



DIPARTIMENTO DI SCIENZE CHIMICHE – UNIVERSITA' DEGLI STUDI DI PADOVA

Assorbimento della luce, fotoprotezione e fotosintesi artificiale

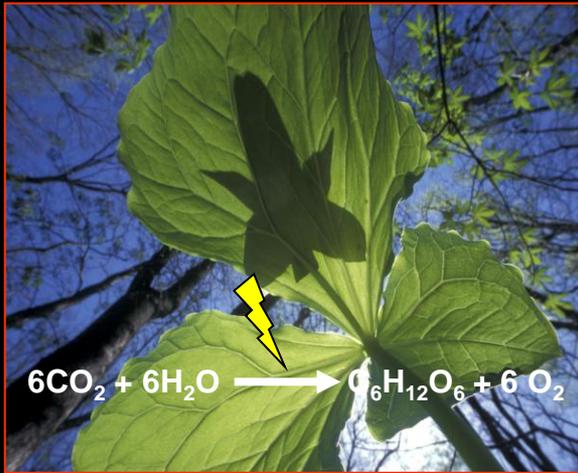
Donatella Carbonera



Accademia dei Georgofili

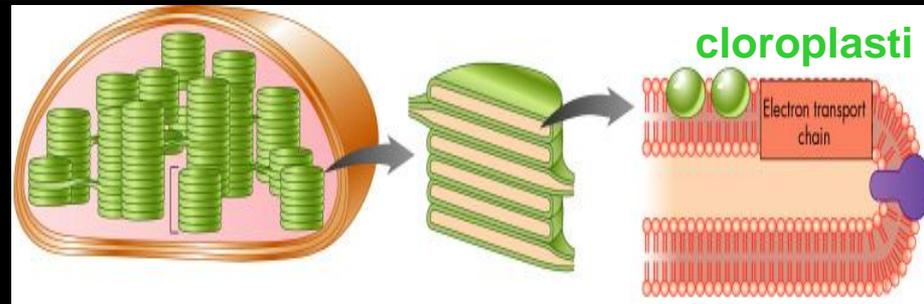
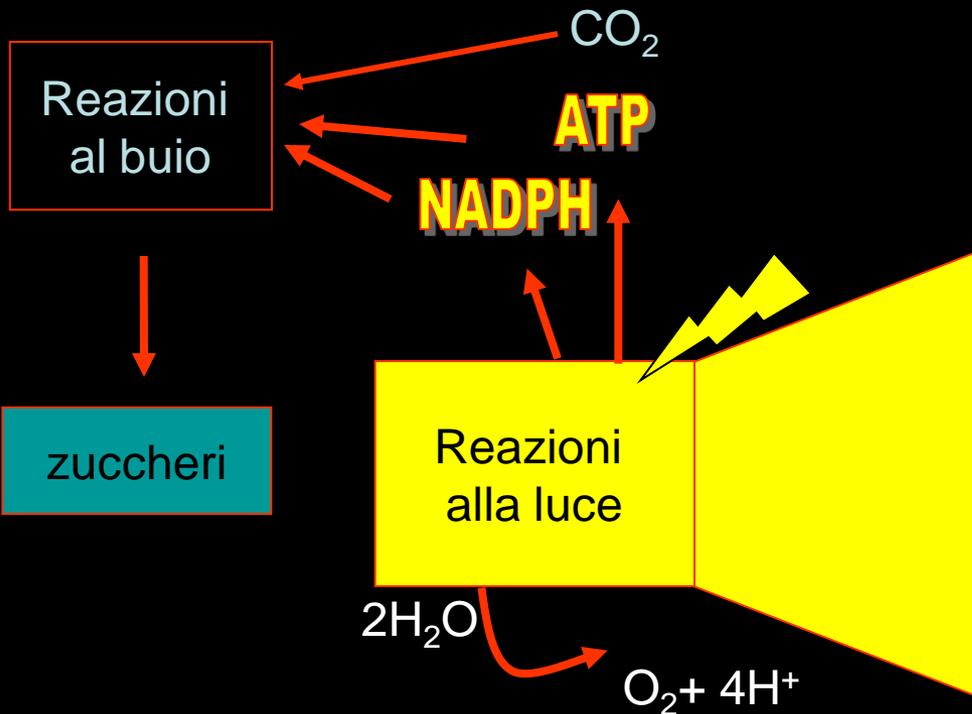
24 maggio 2012

FOTOSINTESI NATURALE

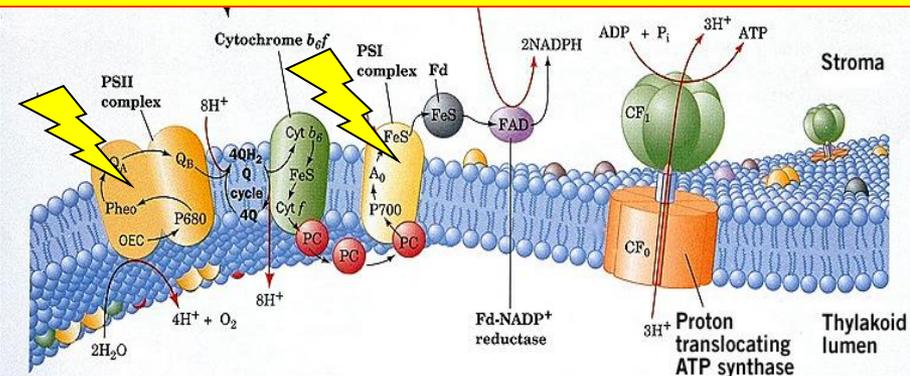


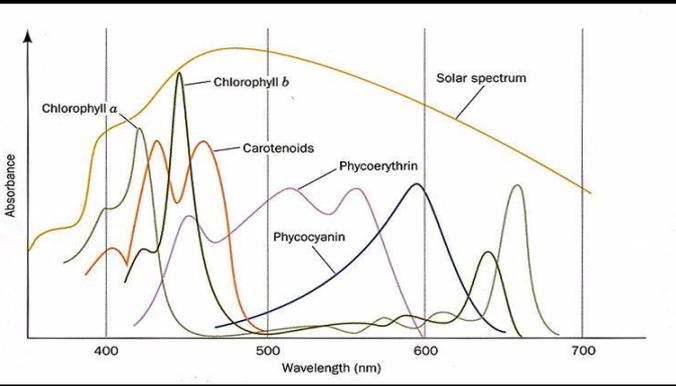
FASE LUMINOSA: produzione di NADPH e ATP mediante utilizzo dell'energia luminosa

FASE AL BUIO: sintesi dei carboidrati, mediante l'utilizzo di NADPH e ATP, a partire da CO_2 e H_2O

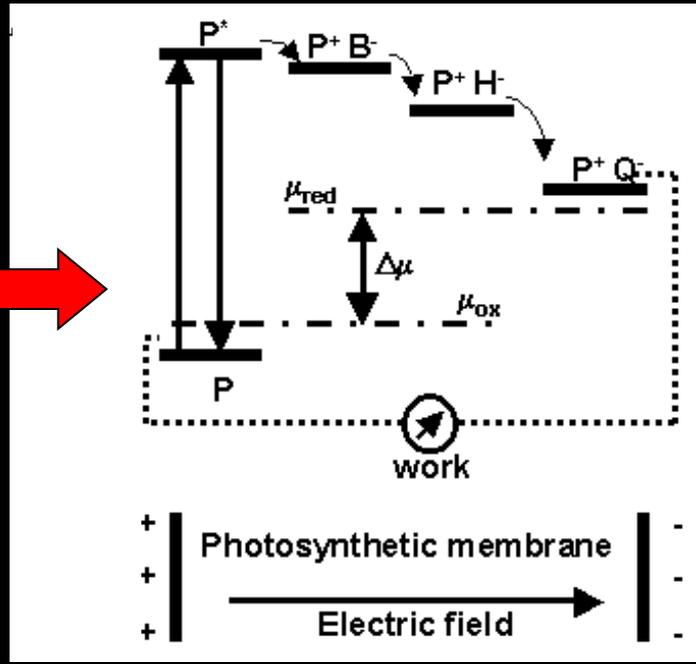
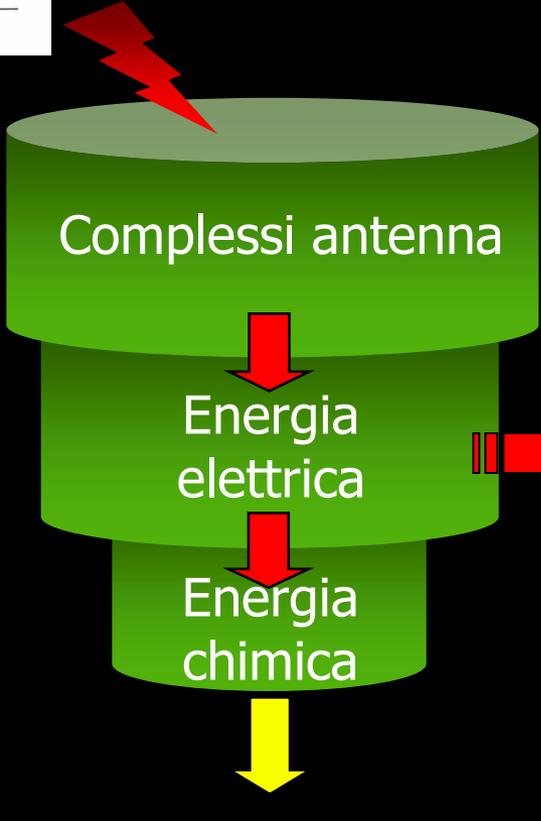


Reazioni alla luce: processo di membrana



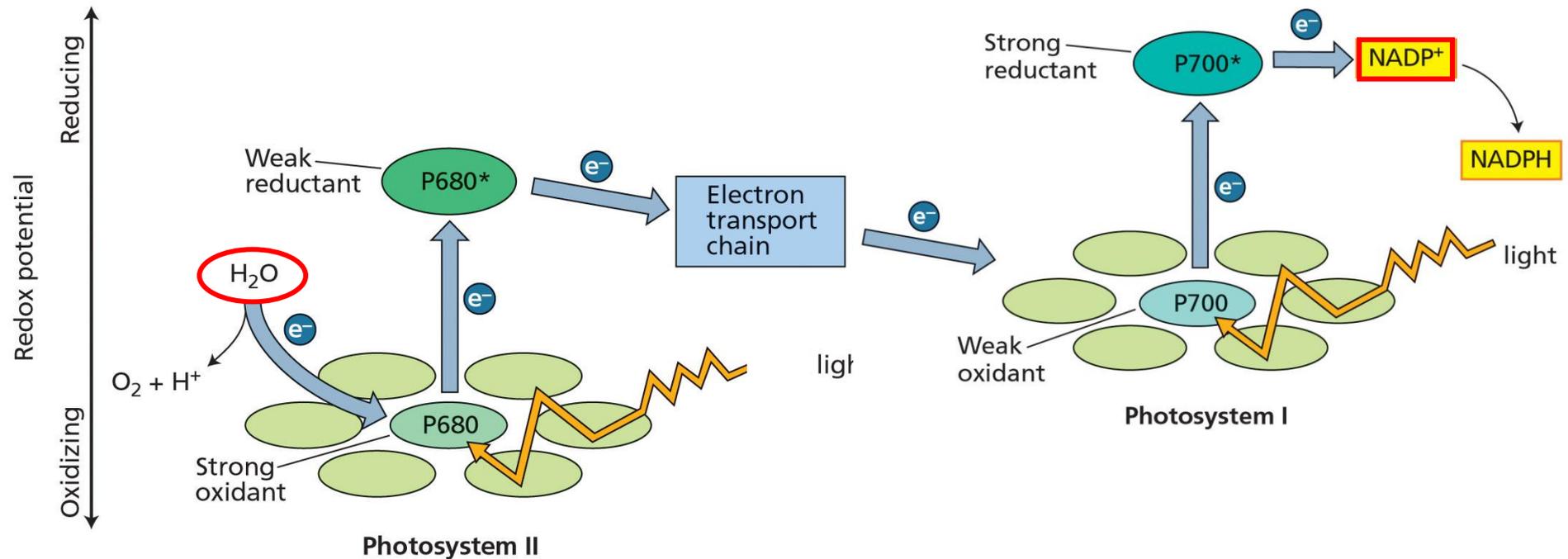


gli organismi fotosintetici rappresentano **nanodispositivi fotovoltaici**



Lavoro biologico utile

Fotosintesi ossigenica: due fotosistemi lavorano in serie



PLANT PHYSIOLOGY, Third Edition, Figure 7.14 (Part 1) © 2002 Sinauer Associates, Inc.

