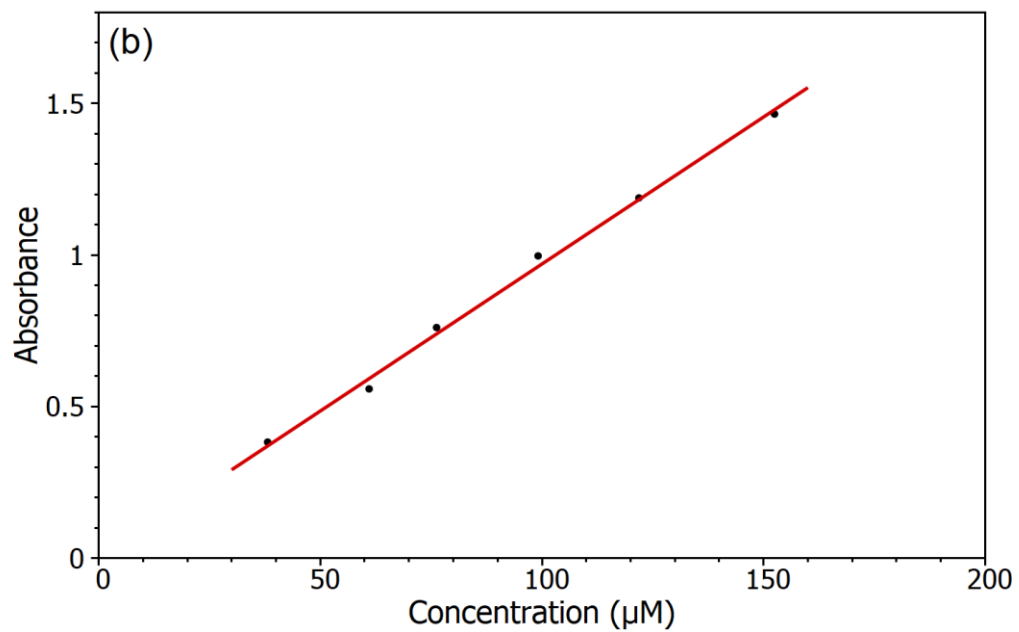
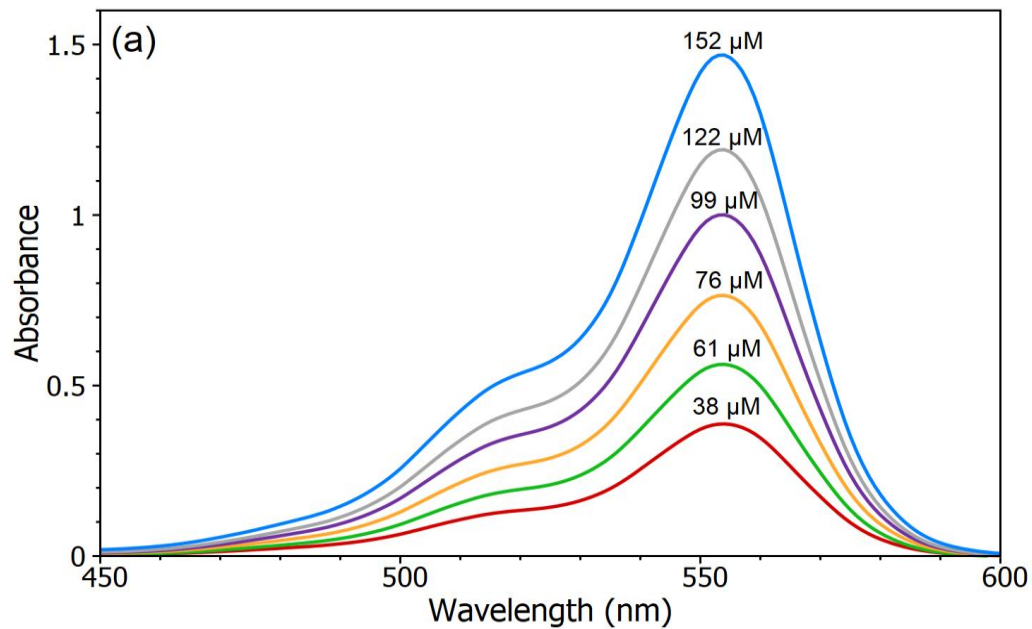
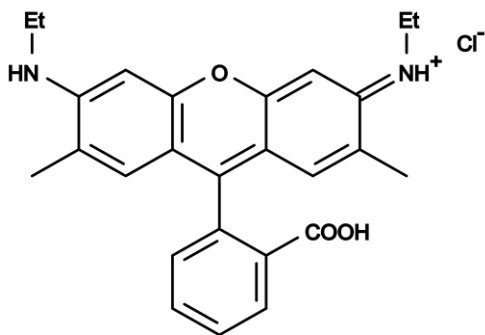
Absorbância

