

# FUNDAMENTOS E APLICAÇÕES EM FOTOQUÍMICA MOLECULAR

**Prof. Dr. Marcelo H. Gehlen**

**Email:** [marcelog@iqsc.sc.usp.br](mailto:marcelog@iqsc.sc.usp.br)



**USP**

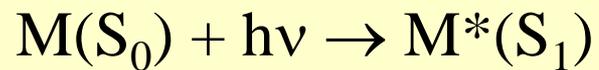
**Universidade de São Paulo**  
B R A S I L

## TÓPICOS E OBJETIVOS

- 1) CONCEITOS BÁSICOS EM FOTOQUÍMICA
- 2) PROCESSOS FOTOQUÍMICOS / EXEMPLOS
- 3) MÉTODOS EXPERIMENTAIS
- 4) FOTOQUÍMICA EM NOSSO COTIDIANO
- 5) PESQUISAS APLICADAS

# CONCEITOS BÁSICOS EM FOTOQUÍMICA

Fotoquímica Molecular = Reações Químicas envolvendo Estados Eletrônicos Excitados



$$E = h\nu = \frac{hc}{\lambda}$$

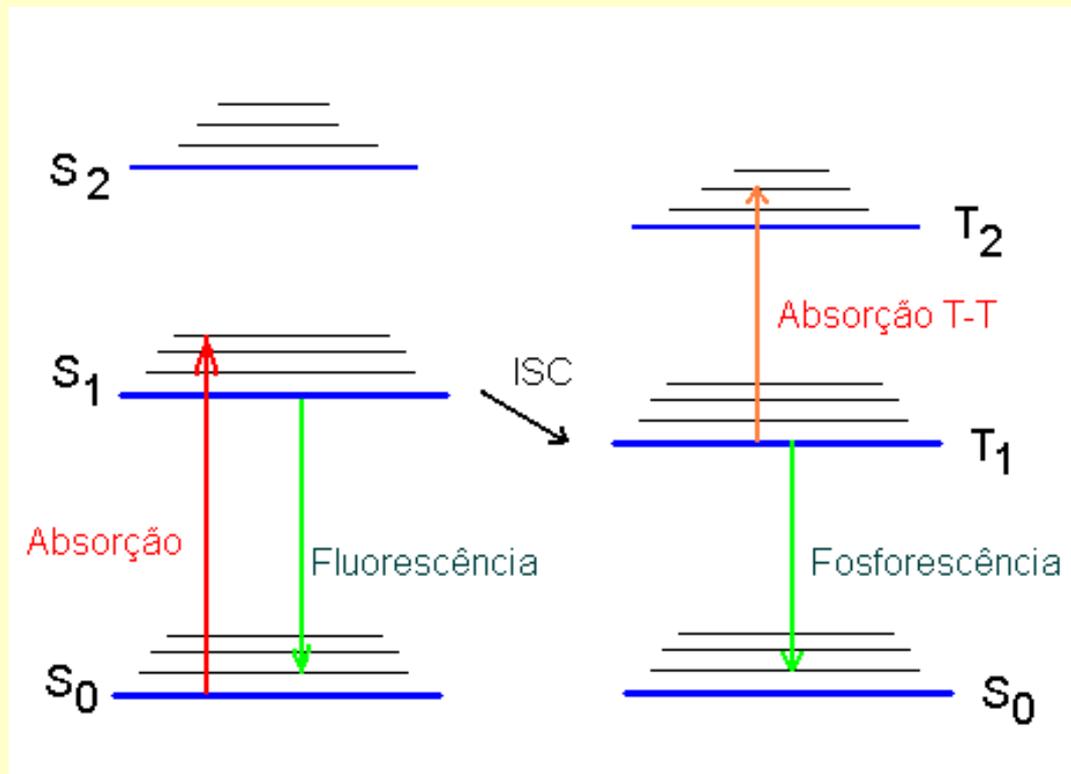


DIAGRAMA SIMPLIFICADO DE JABLONSKI

# PARÂMETROS ESPECTROSCÓPICOS

Absorção / Lei de Lambert-Beer

$$\text{Abs} = \varepsilon_{\lambda} \ell [\text{M}]$$

Emissão / Rendimento Quântico ( $\phi$ ) e Tempo de vida ( $\tau$ )

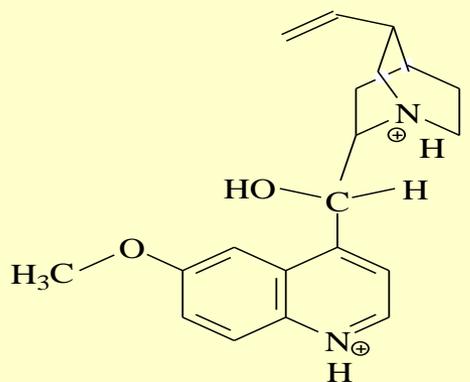
$$\phi = \frac{\text{Fótons emitidos}}{\text{Fótons absorvidos}}$$

Medida do Rendimento Quântico ( $\phi$ ) de uma amostra A usando um padrão de emissão P

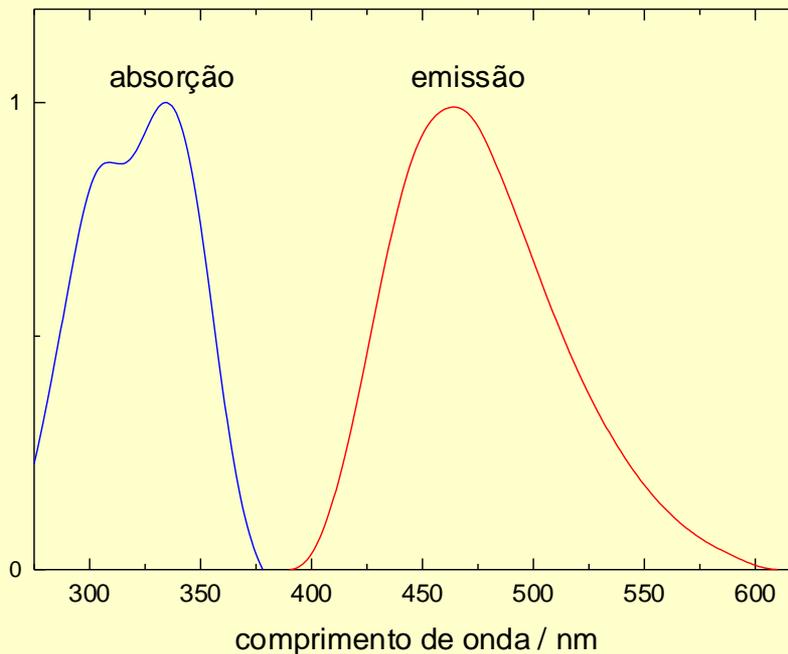
$$\phi_A = \phi_P \frac{\text{Abs}(P)I(A)}{\text{Abs}(A)I(P)}$$

# PADRÕES DE FLUORESCÊNCIA

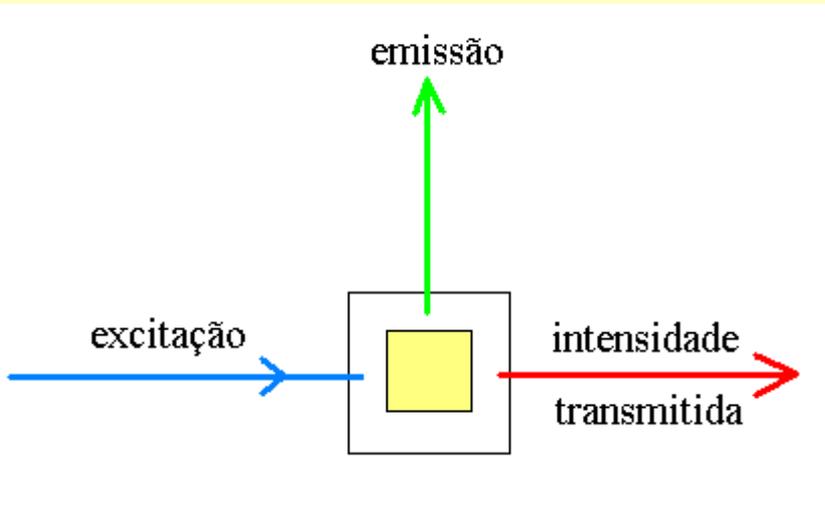
Padrão	Solvente	Região, nm	$\phi_F$
Sulfato de Quinina	0,1 M H <sub>2</sub> SO <sub>4</sub>	400-600	0,546±0,023
9,10-Difenilantraceno	Ciclohexano	400-500	1,000±0,050
2-Aminopiridina	0,1 N H <sub>2</sub> SO <sub>4</sub>	315-480	0,600±0,050
Triptofano	H <sub>2</sub> O pH 7,20	300-380	0,130±0,010
Rodamina 101	Etanol	600-650	1,000±0,020
Violeta de Cresila	Metanol	600-650	0,540±0,030
Antraceno	Etanol	360-480	0,270±0,030
Naftaleno	Ciclohexano	300-400	0,230±0,020
Benzeno	Ciclohexano	270-300	0,050±0,020