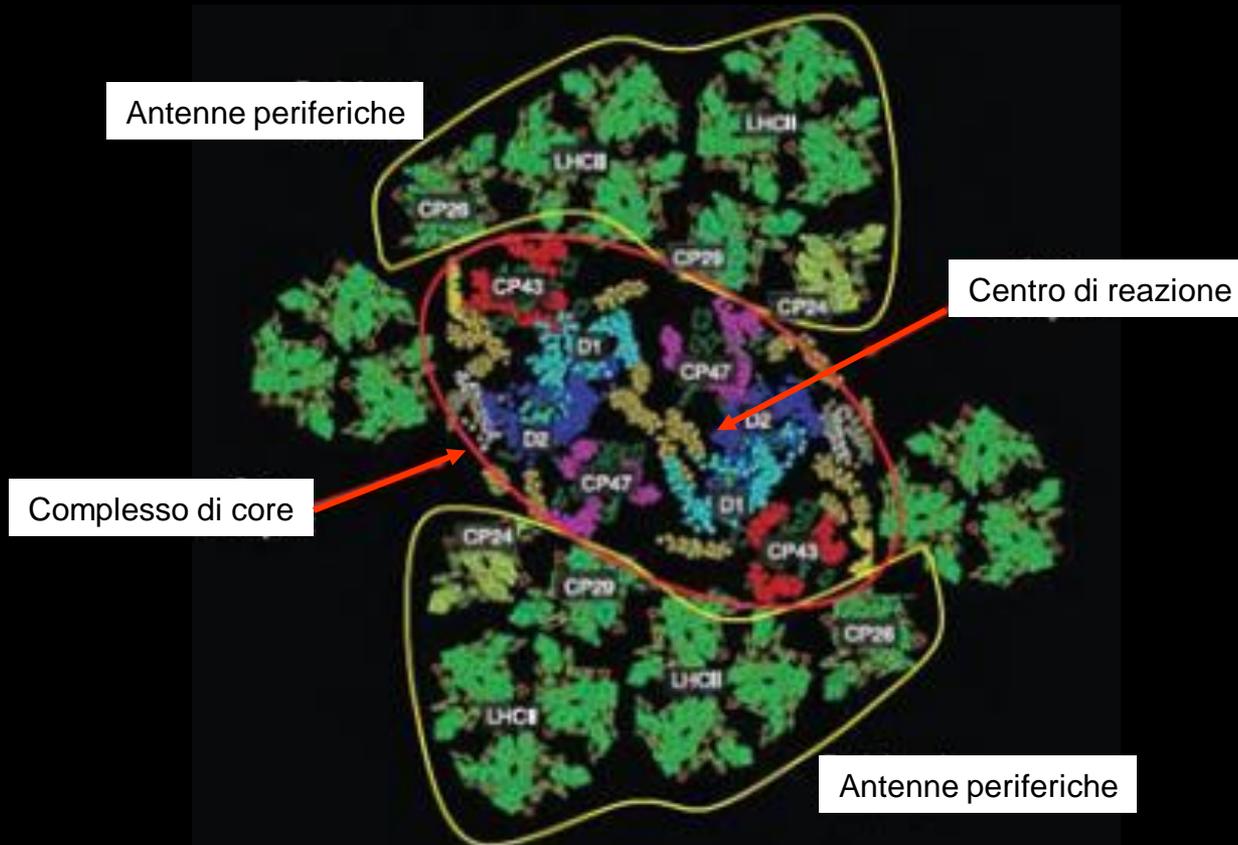
Energia luminosa utilizzata per:

Estrazione di elettroni dall'acqua e riduzione di $NADP^+$

Formazione di gradiente protonico e sintesi di ATP

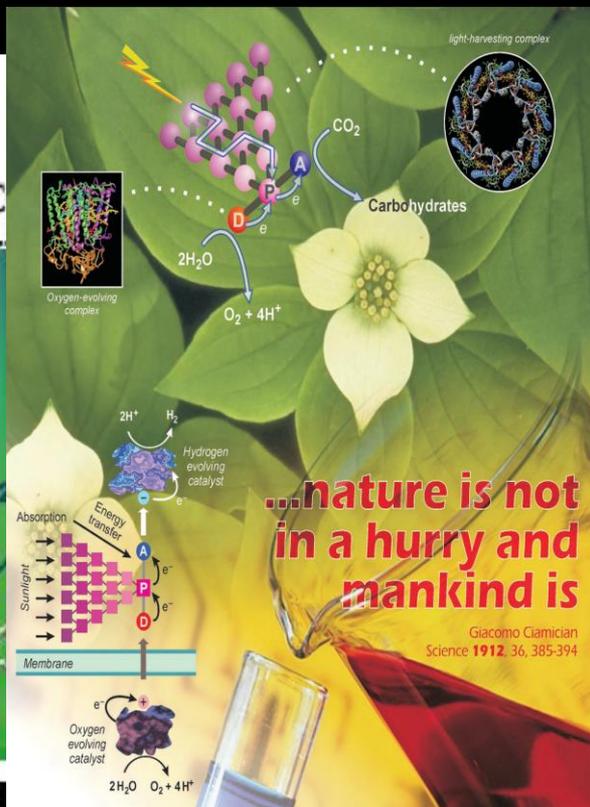
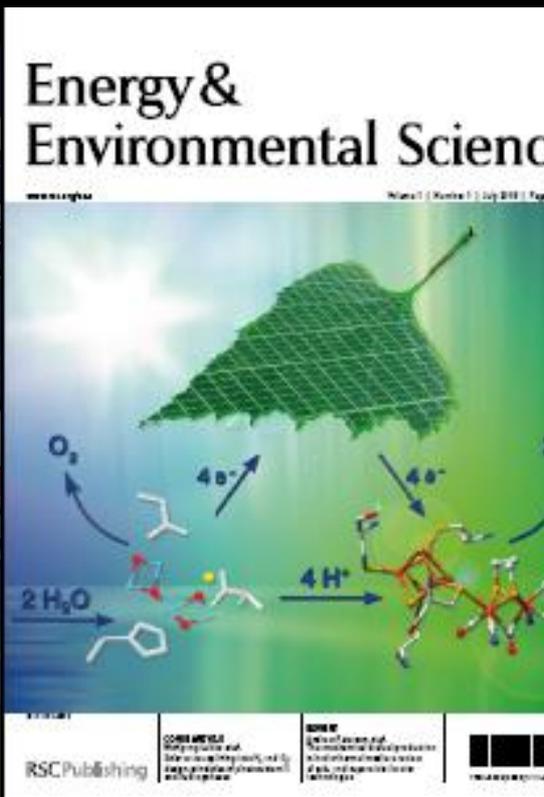
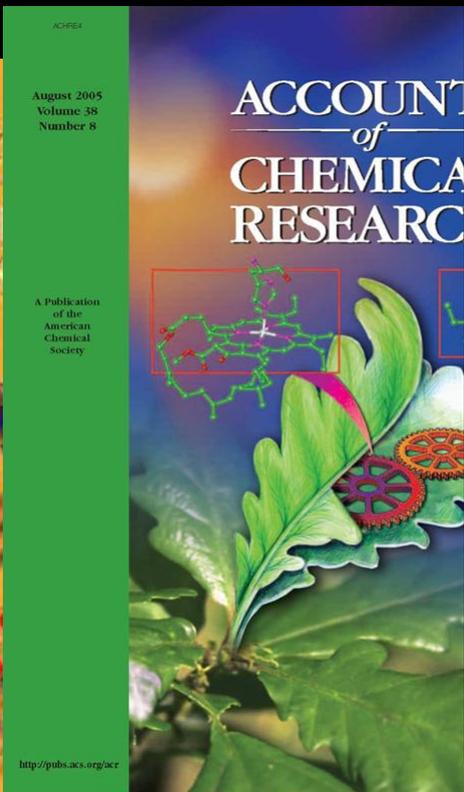
Una macchina molecolare perfetta

- Efficienza di assorbimento in varie condizioni di illuminazione
- Electron Transfer in elevata resa: velocità elevata di ET e lenta di ricombinazione (accoppiamento con reazioni di ossidazione dell'acqua e riduzione di NADP^+)



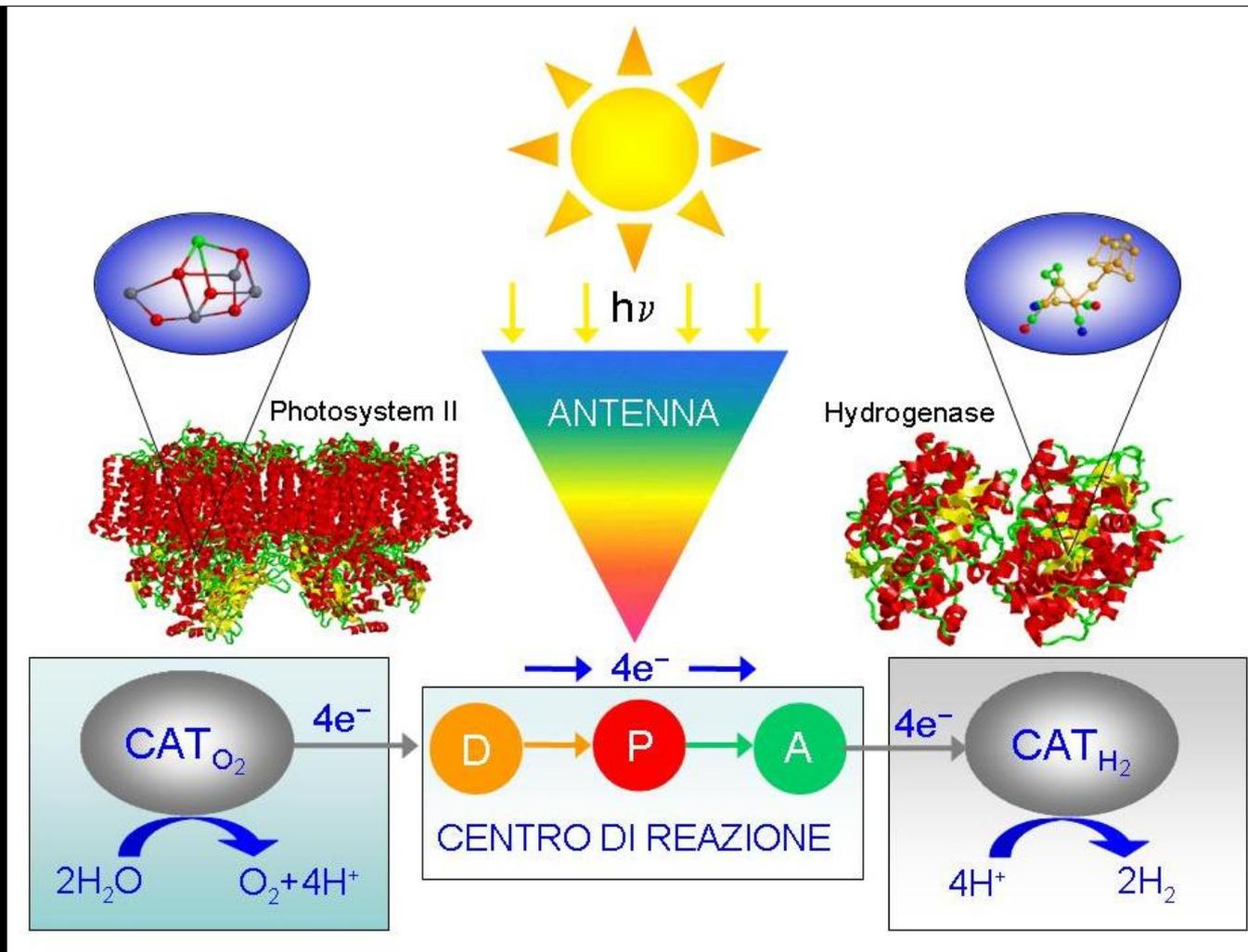
FOTOSINTESI ARTIFICIALE

Nano-scienza ispirata dalla **Fotosintesi**: realizzazione di sistemi molecolari in grado di “mimare” il processo fotosintetico naturale.