$$\text{Abs} = \varepsilon \ell [C]$$

ε = coeficiente de extinção molar ($\text{Lmol}^{-1}\text{cm}^{-1}$)

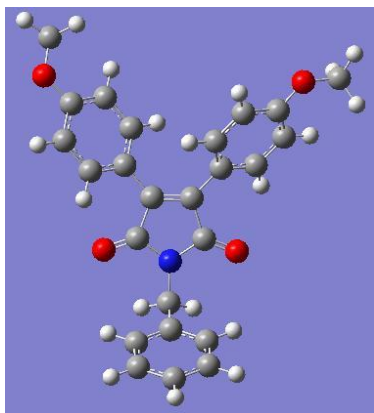
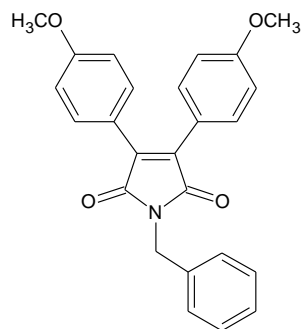
ℓ = percurso (cm)

[C] concentração mol/L

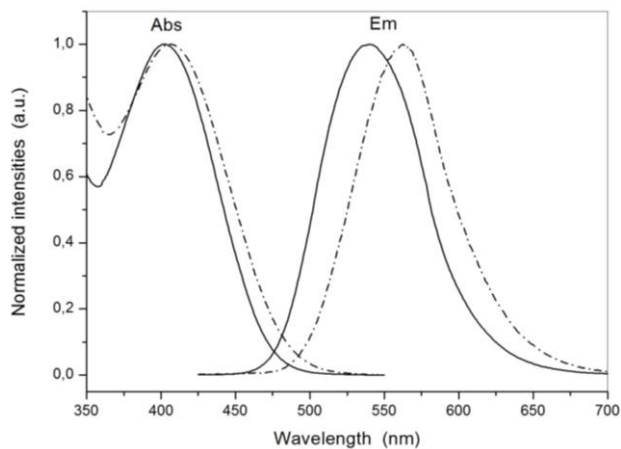
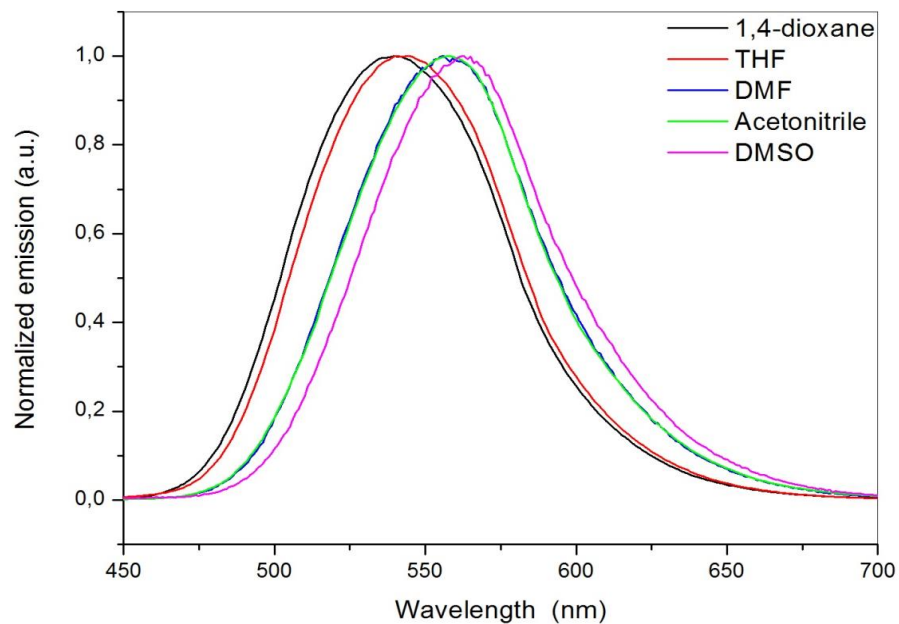