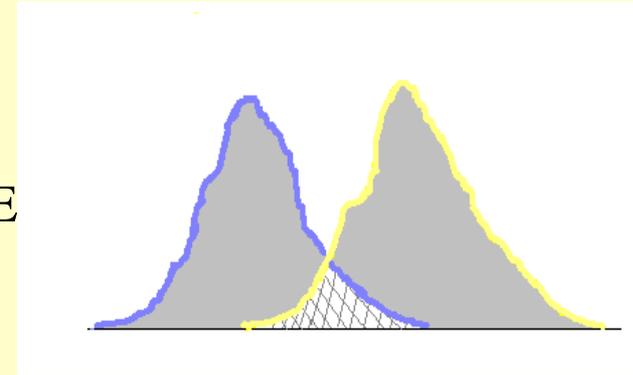
Sulfato de Quinina



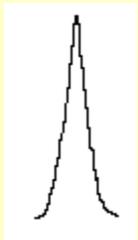
# INTENSIDADE DE EMISSÃO



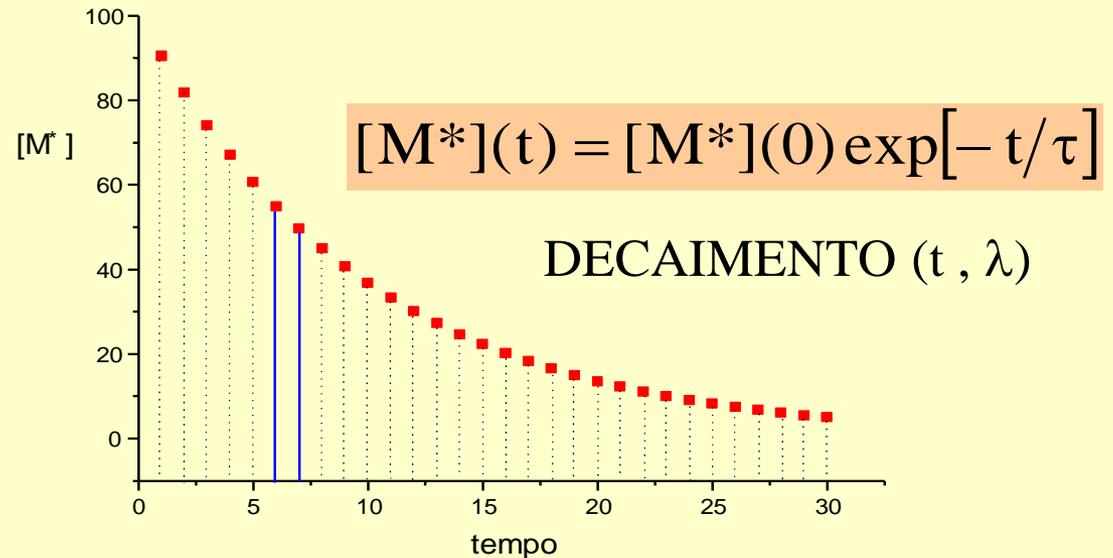
LUZ CONSTANTE



ESPECTROS ( $\lambda$ )



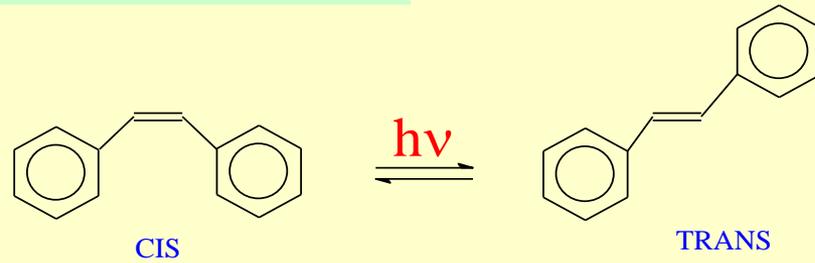
PULSO LUZ



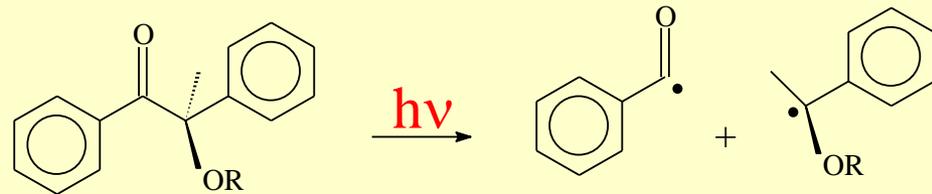
# PROCESSOS FOTOQUÍMICOS

## UNIMOLECULARES

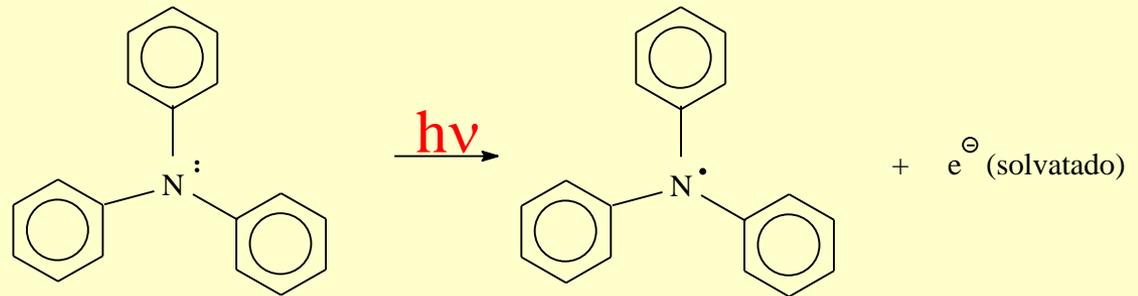
Fotoisomerização



Fotodissociação

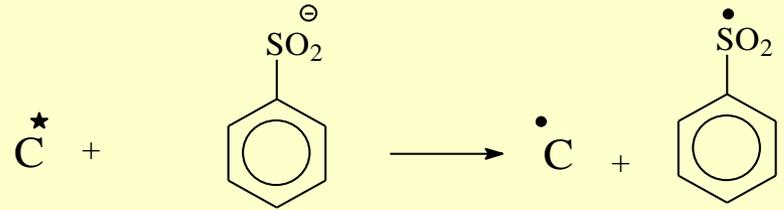


Fotoionização

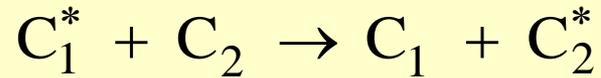


# BIMOLECULARES

→ Transferência de carga (elétron)