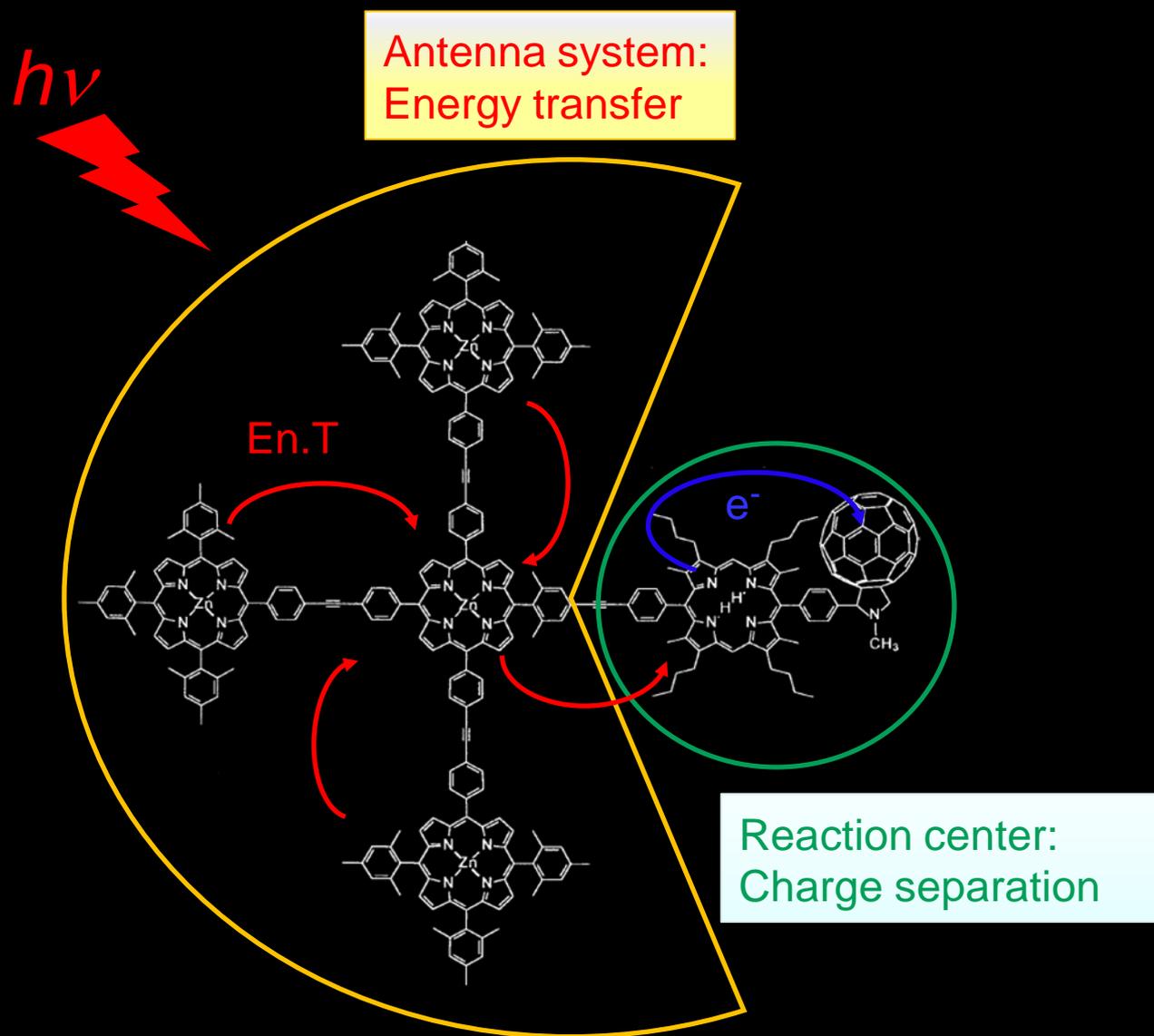
FOTOSINTESI ARTIFICIALE:

Nano-scienza ispirata dai processi biologici di fotosintesi



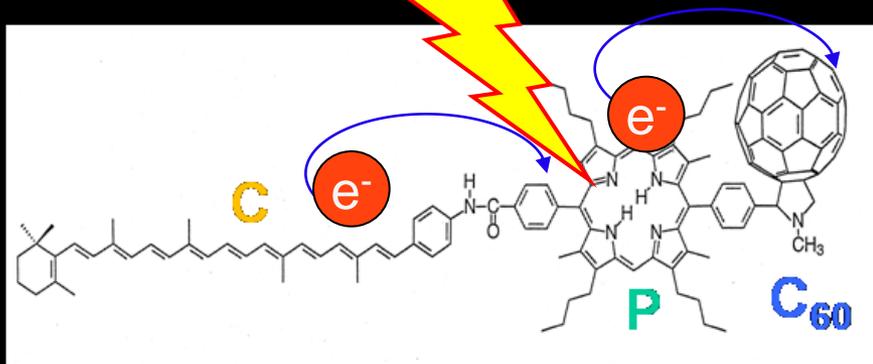
Lego Chimico che utilizza le unità minime necessarie al processo di sintesi di un "combustibile" a partire da acqua e luce

Sistemi combinati antenna- centro di reazione

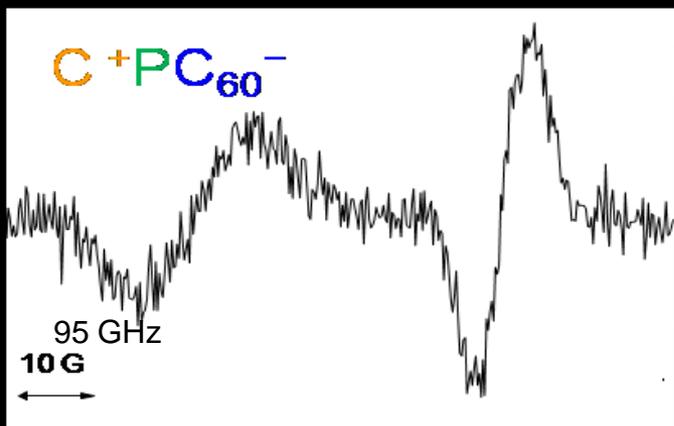


centri di reazione artificiali

Gust, Moore, et al.



Photoexcited radical pair



Carbonera *et al.* JACS (2004) 126, 17074

TIME-RESOLVED EPR

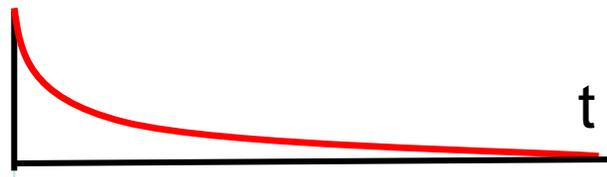
MWs



LASER

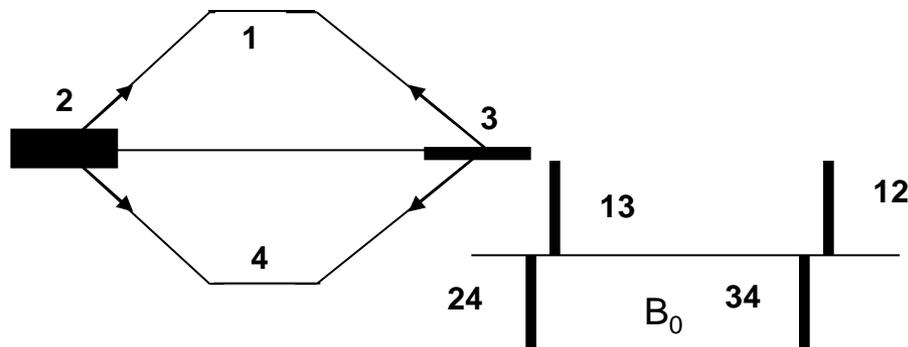


EPR SIGNAL

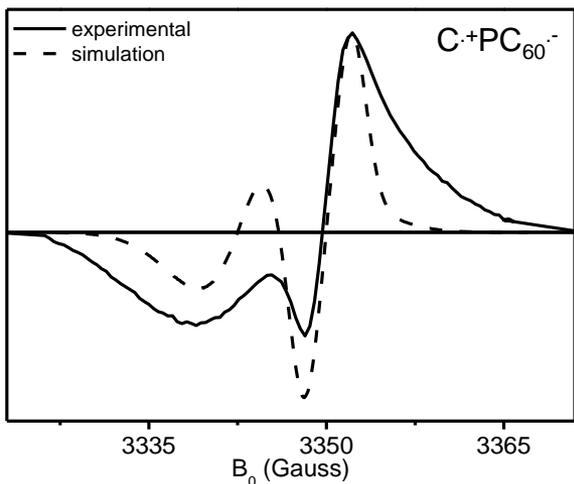
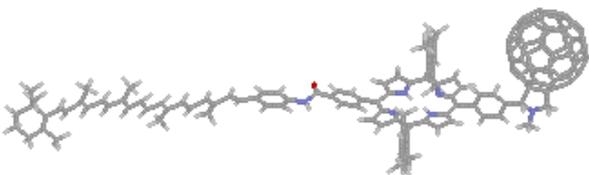


Spin-correlated radical pair mechanism

$$\hat{H} = \omega_A \hat{S}_{ZA} + \omega_B \hat{S}_{ZB} - J(\hat{S}^2 - 1) + \frac{1}{2} D (\cos^2 \xi - \frac{1}{3}) (3\hat{S}_Z^2 - \hat{S}^2)$$

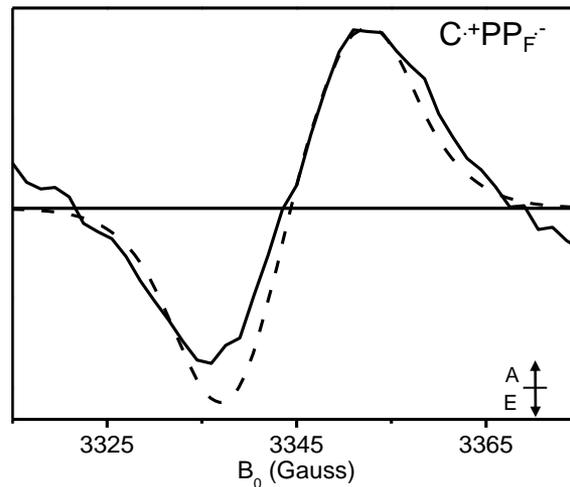
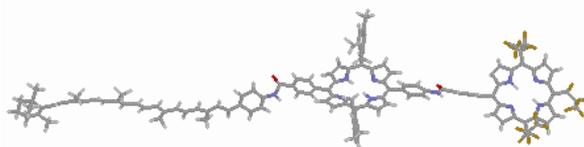


CPC₆₀ triad



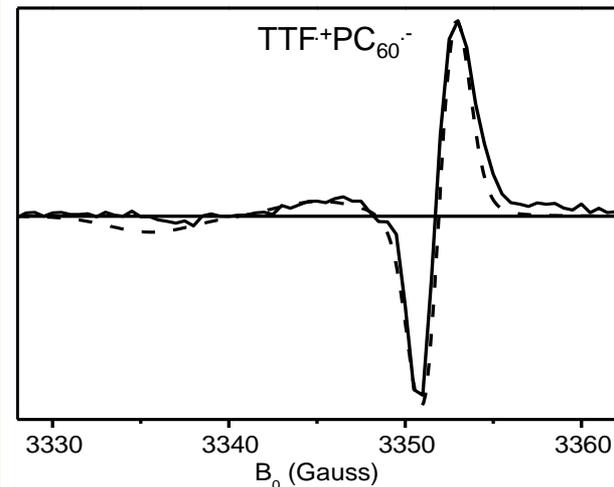
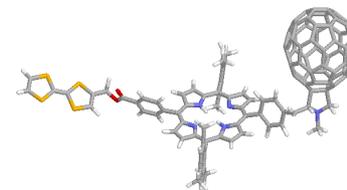
$$D = -0.6 \text{ Gauss } (d_{cc} = 36 \text{ \AA})$$
$$J = 1.8 \pm 0.2 \text{ Gauss}$$

CPP_F triad



$$D = -0.3 \text{ Gauss } (d_{cc} = 44 \text{ \AA})$$
$$J = 1.4 \pm 0.2 \text{ Gauss}$$