$$\text{Abs} = \epsilon \ell [C]$$

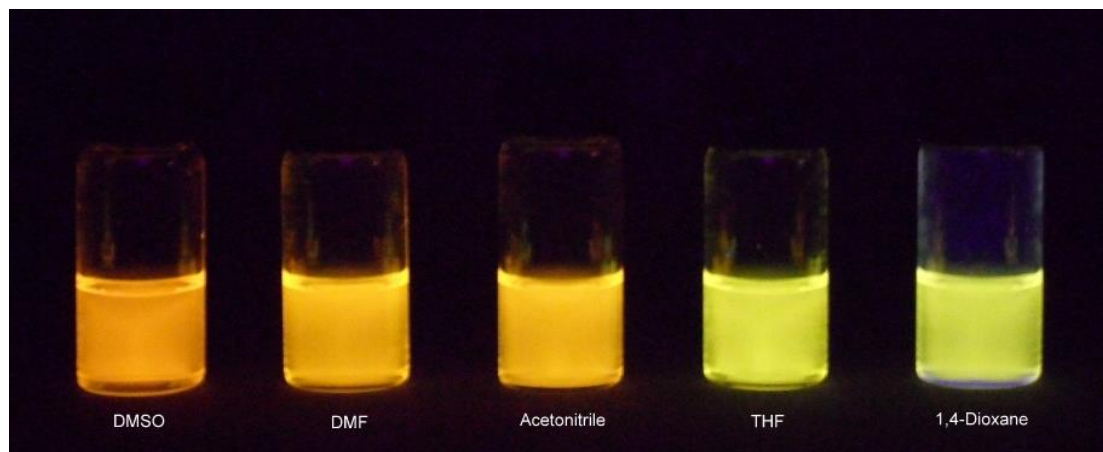
MALEIMIDA DERIVATIVE



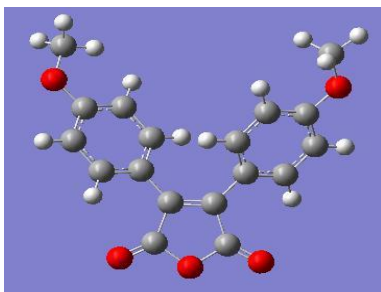
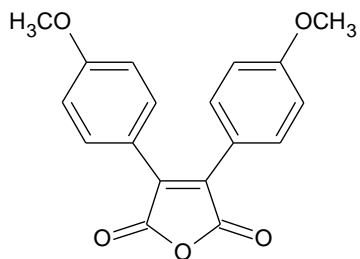
DFT – B3LYP – 6-311G++ (2d, 2p)



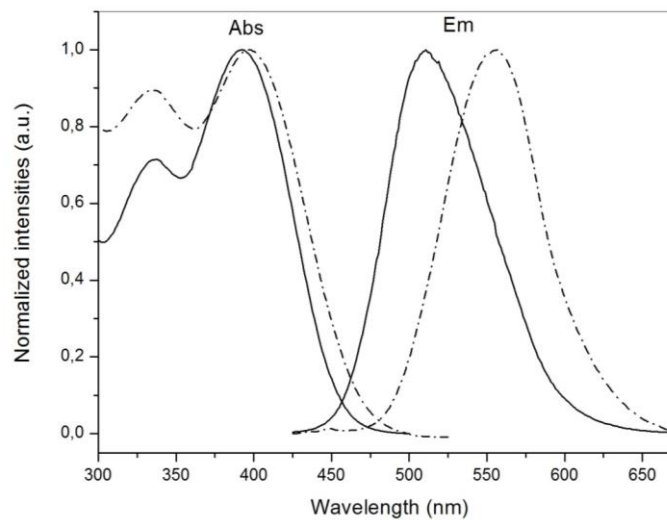
Normalized absorption and emission spectra of compound **II-1** in 1,4-dioxane (solid) and in DMSO (dash dot)