→ Transferência de energia



Abstração de H

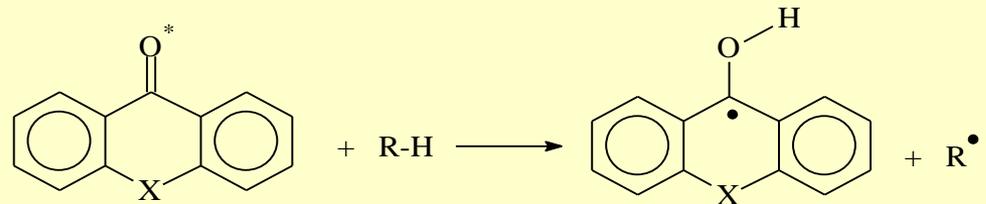
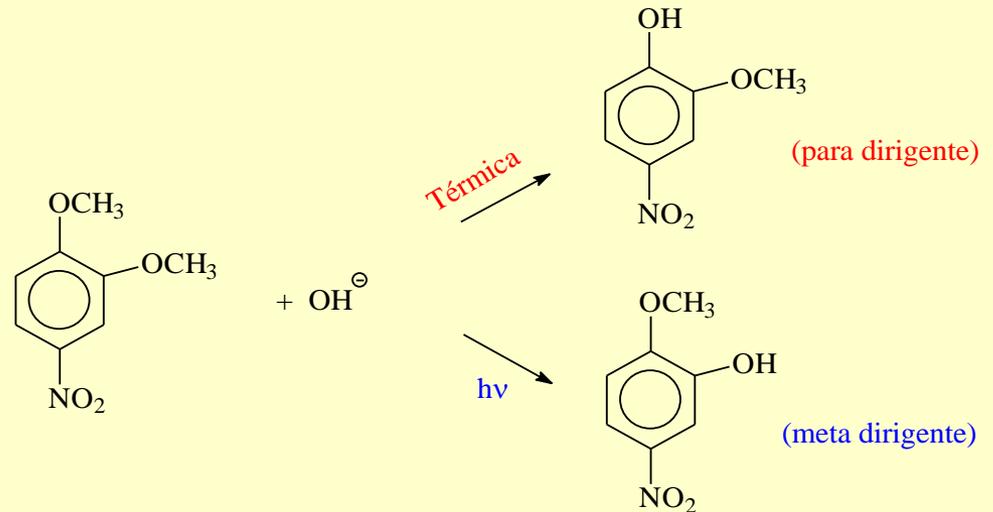
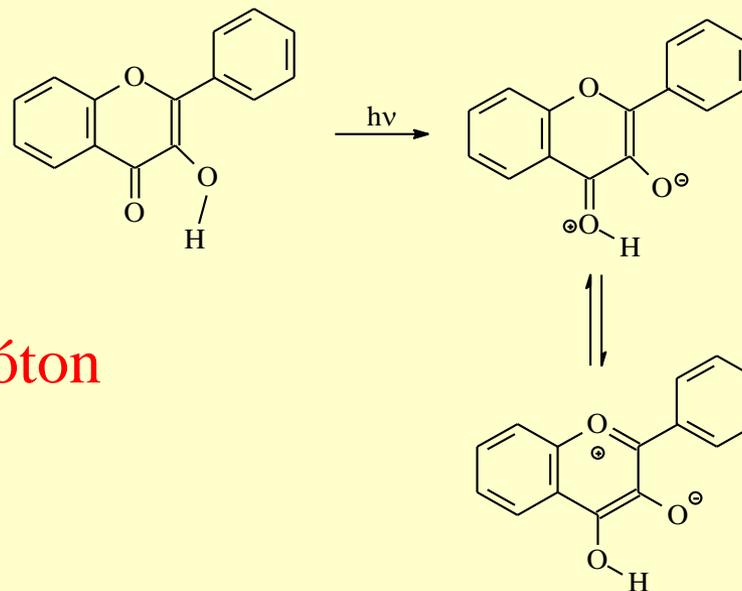
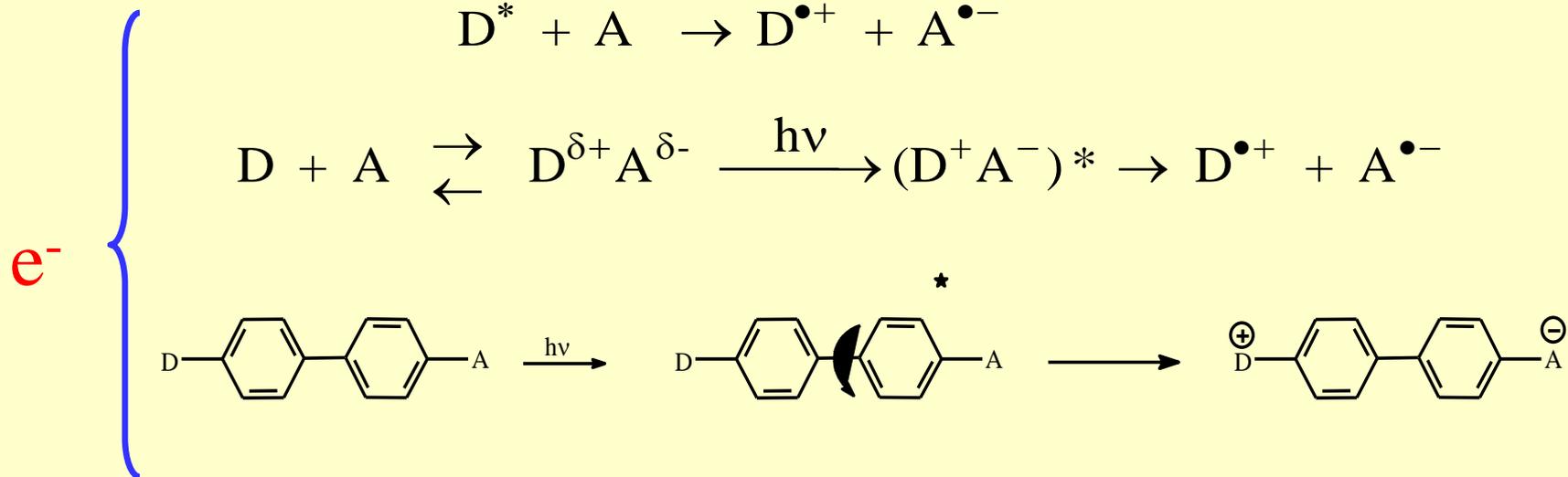


Foto-substituição

Nucleofílica



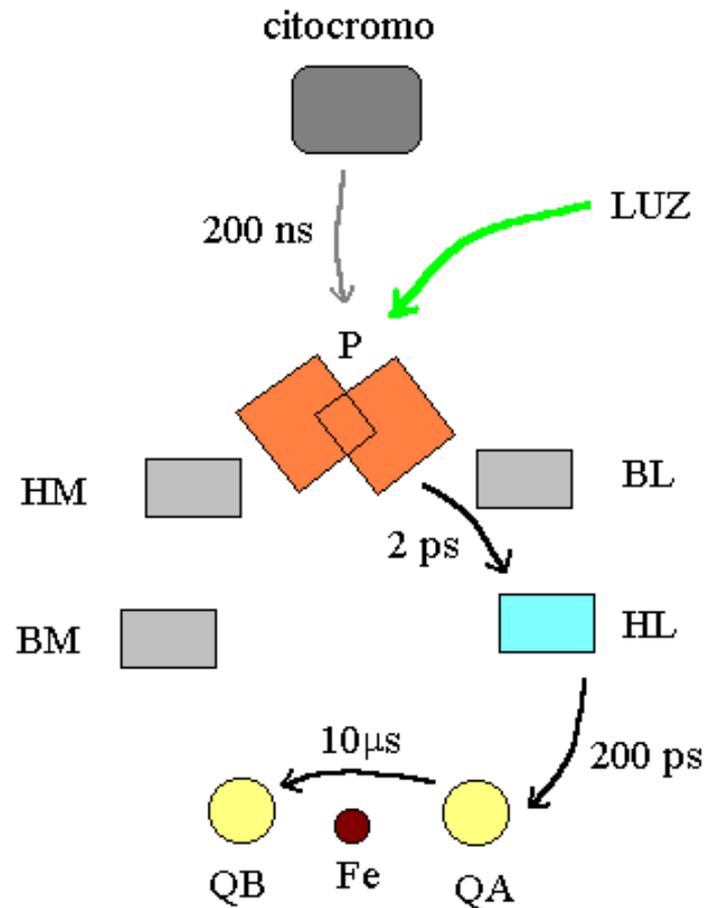
# Transferência de Carga Foto-induzida



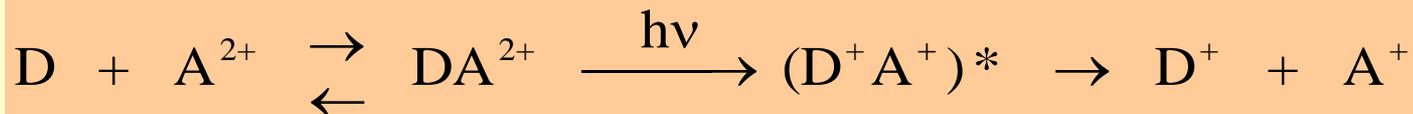
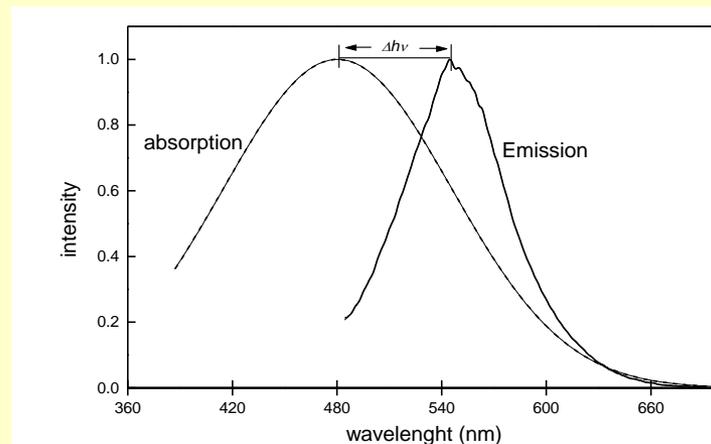
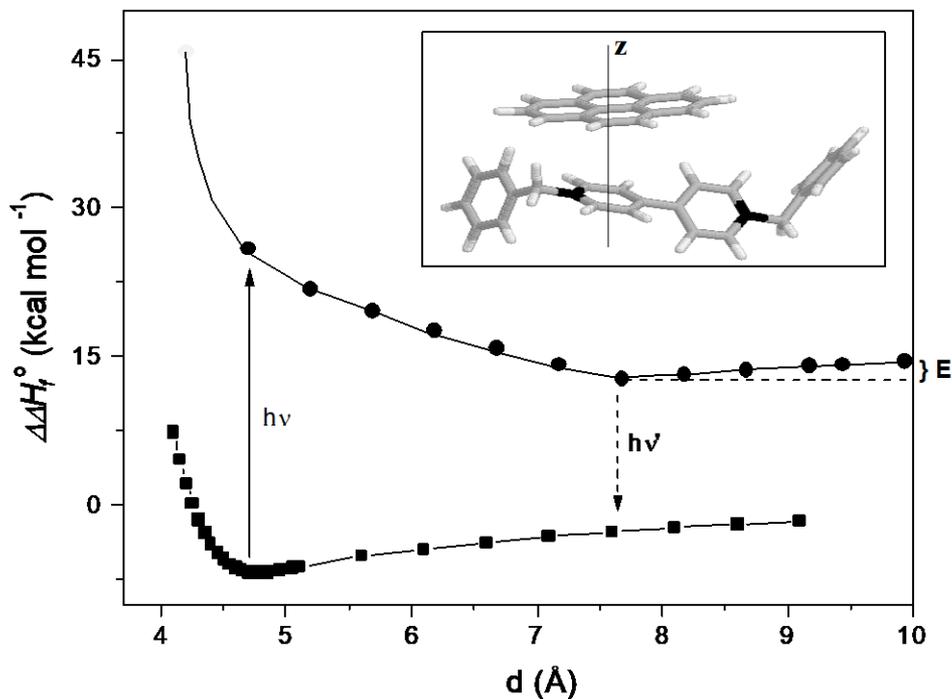
Fototautômeros da  
3-hidroxi-flavona