TTFPC₆₀ triad

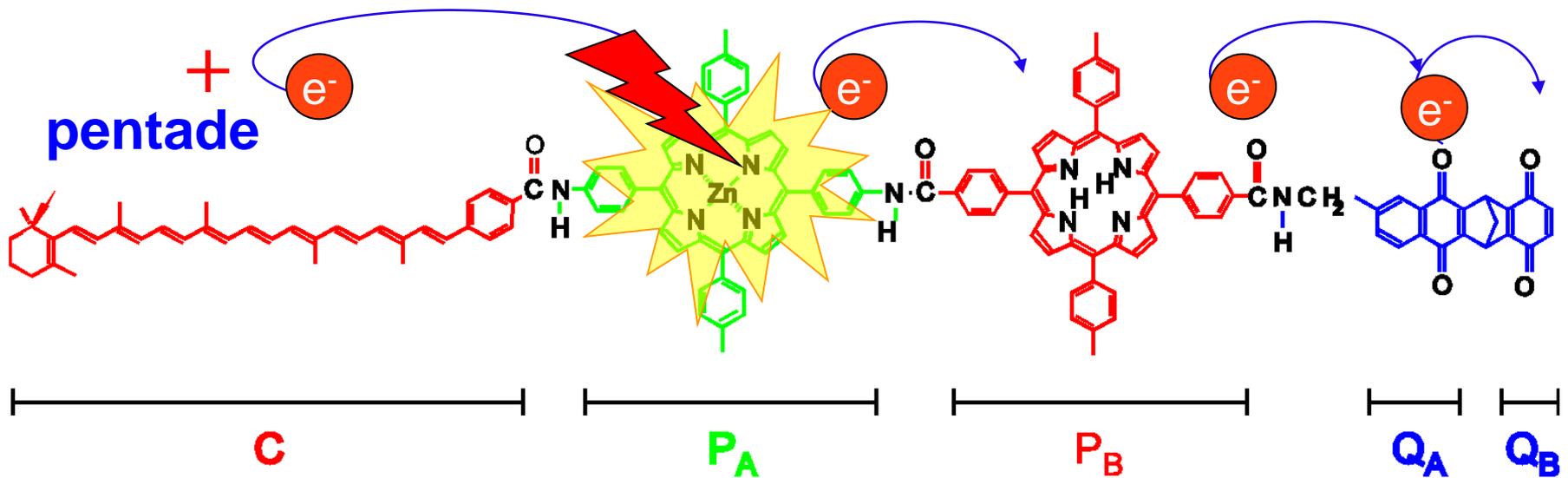


$$D = -1.4 \text{ Gauss } (d_{cc} = 27 \text{ \AA})$$
$$J = 0.45 \pm 0.05 \text{ Gauss}$$

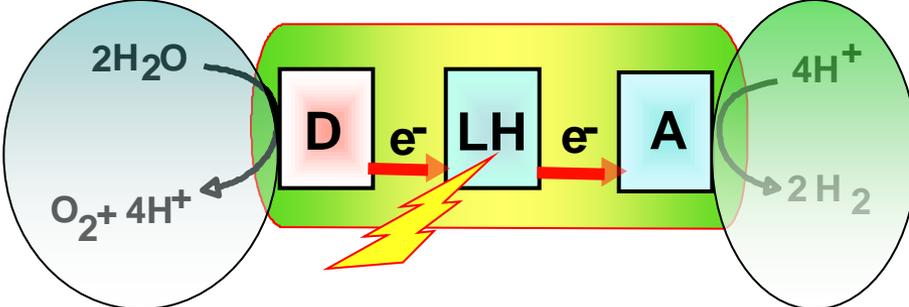
Di Valentin, M., Bisol A., Fuhs M., Liddell PA., Moore AL., Moore TA., Gust D., Carbonera D. (2004). Photochemistry of artificial photosynthetic reaction center in liquid crystals probed by multifrequency EPR (9.5 and 95 GHz). *JACS* 126. 17074-17086

Di Valentin, M.; Bisol, A.; Agostini, G.; Carbonera, D.; Electronic Coupling Effects on Photoinduced Electron Transfer in Carotene-Porphyrin-Fullerene Triads Detected by Time-Resolved EPR *J. Chem. Inf. Model*; (2005)

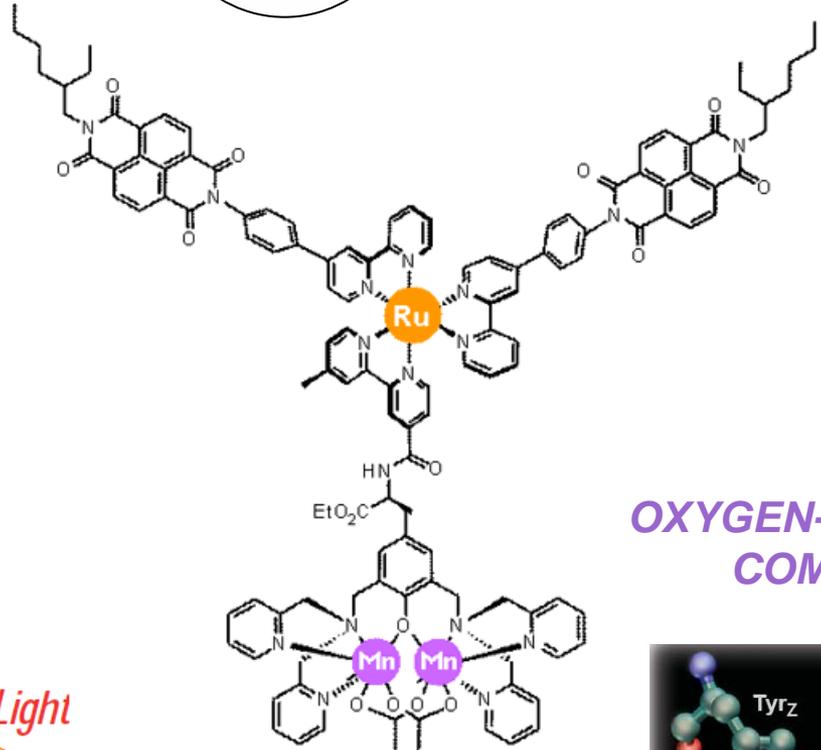
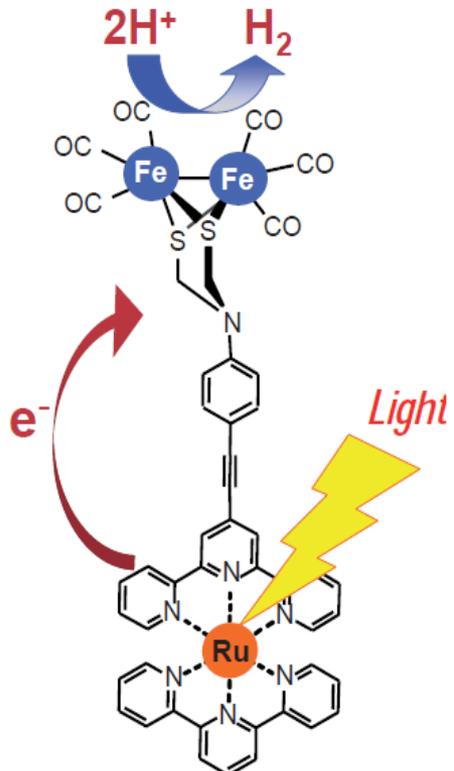
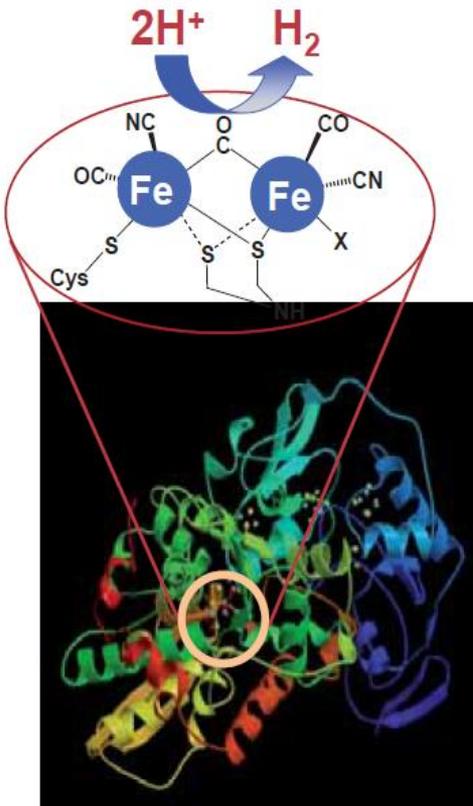
Centro di reazione “multi step” separazione spaziale delle cariche



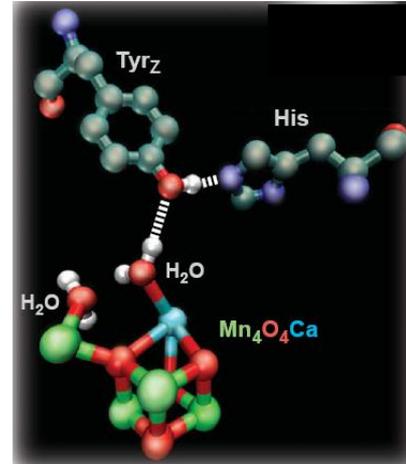
Catalizzatori "bio-inspired"



hydrogenase



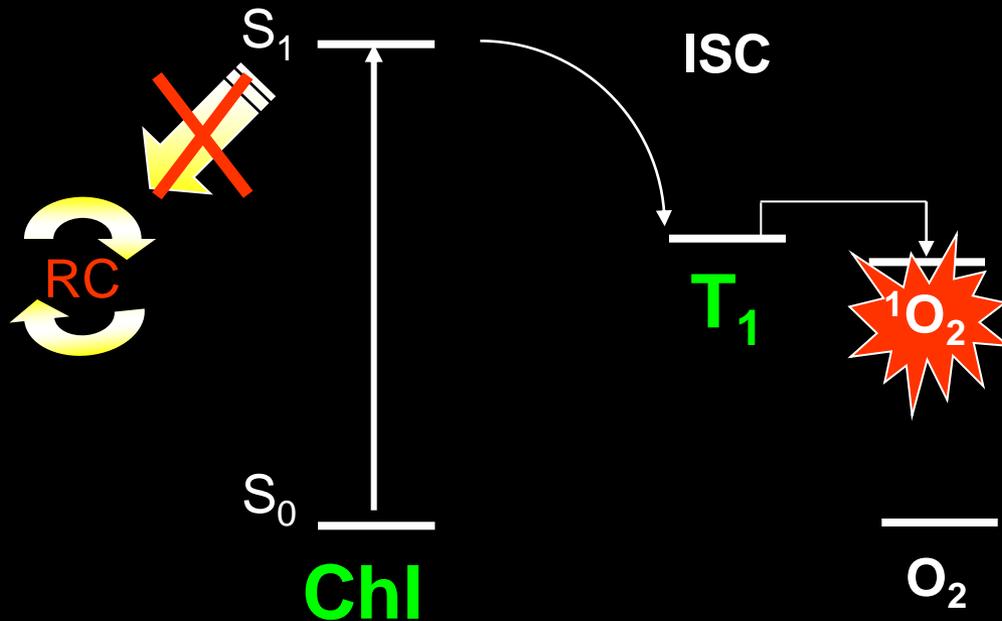
OXYGEN-EVOLVING COMPLEX



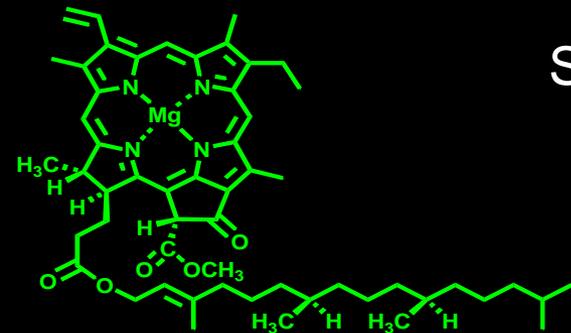
Problemi

- Resa quantica della separazione di carica
- Integrazione dei vari componenti in un sistema completo
- Risposta alle variazioni di illuminazione naturale (grandezza dell'antenna)
- Fotostabilità dei componenti