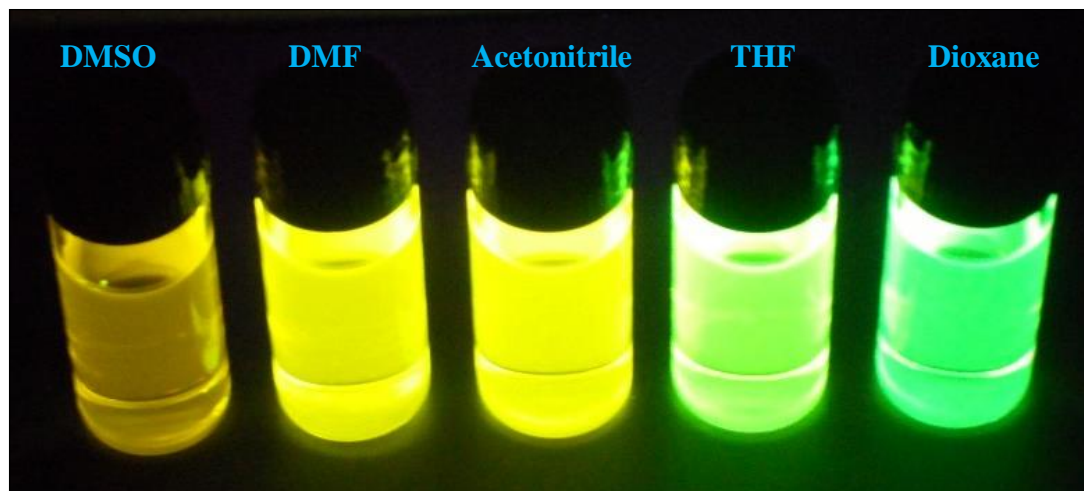
Diarylated maleic anhydrides



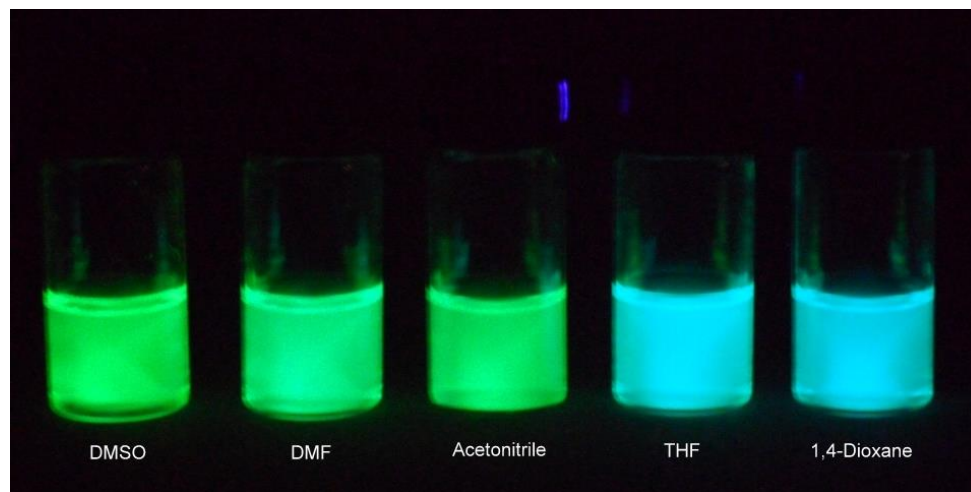
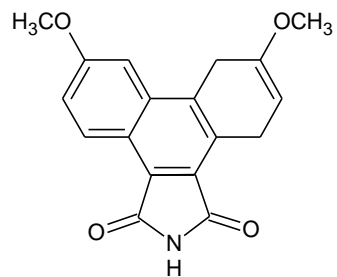
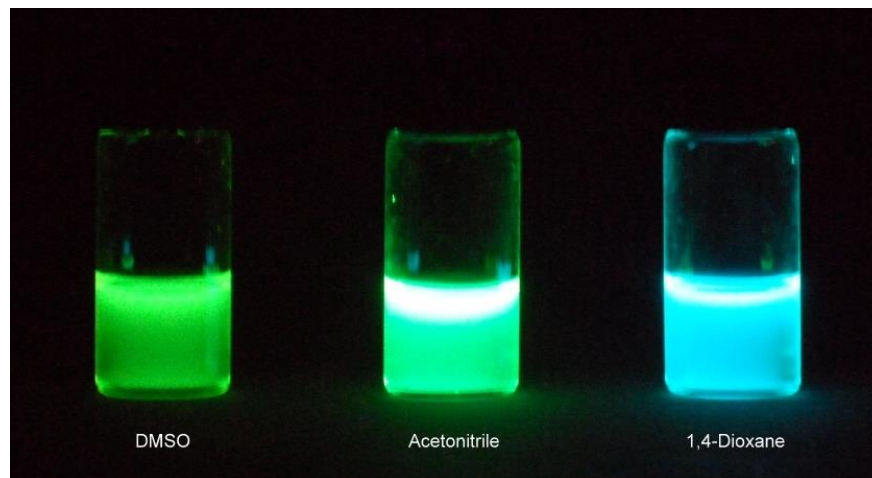
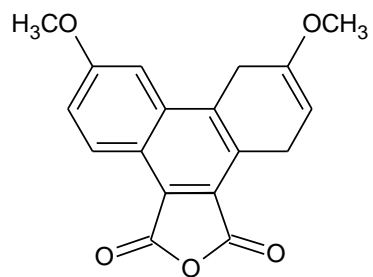
DFT – B3LYP – 6-311G++ (2d, 2p)