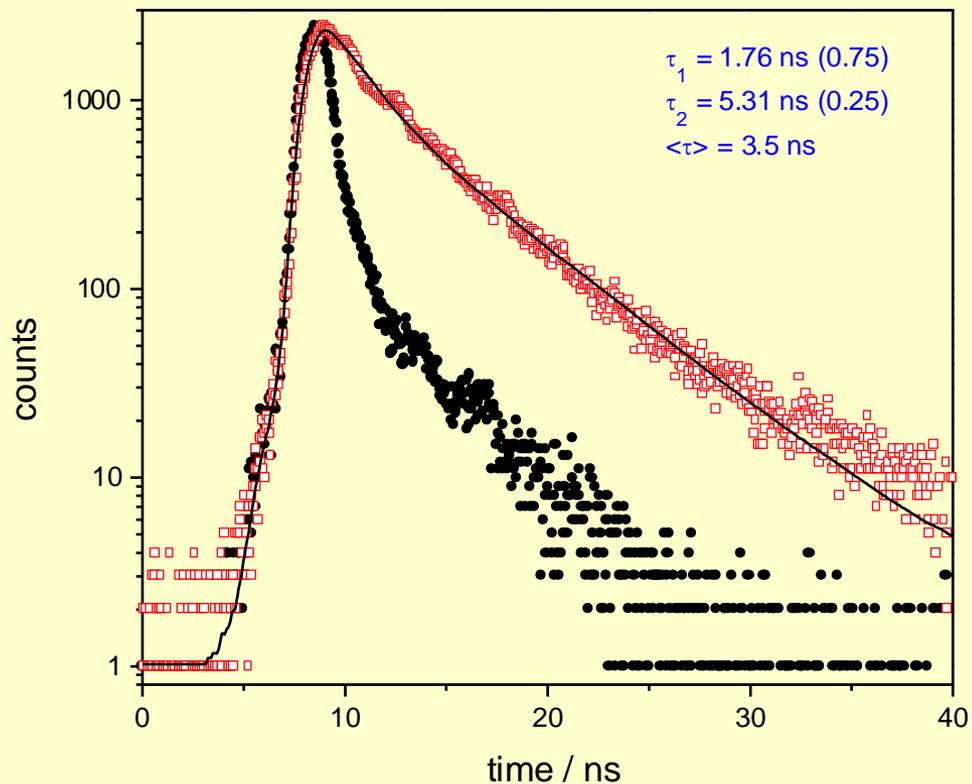
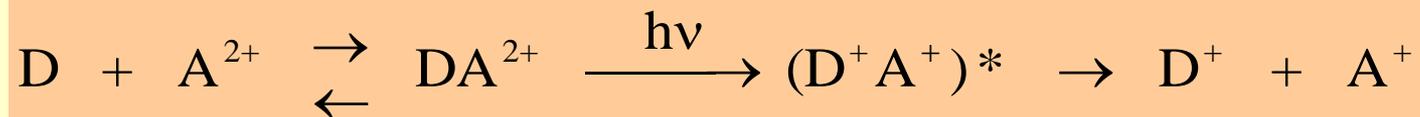
Transferência de próton

# FOTOSÍNTESE (RC1)



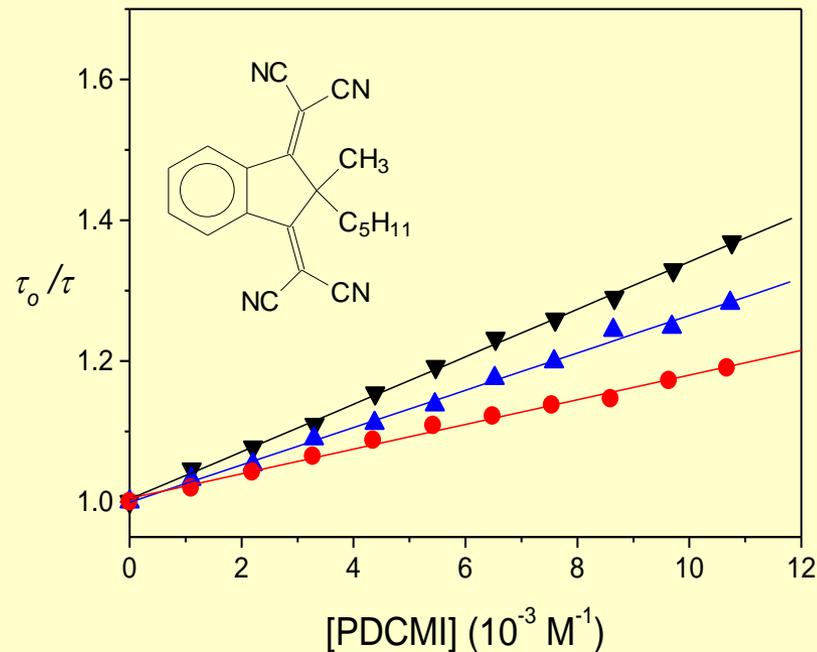
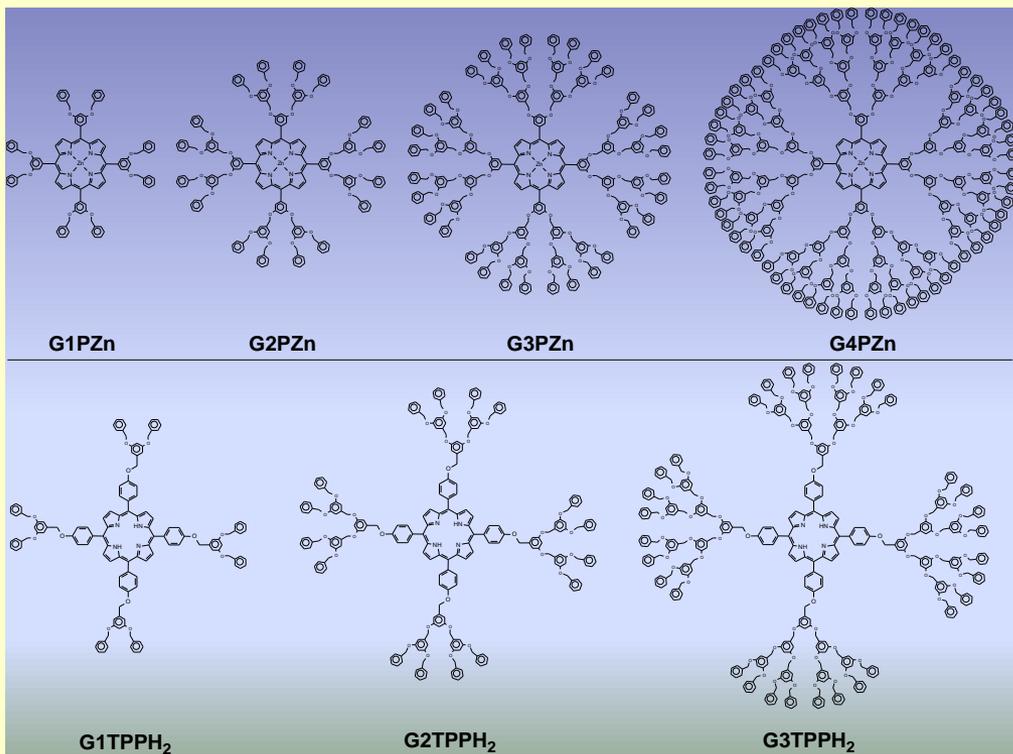
# COMPLEXO DE TRANSFERÊNCIA DE CARGA ENTRE PIRENO (D) E BENZIL VIOLOGENO ( $A^{2+}$ )