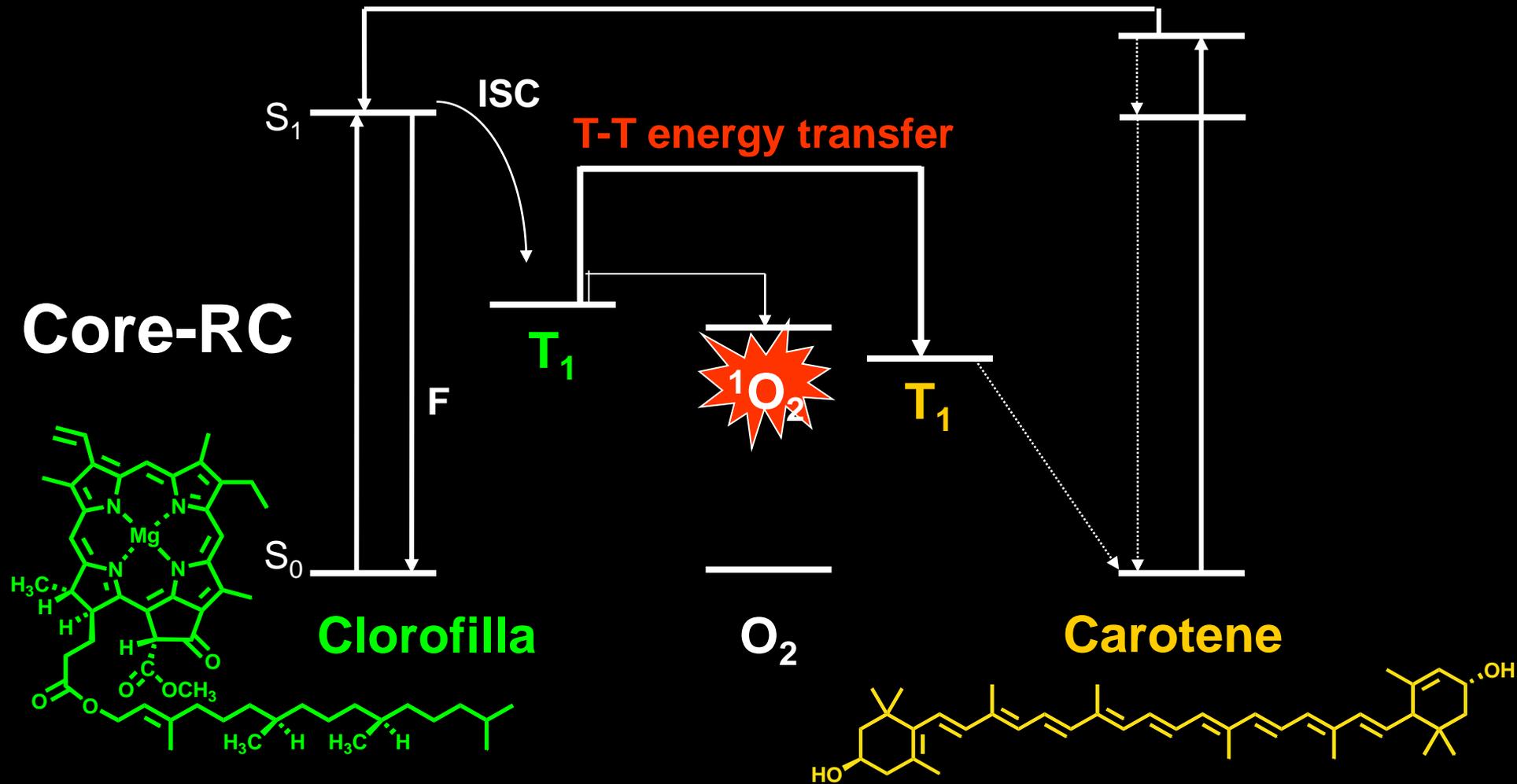
Fotoprotezione naturale



danno ossidativo
dell'apparato
fotosintetico

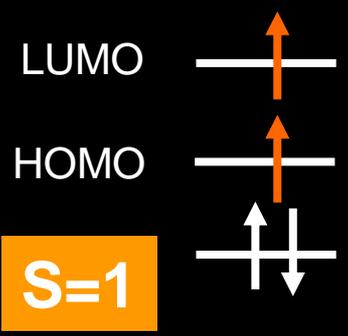


Fotoprotezione mediante trasferimento tripletto-tripletto



Gli stati di tripletto sono paramagnetici

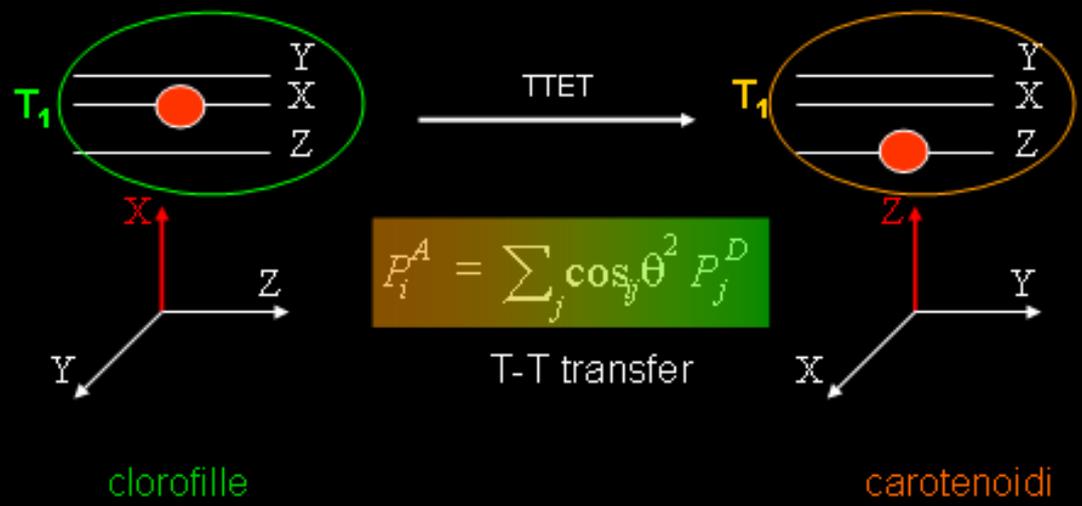
risonanza magnetica di spin elettronico (EPR)



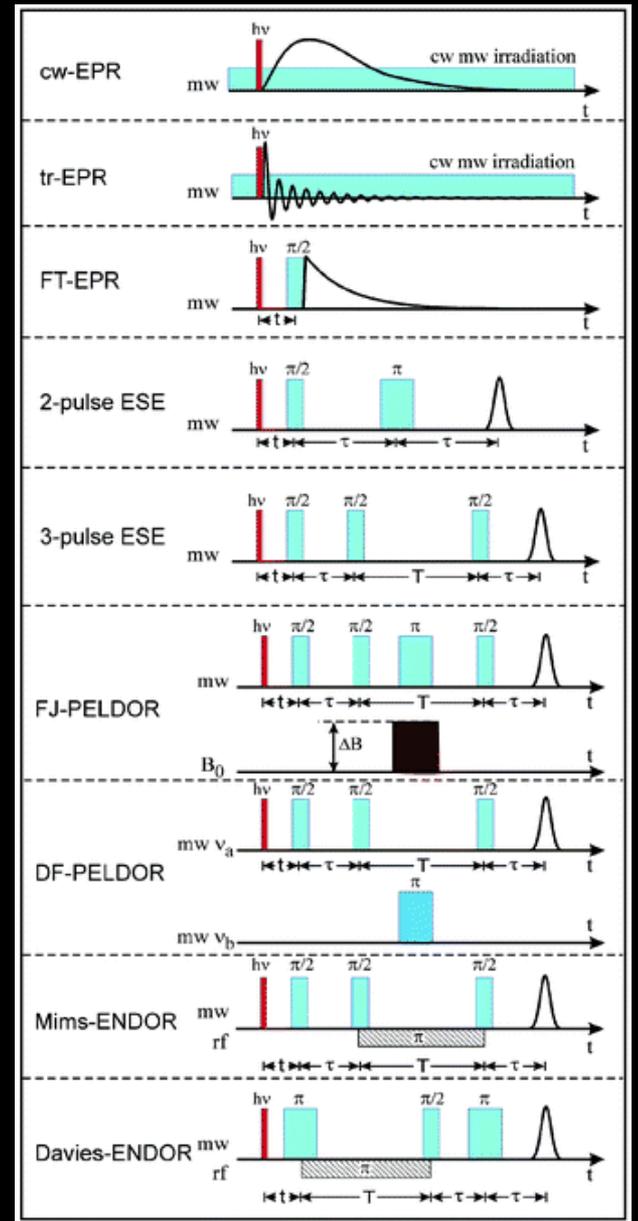
Conservazione del momento di spin nel trasferimento di energia tripletto-tripletto (TTET)

Donatore dello stato di tripletto

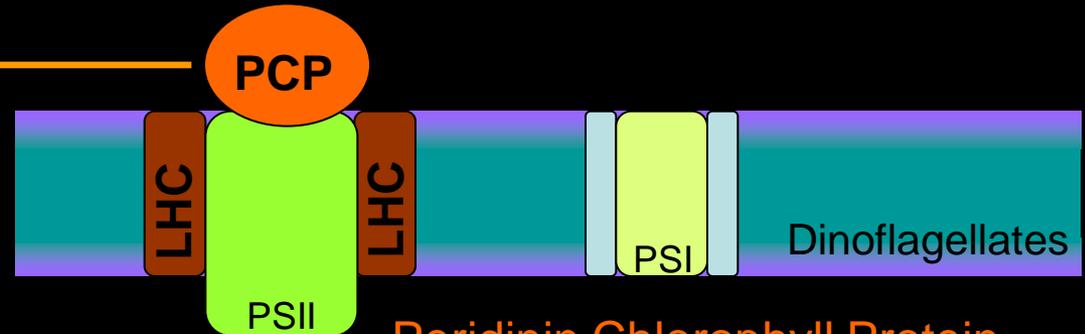
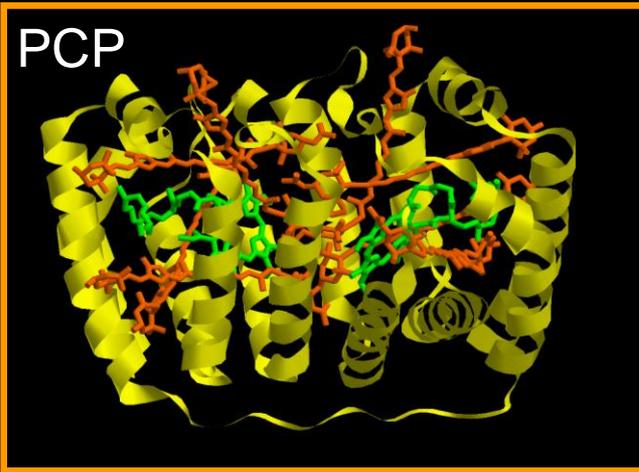
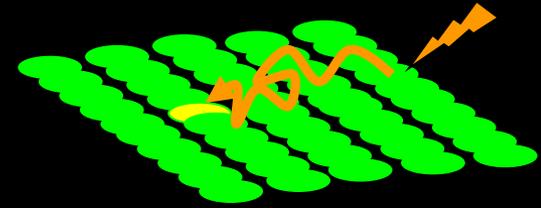
Accettore dello stato di tripletto



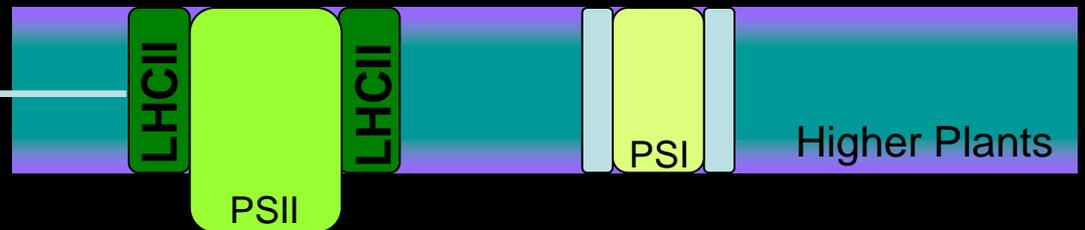
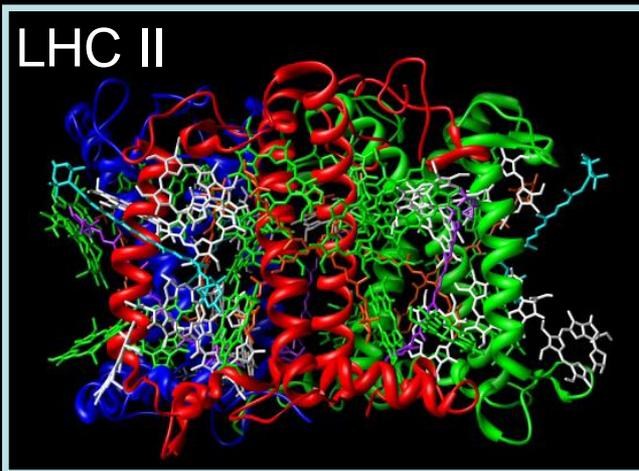
^TCar eredita la polarizzazione di spin da ^TChl



Quali sono i requisiti strutturali per un “quenching” efficace dei tripletti di clorofilla da parte dei carotenoidi?