Normalized absorption and emission spectra of compound **I-4** in 1,4-dioxane (solid) and in DMSO (dash dot).

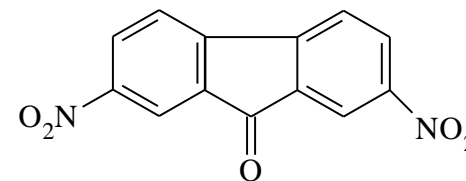
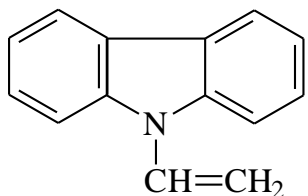


PHENANTHRENE DERIVATIVES



VARIAÇÃO ESPECTRAL EM SISTEMAS MOLECULARES

- 1) Efeito de substituintes no cromóforo
- 2) Efeito de solvente / equilíbrio ácido-base
- 3) Processos de associação (autoagregação / complexos CT bimoleculares)

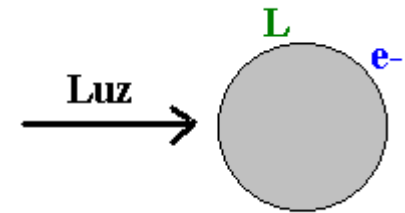
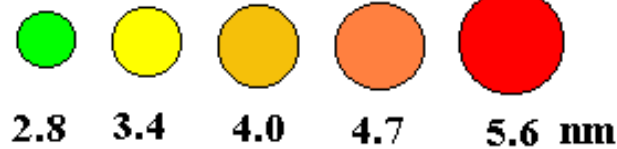


Metais e semicondutores: Podemos variar a cor ???