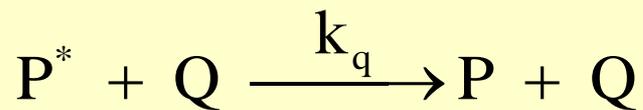


$$\langle \tau \rangle = \langle \tau \rangle_d + \langle \tau \rangle_e = \frac{\ell^2}{2D} + \left( v_{\text{ex}}^{\neq} e^{-E/RT} \right)^{-1} = 3.0 \text{ ns}$$

# Transferência de elétron em Dendrímeros



Supressão de Fluorescência

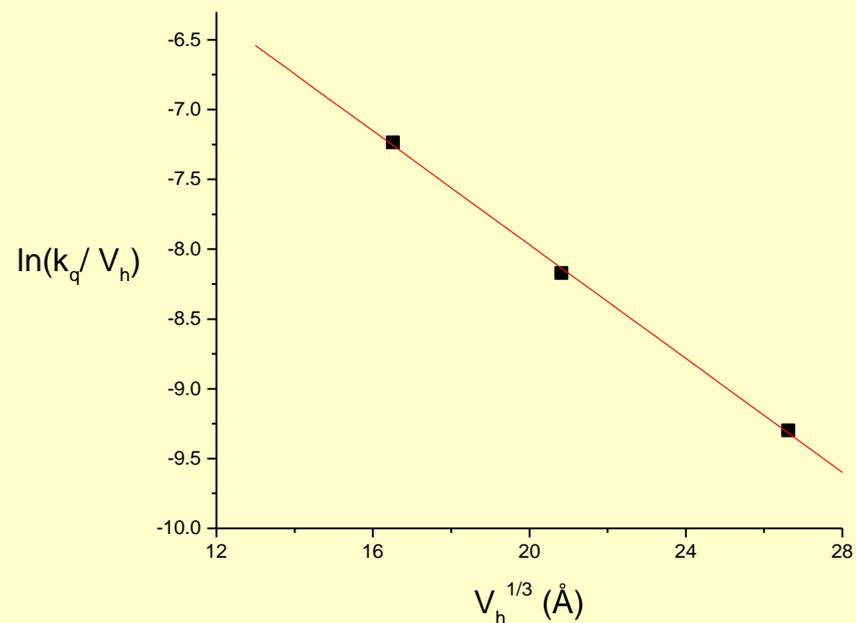


Equação de Stern-Volmer

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] = \frac{\tau_0}{\tau}$$

# RESULTADOS

dendrímero	$V_h ; V_{vw} ; V_{free} (\text{Å}^3)^*$	$k_q (\text{M}^{-1} \text{s}^{-1})$
G1TPPH <sub>2</sub>	4514; 1660; 2854	$3.2 \times 10^9$
G2TPPH <sub>2</sub>	9051; 3148; 5903	$2.6 \times 10^9$
G3TPPH <sub>2</sub>	18890; 6124; 12766	$1.7 \times 10^9$



$$k_q = cV_h \exp[-0.62\beta V_h^{1/3}]$$

$$\text{Valor de } \beta = 0.33 \text{Å}^{-1}$$

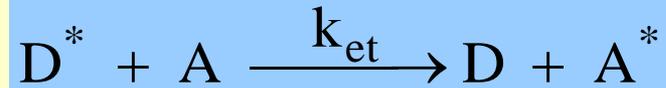
# TRANSFERÊNCIA DE ENERGIA

(a) Troca eletrônica ou mecanismo de Dexter



(interação de curto alcance)

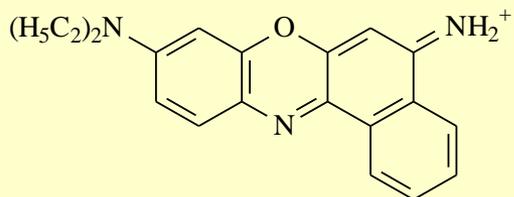
(b) Interação de dipolos ou mecanismo de Förster



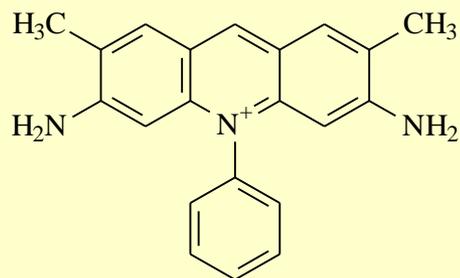
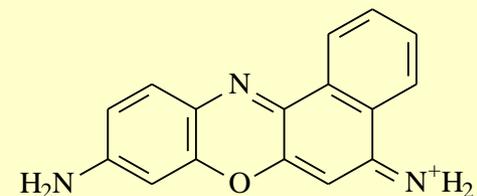
(interação de longa distância)

# Corantes Orgânicos

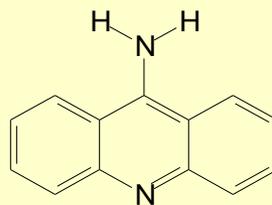
## Azul do Nilo



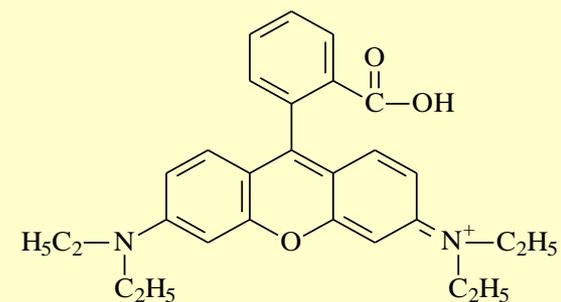
## Violeta de cresila



## Safranina

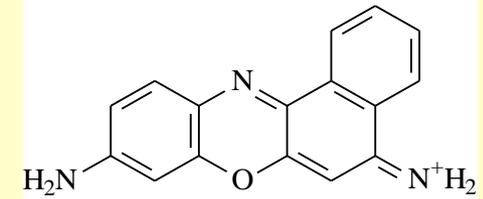
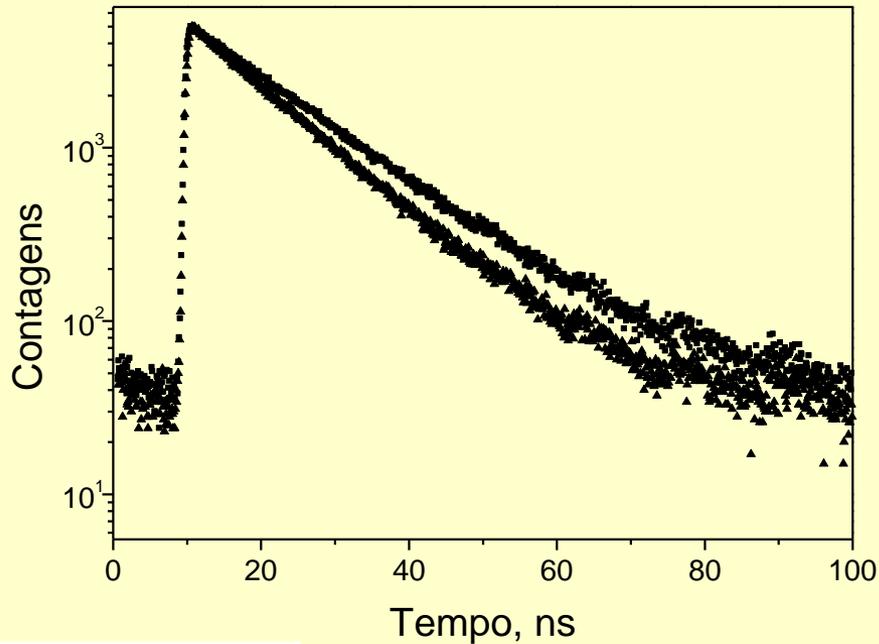
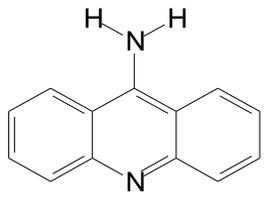
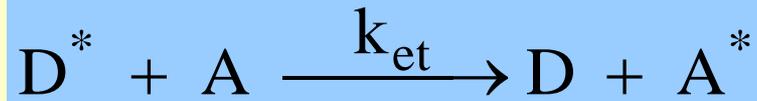