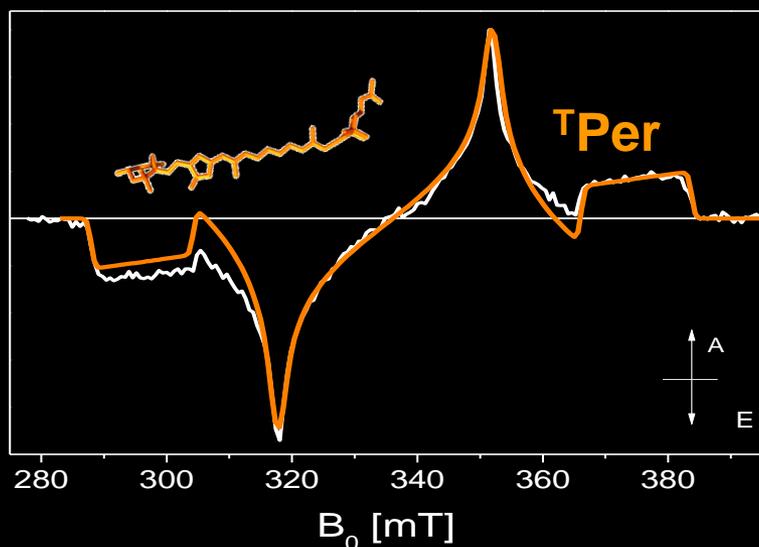
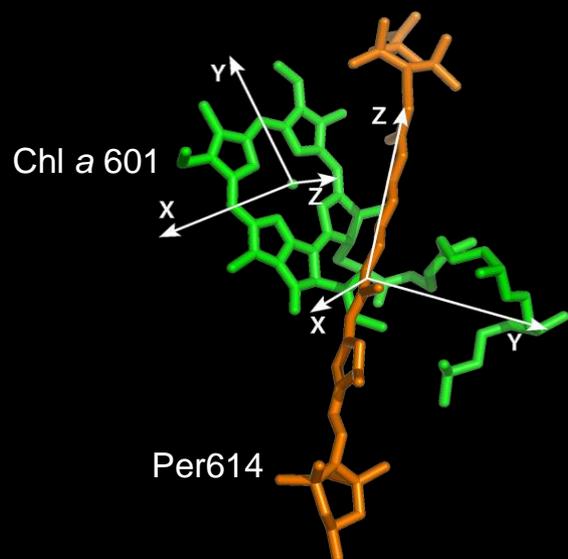
Peridinin Chlorophyll Protein (PCP)
da *Amphidinium carterae*



Light-Harvesting complex II (LHC II)
da *Spinacia oleracea*

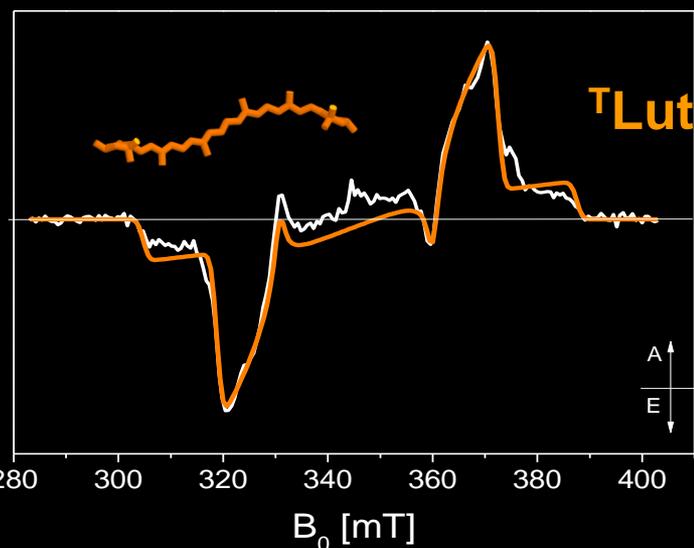
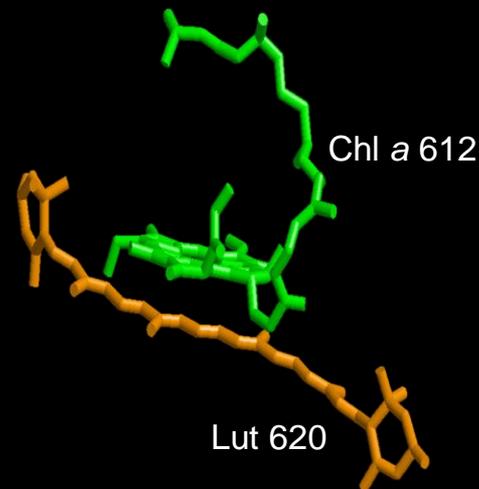
Individuazione delle coppie Chl-Car deputate alla fotoprotezione

PCP



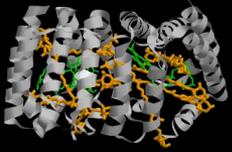
Di Valentin *et al.* BBA (2008) 1777, 186

LHCII



Di Valentin *et al.* J. Phys. Chem. B (2009) 113, 13071

PCP



Caratteristiche dei siti di quenching

LHCII



His

H₂O

Per4

Ponte molecolare

Asn

Cla612

PCP

LHCII

 Π - Π
distance (Å)

 Centre to centre
distance (Å)

 Π - Π
distance (Å)

 Centre to centre
distance (Å)

Chl a-Per611

4.50

8.57

Chl a-610-Lut

3.61

9.91

Chl a-Per612

3.70

8.97

Chl a-612-Lut

3.65

6.03

Chl a-Per613

4.14

9.94

Chl a-611-Lut

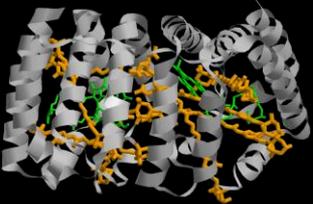
3.77

9.76

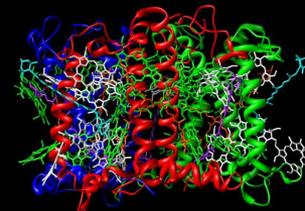
Chl a-Per614

4.71

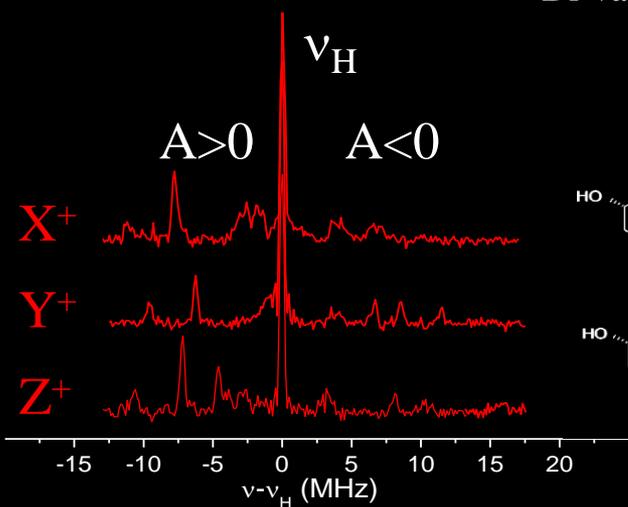
5.36



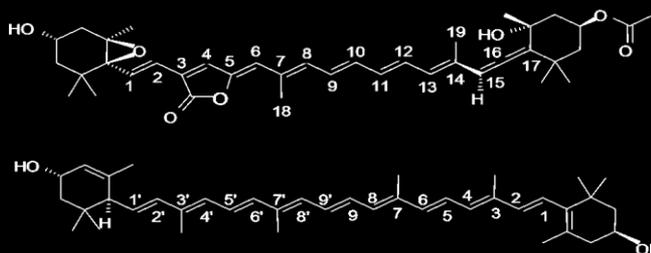
Triplet Pulsed-ENDOR PCP *versus* LHCII



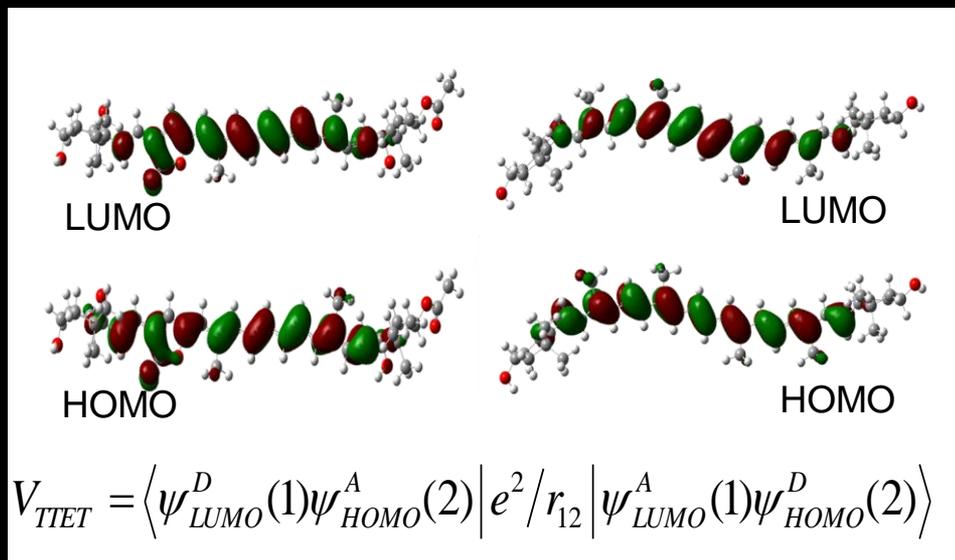
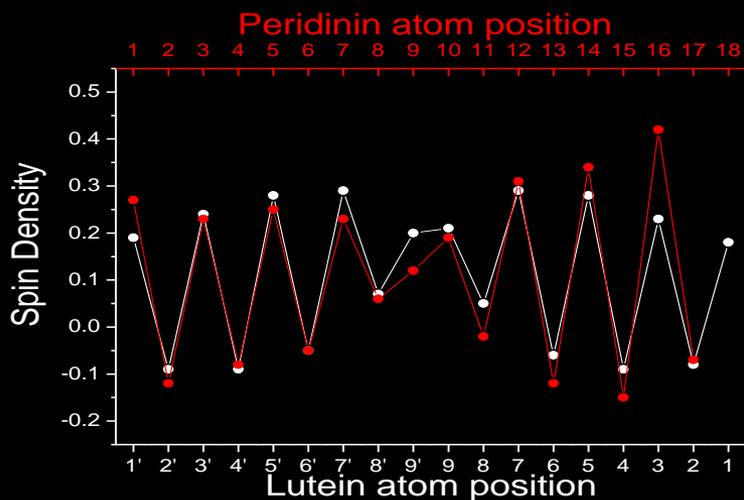
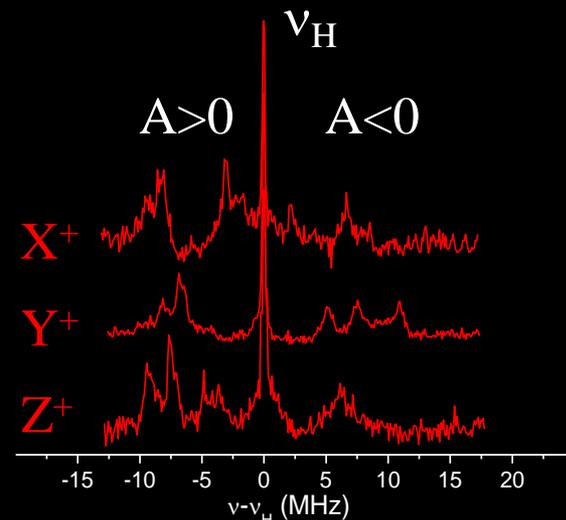
Di Valentin *et al.* BBA (2008) 1777, 295