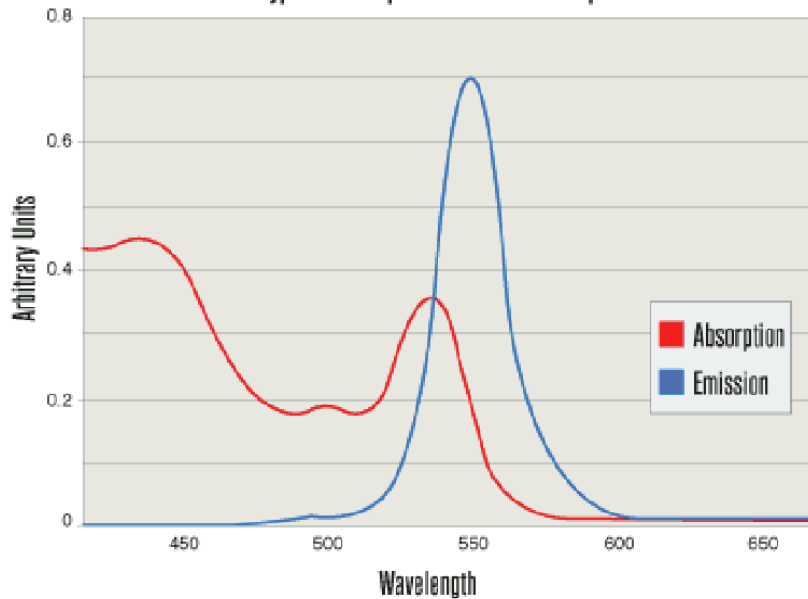


Nanopartículas de CdSe

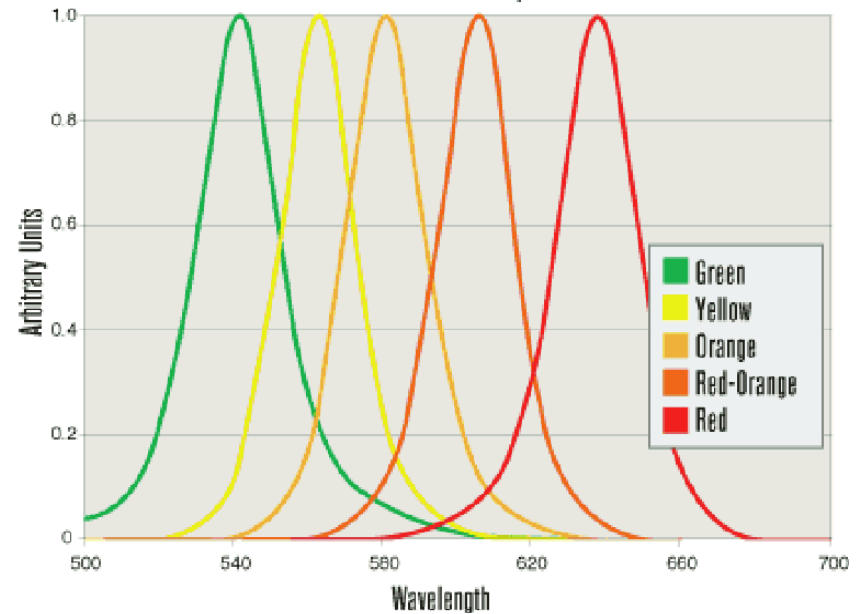
Efeito Quântico
de tamanho



Typical Absorption and Emission Spectra



5 Color Kit Emission Spectra



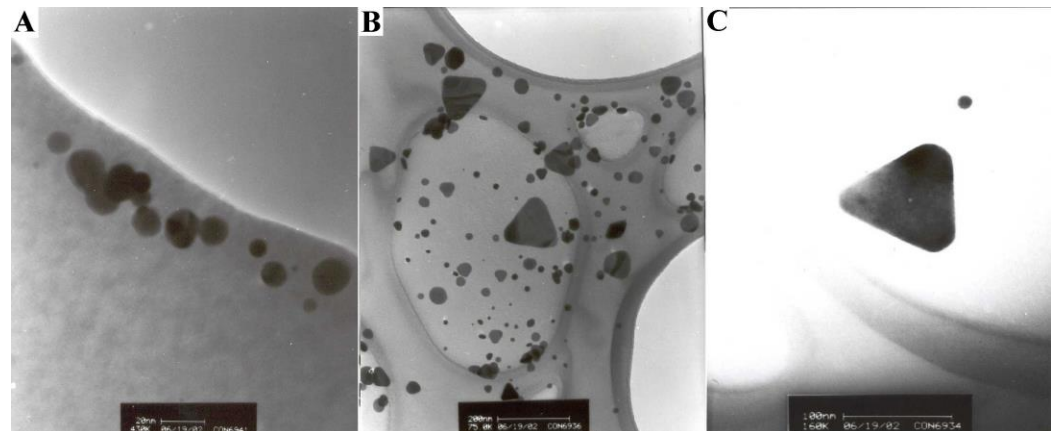
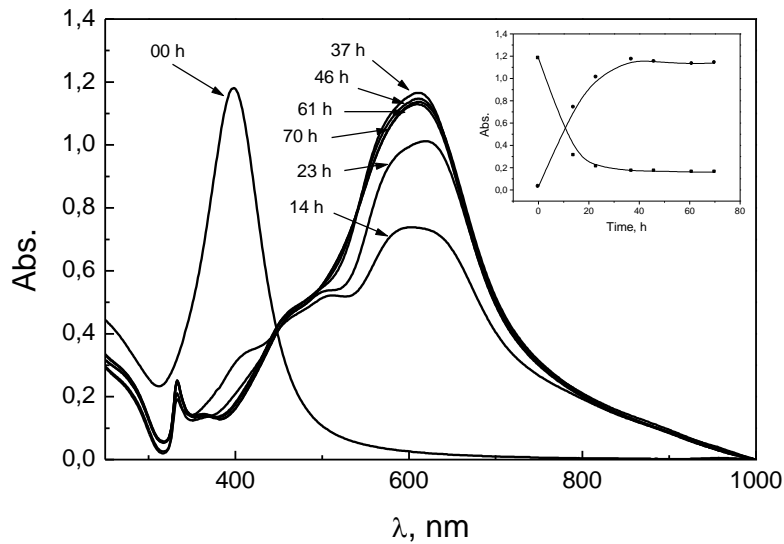
NANOPARTÍCULAS METÁLICAS (Ag ; Au ...)