## 9-amino acridina



## Rodamina B

# Transferência de Energia entre Corantes

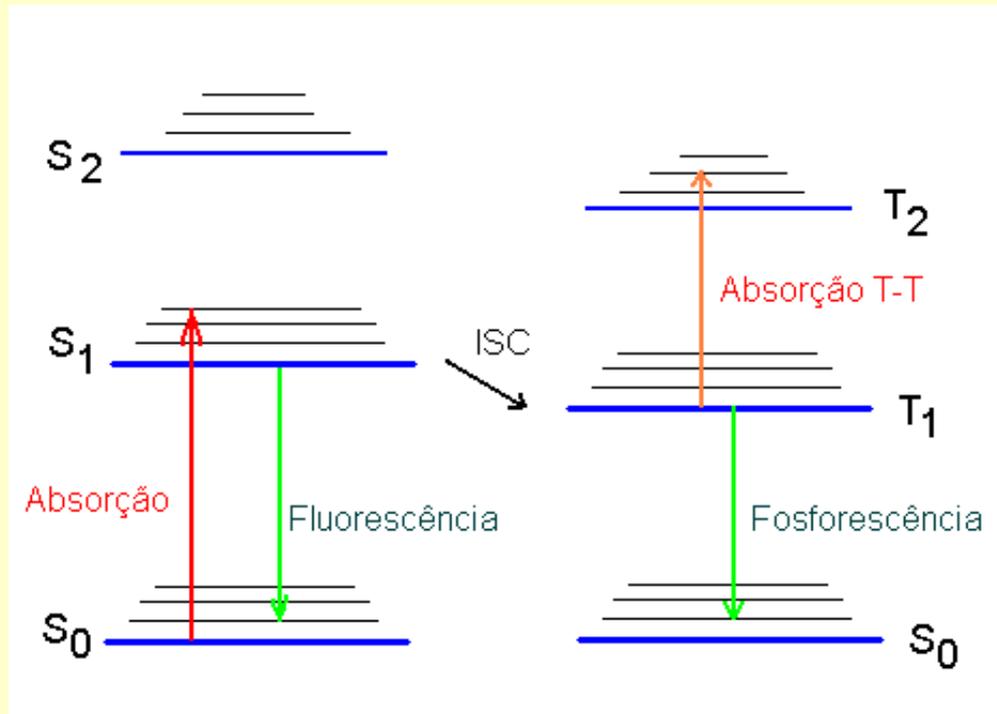


$$f(t) = \exp\left[\frac{-t}{\tau_0} - 2\Gamma\left(\frac{t}{\tau_0}\right)^{\frac{1}{2}}\right]$$

$$2\Gamma = \frac{4}{3}\pi^2 n_a R_0^3$$

Valor de  $R_0 = 60 \text{ \AA}$

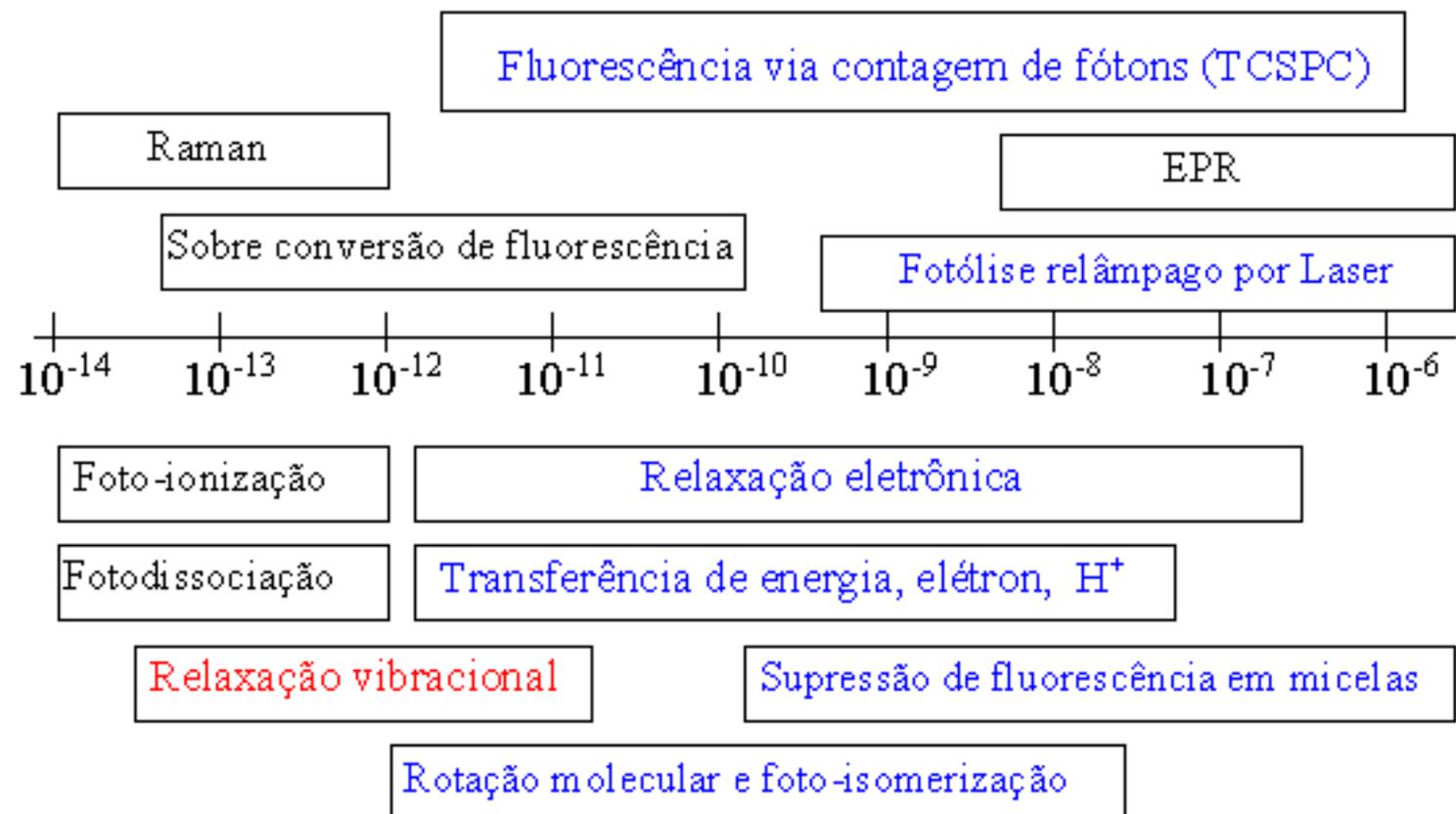
# MÉTODOS EXPERIMENTAIS



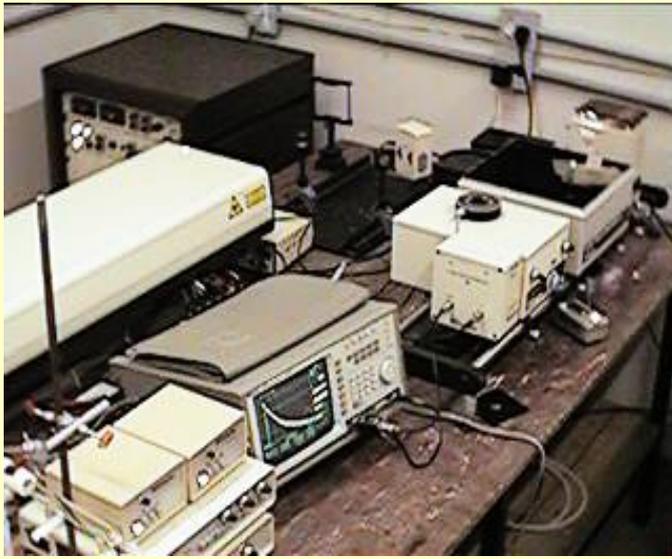
1) Absorção de Transiente

2) Emissão e Contagem de Fótons

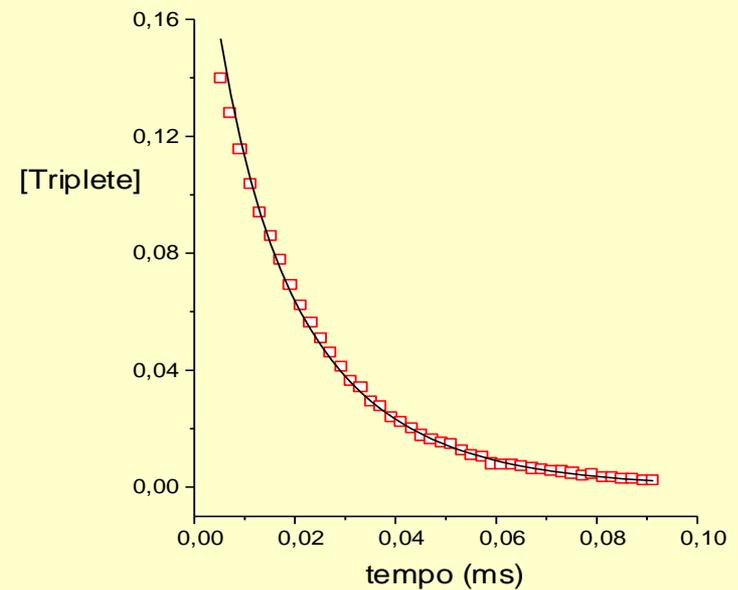
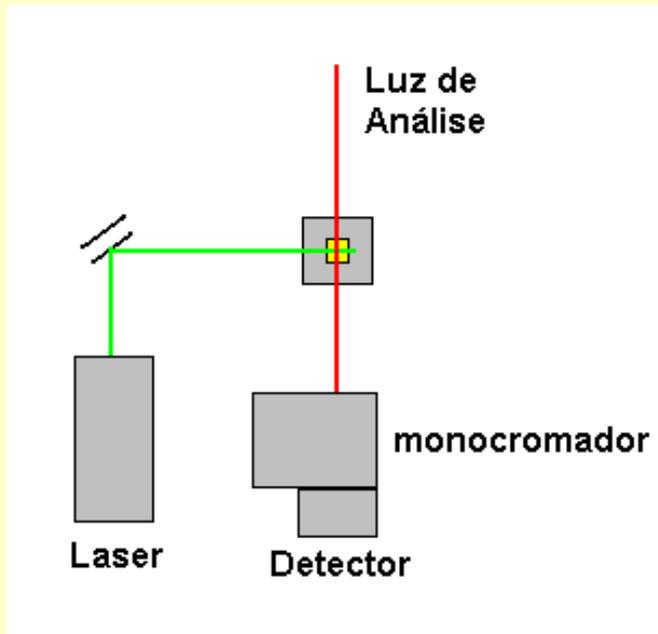
## Técnicas espectroscópicas e escala de resolução de processos dinâmicos em fotofísica e fotoquímica molecular.