Peridinin



Luteina

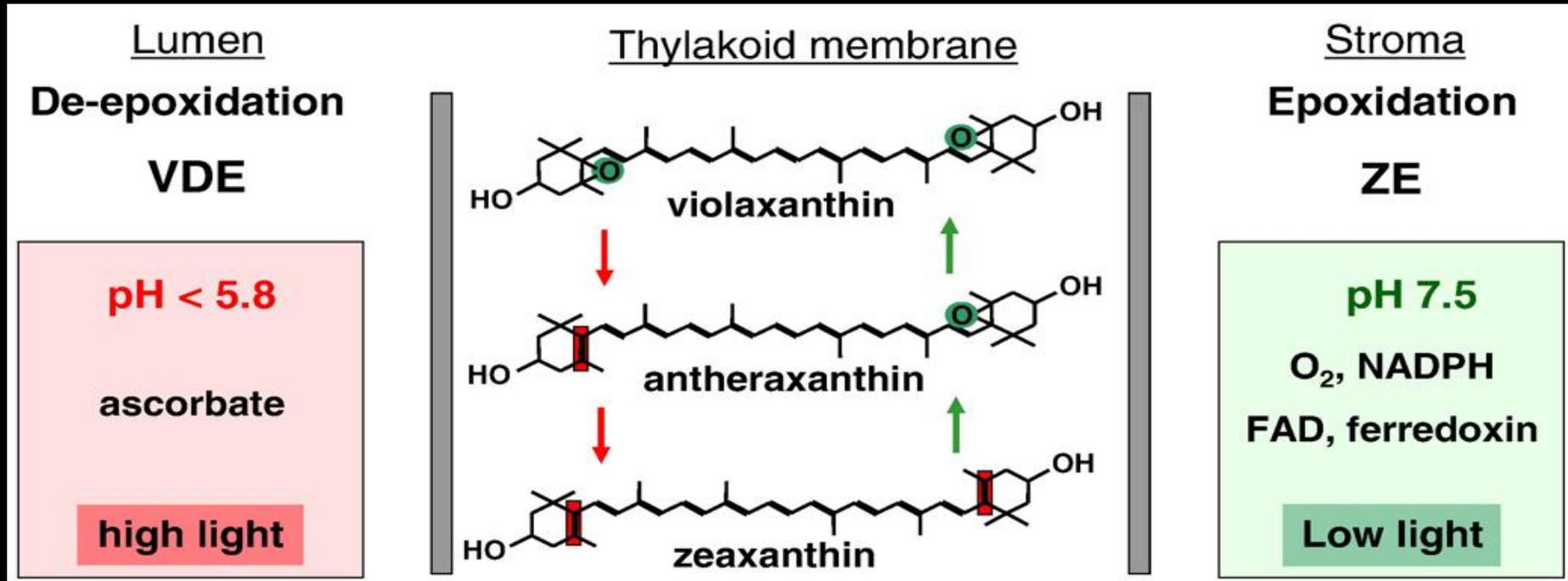


TR-EPR ha permesso di individuare le coppie **clorofilla-carotene** attive nel meccanismo di fotoprotezione

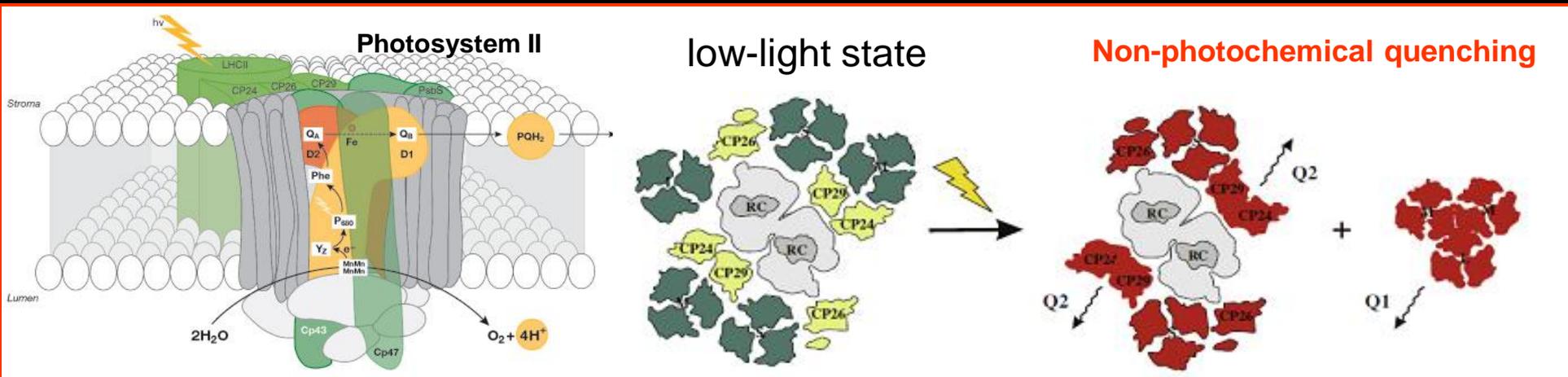
Aspetti strutturali comuni:

- **distanze corte centro-centro** *Chl a - Car*
- **ponte molecolare** interposto tra la coppia (Mg ligand)
- **densità elettronica estesa** ed omogenea negli orbitali dei caroteni coinvolti nel transfer

Non-photochemical quenching: il ciclo dell xantofille

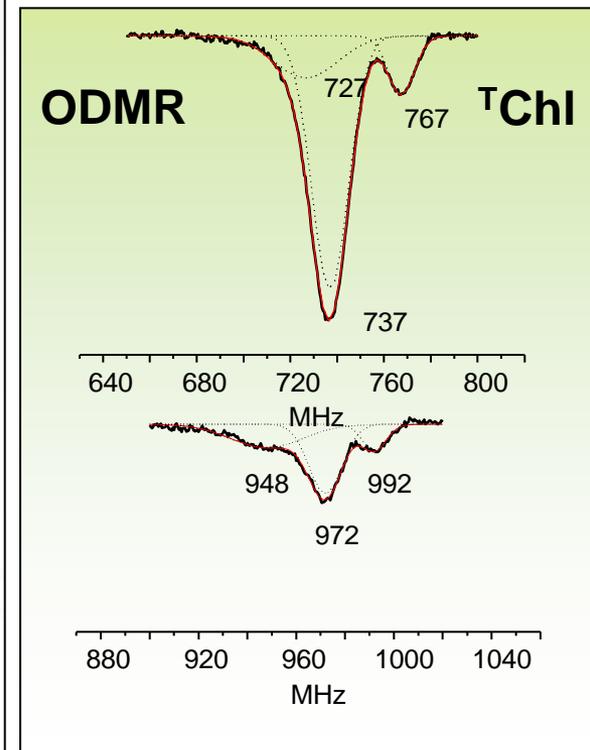
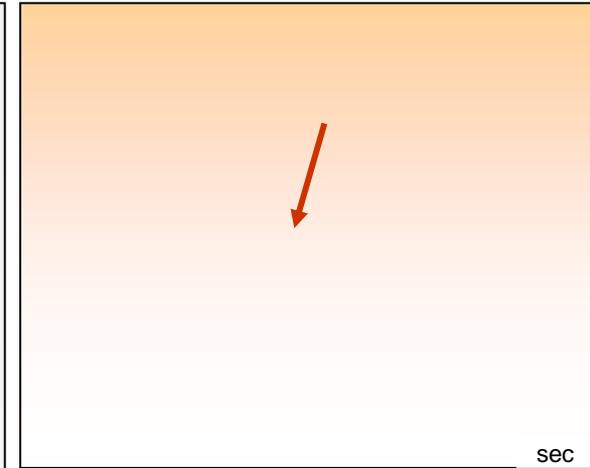
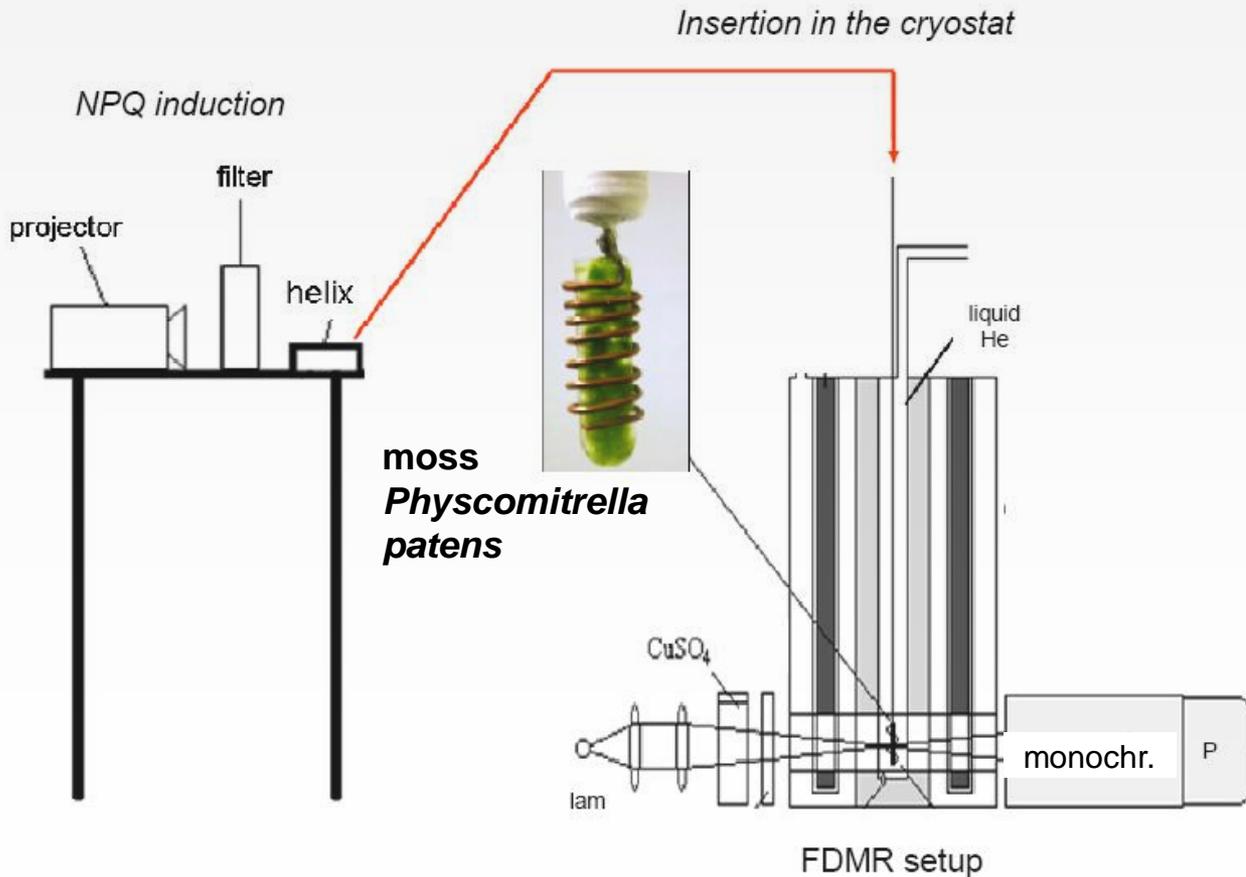


Modello per il riarrangiamento strutturale del PSII

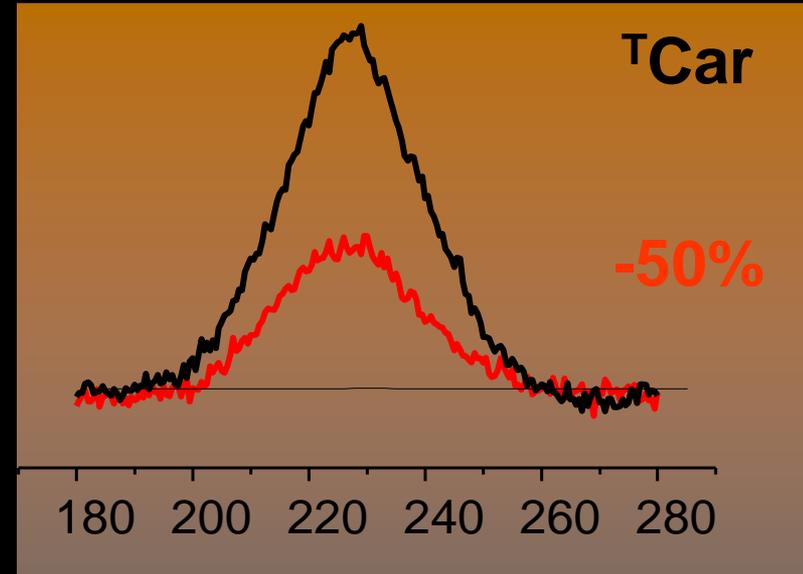
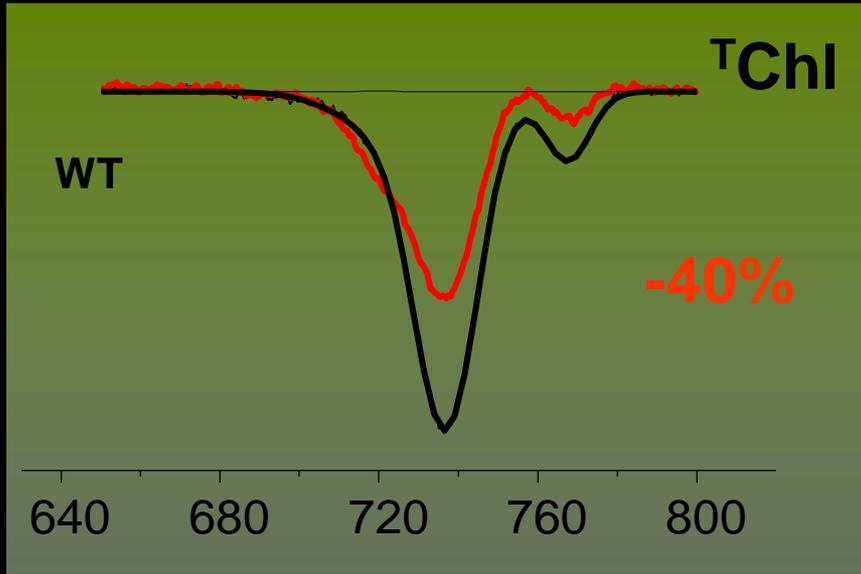