Teoria de Mie-Drude:
Absorção e
espalhamento

Esferas: $d = 14 \text{ nm}$

Prismas: aresta 100 nm



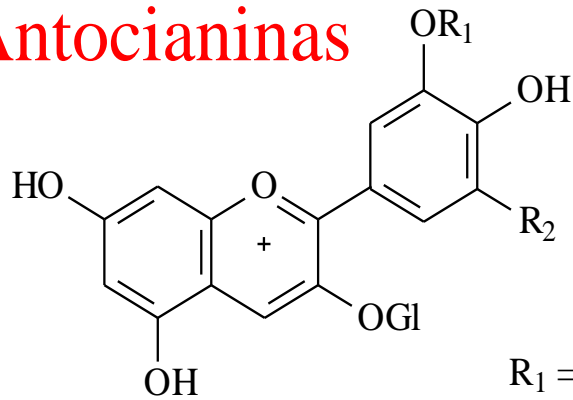


Morpho Menelaus / Flor

Qual a razão das cores?

A razão das Cores

Antocianinas



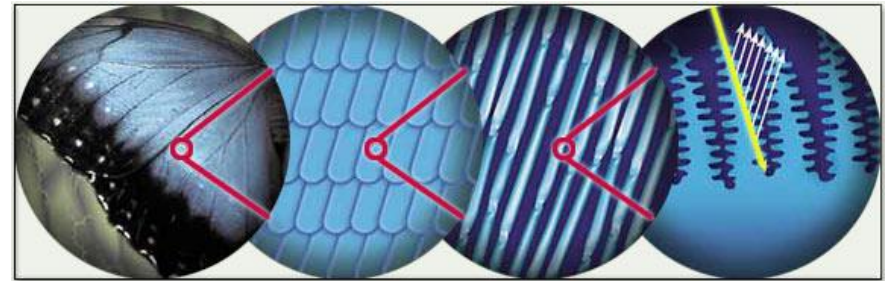
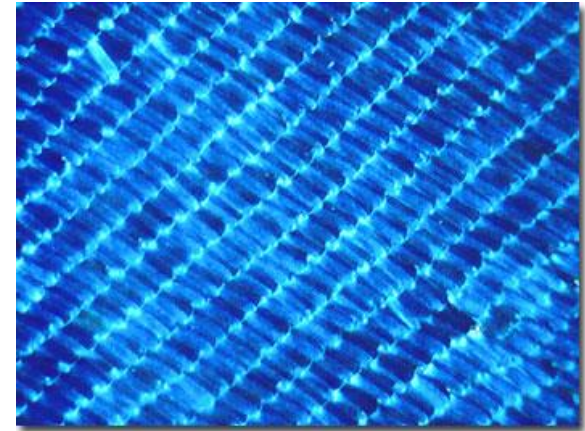
R₁ = H, CH₃

R₂ = H, OR₁

Cátion Flavílio

Efeito de absorção

Transição eletrônica



Efeito de interferência construtiva
da radiação 400 – 480 nm

Espaçamento \approx 200 nm