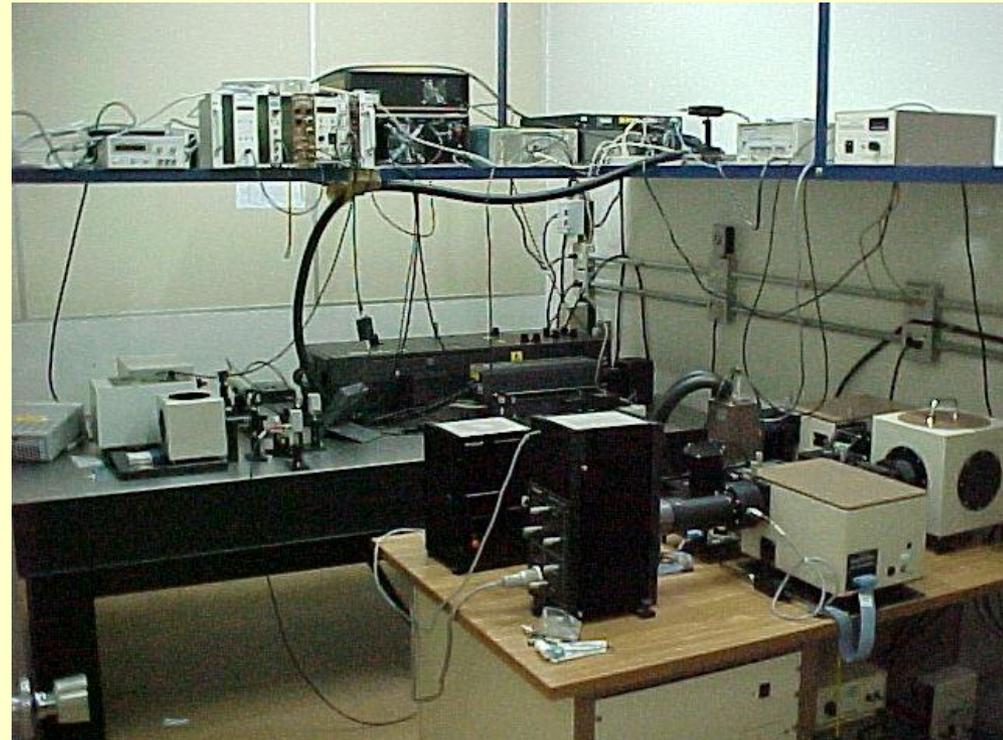
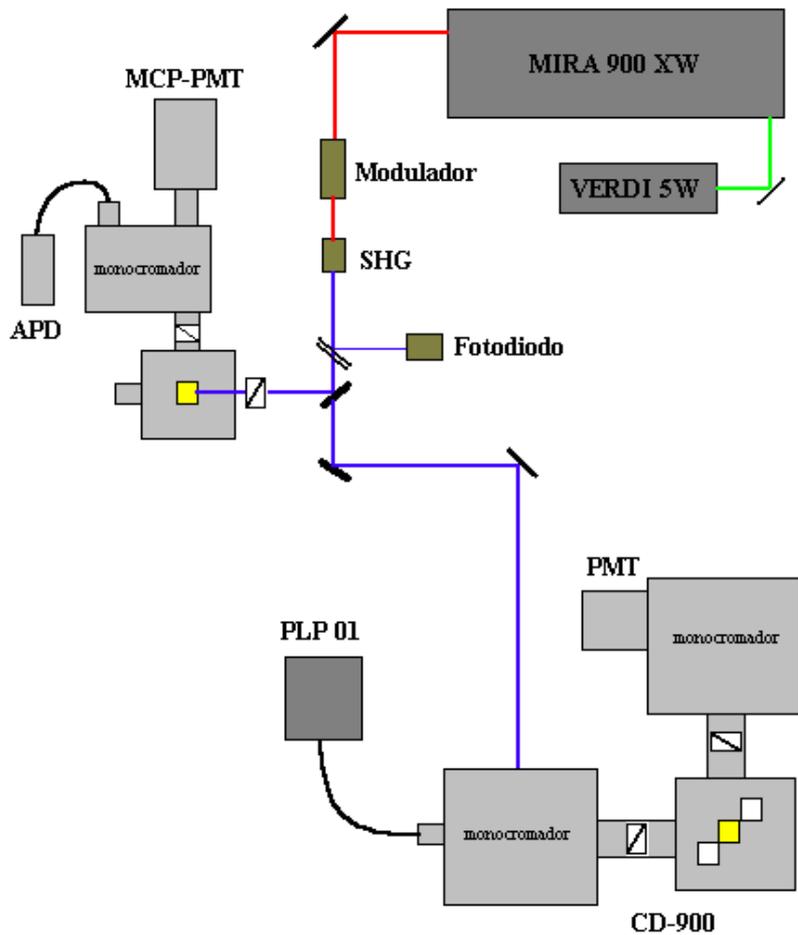
# Equipamento de Fotólise por Pulso de Laser



Decaimento de triplete do corante Safranine em solução micelar de SDS



# INSTRUMENTAÇÃO EM FLUORESCÊNCIA



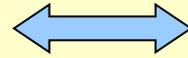
# FONTES DE EXCITAÇÃO E DETECTORES



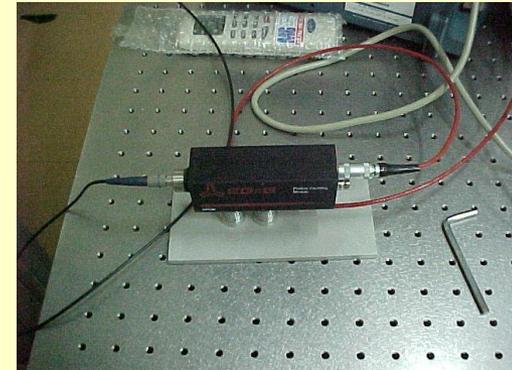
Lento (ns)



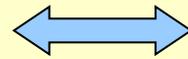
PMT



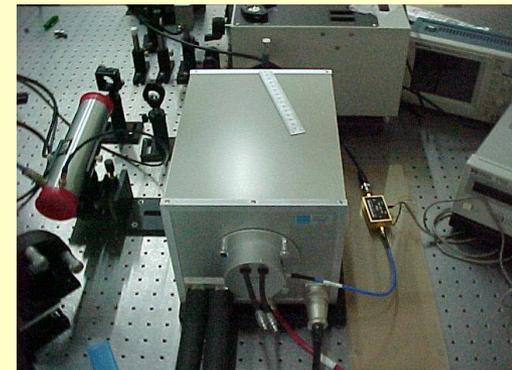
Médio (ps)



APD



Rápido (fs – ps)