Rivelazione degli stati di tripletto in *Physcomitrella patens*

Optically Detected Magnetic Resonance (ODMR)

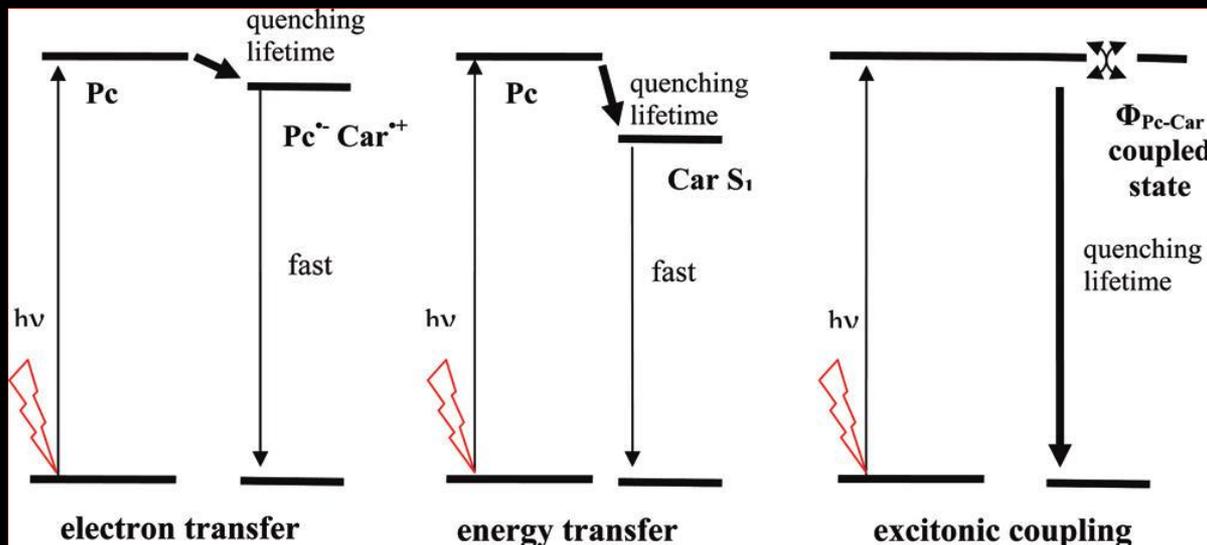
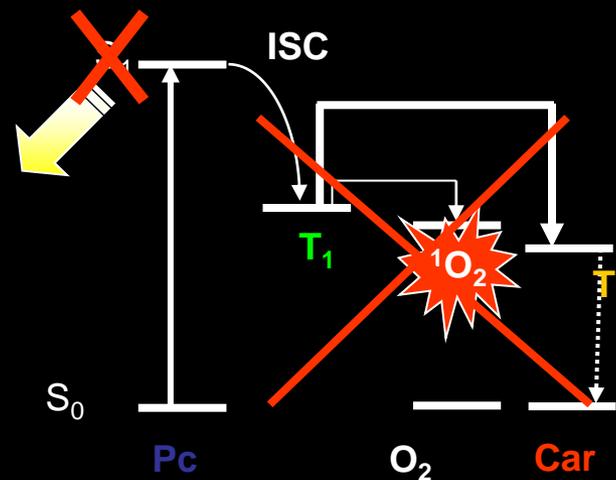
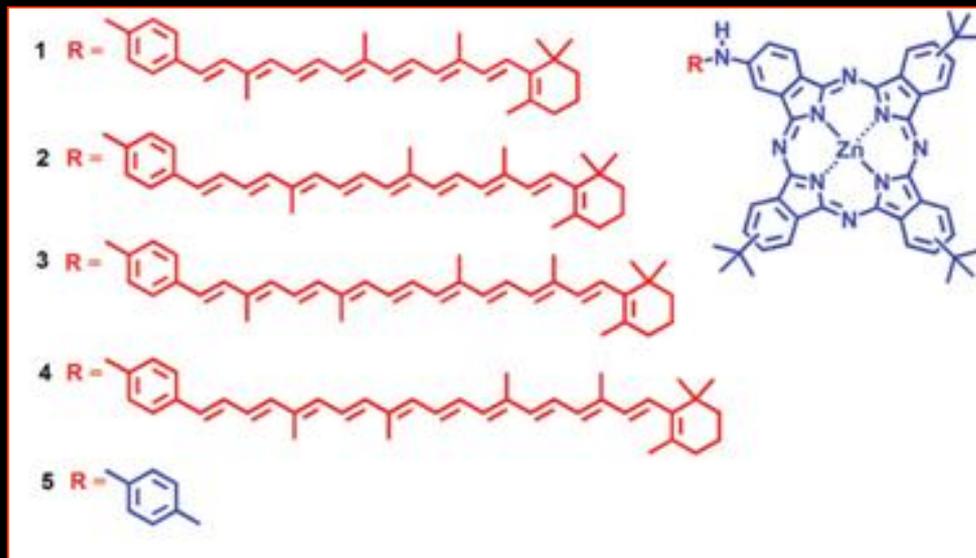


L'attivazione di NPQ riduce la formazione di stati di tripletto di tutte le componenti osservate, appartenenti ai complessi antenna, periferici e di core del PSII



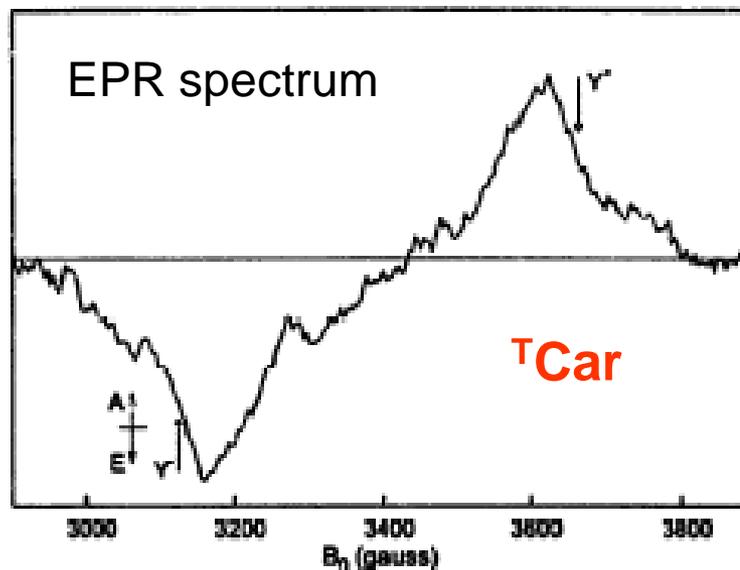
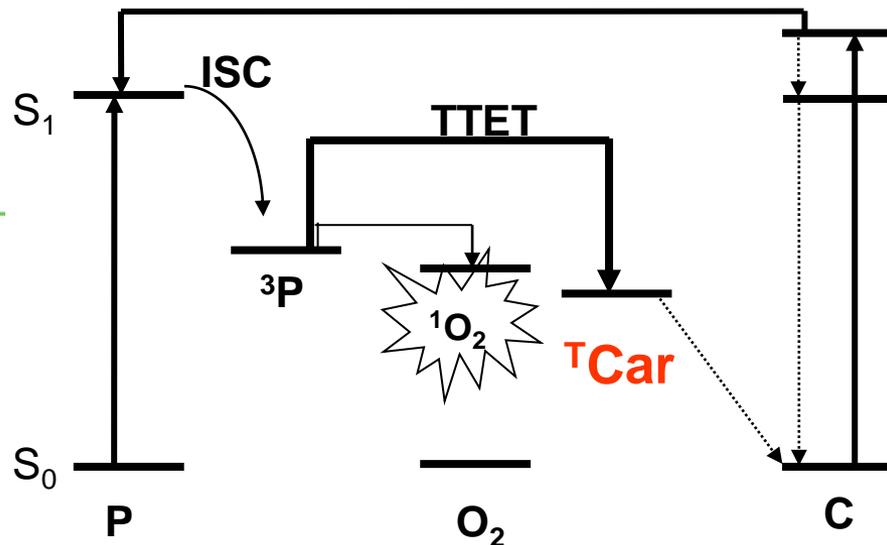
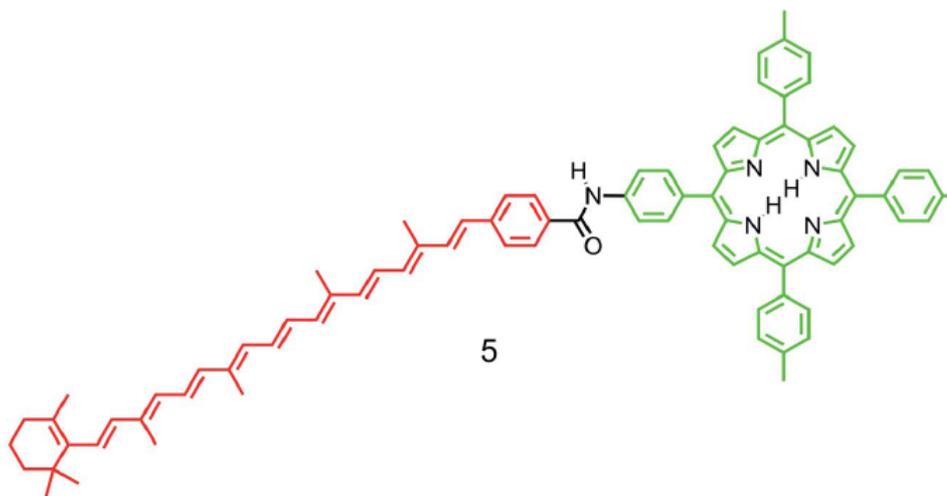
	x_c [MHz]	w [MHz]		
			<i>dark</i>	<i>illuminated</i>
T_1	737 0.5	16 0.2	-1	-0.59 0.05
T_2	726 0.5	27 0.2	-0.29 0.02	-0.19 0.02
T_3	767 0.5	11 0.2	-0.165 0.02	-0.05 0.002
T_4	719 0.5	11 0.2	0	+0.11 0.01

Diadi artificiali **carotene-ftalocianine** riproducono gli effetti di quenching degli stati di singoletto osservati nei complessi di “Light harvesting naturali”



Meccanismi di quenching proposti

Carotenoporfirina (C-P) in grado di dare fotoprotezione da ossigeno di singoletto, mediante TTET



Considerazioni finali

Solo recentemente la ricerca di base sulla fotosintesi e la definizione dei meccanismi molecolari che la regolano ha consentito alla ricerca finalizzata alla fotosintesi artificiale di raggiungere la fase di maturità che permetterà **l'integrazione dei singoli componenti** sviluppati per la realizzazione di un sistema composito atto alla produzione di combustibile.

In questa prospettiva, le strategie future per la fotosintesi artificiale dovrebbero includere anche la mimesi della fotosintesi per quanto concerne i **meccanismi di fotoprotezione** adottati dalla fotosintesi naturale.



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Fotosintesi

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Pisa

Prof. Vincenzo Barone
Prof. Orlando Crescenzi
Dr. Alfonso Pedone

Department of Biology, Macquarie
University Australia

Prof. Roger G. Hiller

Research Department of Structural and
Molecular Biology, University of London

Dr. Christopher Kay

Fotosintesi artificiale

Department of Chemistry & Biochemistry
Center for Bioenergy & Photosynthesis
Arizona State University

Prof. Devens Gust
Prof. Ana Moore
Prof Thomas MOORE