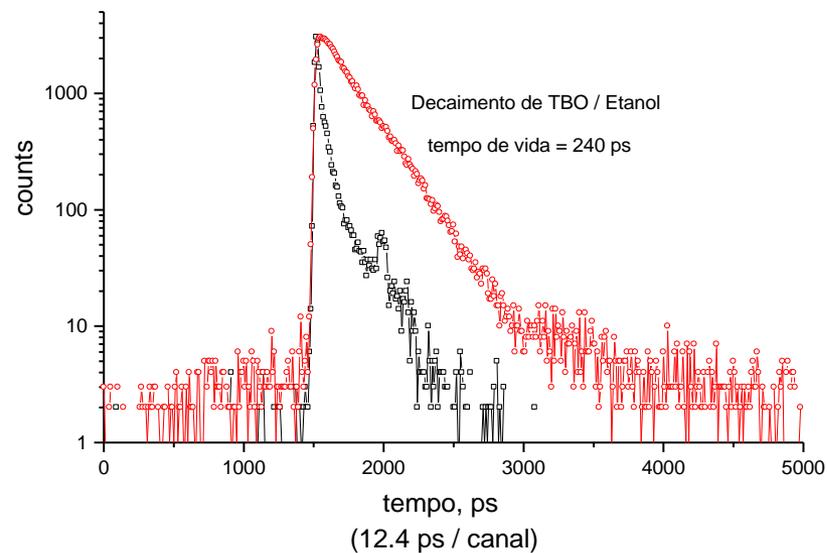
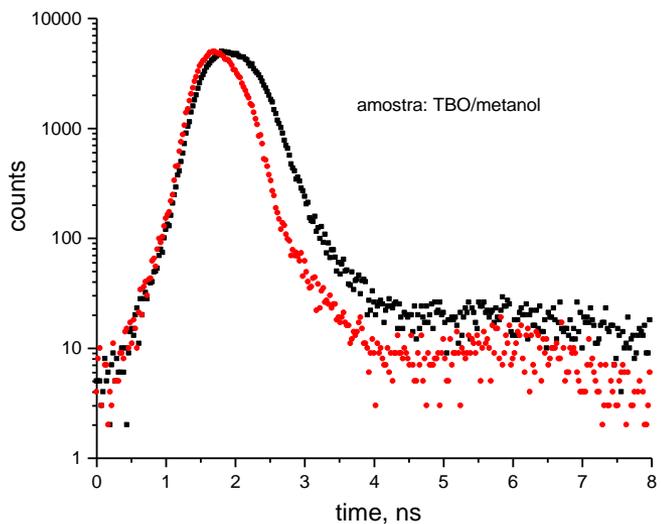


MCP

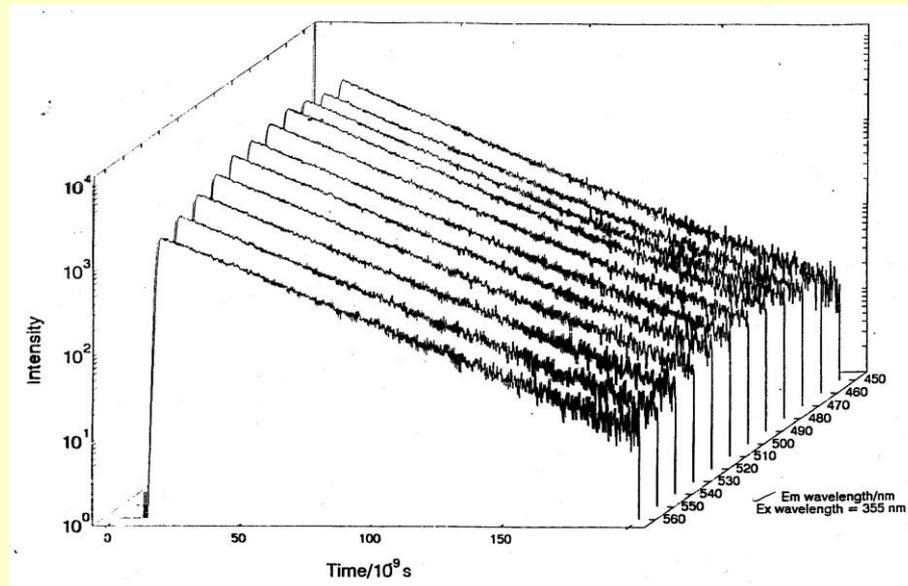
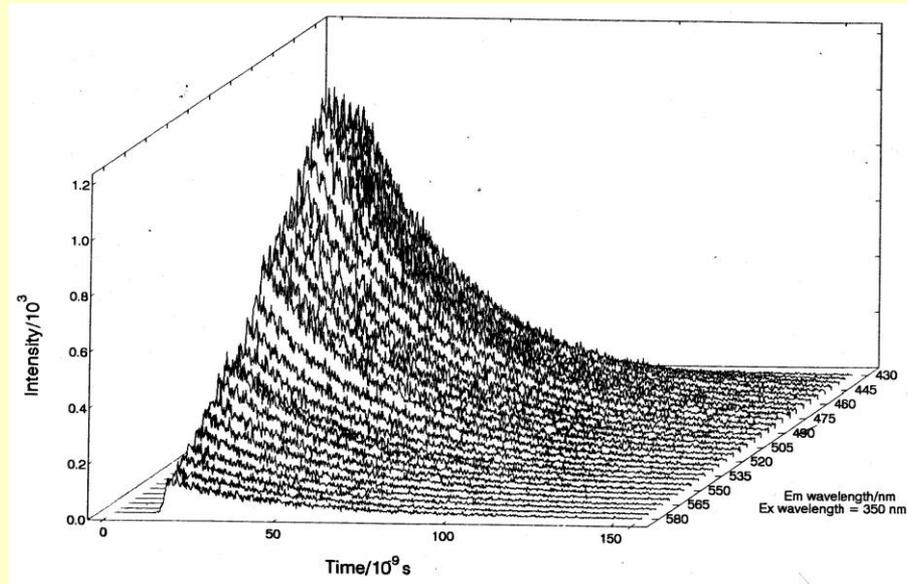


# RESOLUÇÃO

Fonte	Detector	irf (ps)	menor $\tau$ (ps)
Lâmpada H <sub>2</sub>	PMT	1500	500
Diodo laser (633 nm)	PMT	800	200
	APD	360	80
	MCP	120	40
Verdi/Mira laser 350 - 450 nm	PMT	800	200
	APD	360	80
	MCP	40	20



# SUPERFÍCIE DE DECAIMENTO ( $t, \lambda_{em}$ )



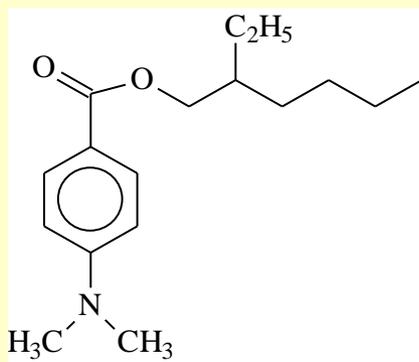
# FOTOQUÍMICA EM NOSSO COTIDIANO

## a) Protetor ou Filtro Solar

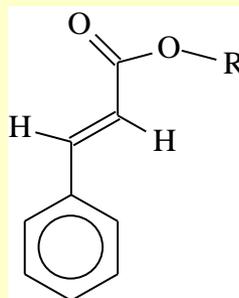
UVA (400 – 320 nm)

UVB (320 – 290 nm)

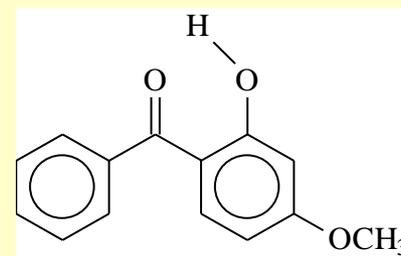
UVC (290 – 200 nm)



aminobenzoatos (PABA)  
(UVB)

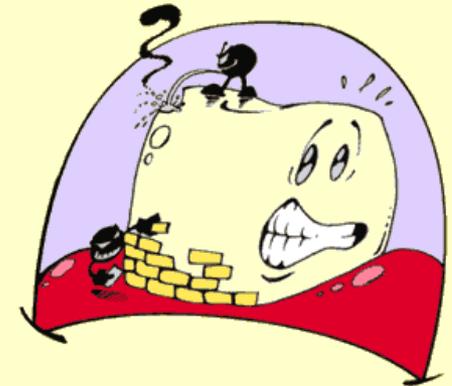
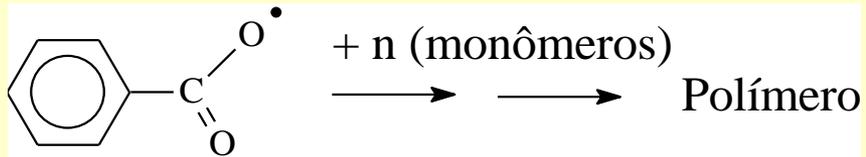
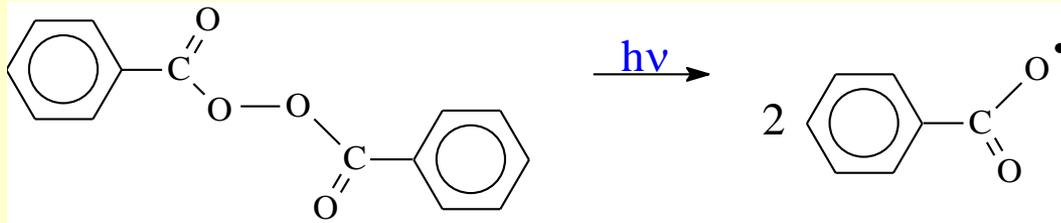


Cinamatos  
(UVB)

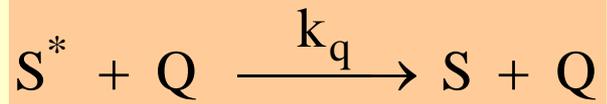


Benzofenonas  
(UVA / UVB)

## b) Fotopolimerização



# APLICAÇÃO – SENSORES FOTOQUÍMICOS



$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] = \frac{\tau_0}{\tau}$$

