



Optyka nanostruktur

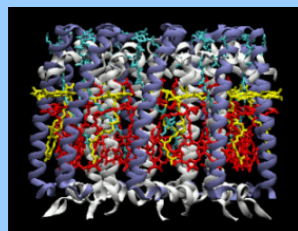
Sebastian Maćkowski

Instytut Fizyki

Uniwersytet Mikołaja Kopernika

Adres poczty elektronicznej: mackowski@fizyka.umk.pl

Biuro: 365, telefon: 611-3250



SL 2008/2009



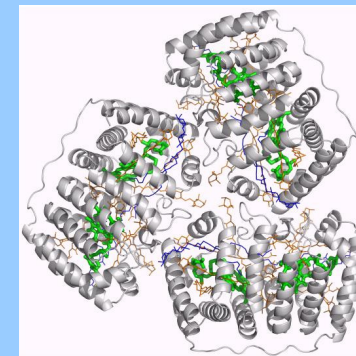
Perydynina-chlorofil-białko



Amphidinium carterae



struktura (krystalografia promieni X)

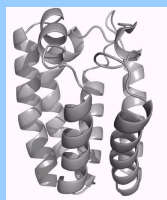


E. Hofmann et al., Science (1996)

SL 2008/2009

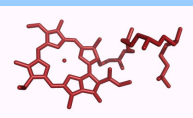


Rekonstytucja Chl a



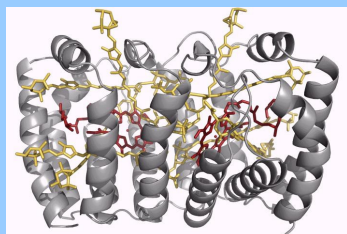
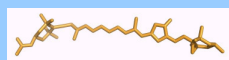
+

1 Chl a



+

4 Per



(Chl a)₂-N-PCP

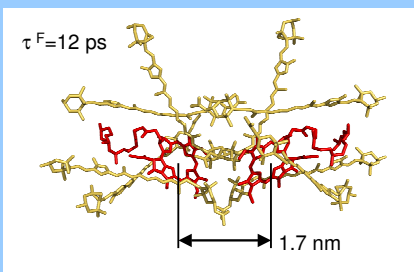
T. Brotsudarmo, SM, et al.,
FEBS Lett. 580 (2006) 5257

SL 2008/2009



Perydynina-chlorofil-białko

monomer PCP



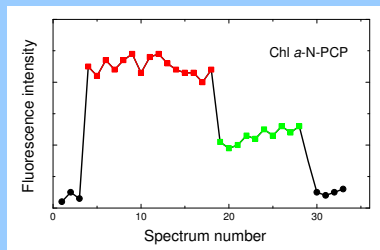
Chl:Per - 1:4

dominująca absorpcja - karotenoidy
słabe oddziaływanie między Chl

SL 2008/2009

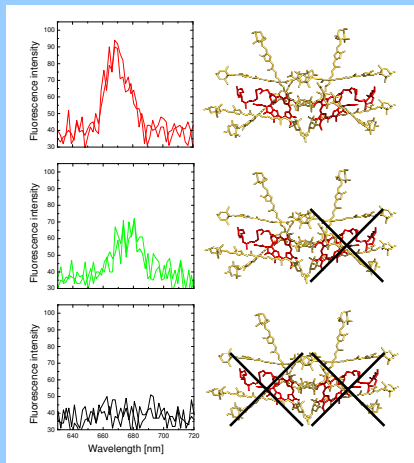


Oddziaływanie Chl-Chl



dwustopniowy zanik intensywności
świecenia – słabe oddziaływanie

niezależny pomiar fluorescencji
z obu Chl w monomerze

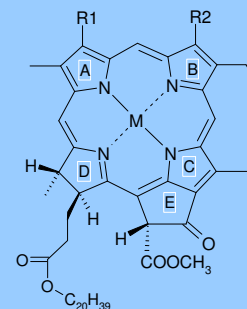


S. Wörmke, SM, *et al.*, BBA - Bioenergetics 1767 (2007) 956

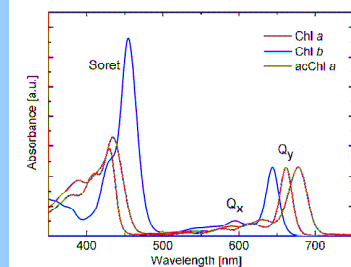
SL 2008/2009



Chlorofile



Name	M	R1	R2
Chlorophyll a	Mg	CH=CH ₂	CH ₃
Chlorophyll b	Mg	CH=CH ₂	CHO
Acetyl-chlorophyll a	Mg	COCH ₃	CH ₃

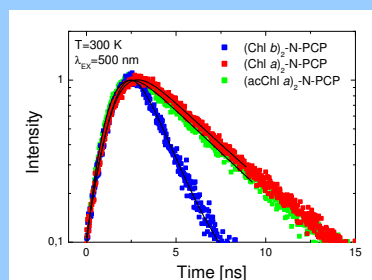
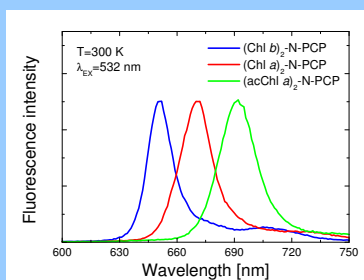


SL 2008/2009



Inne typy chlorofilu

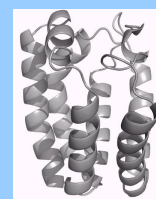
Pigment	Fluorescence maximum [nm]	Extinction coefficient [mM ⁻¹ cm ⁻¹]	Lifetime [ns]	Quantum yield [%]	Per to Chl transfer time [ps] ¹
Chl a	672	78.8 at 662 nm	3.68	24	3.55
Chl b	651	46.9 at 644 nm	1.4	11	9.4
acChl a	692	65.2 at 667 nm	3.86	21	2.55



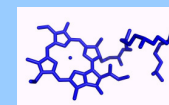
SL 2008/2009



Układy z innymi chlorofilami



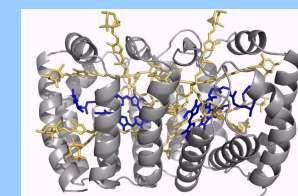
1 Chl b



4 Per



Chl b-N-PCP

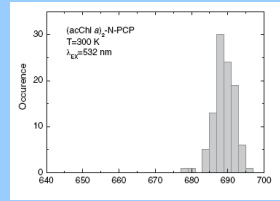
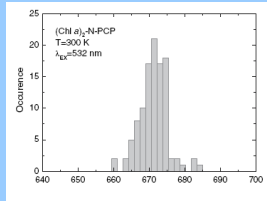
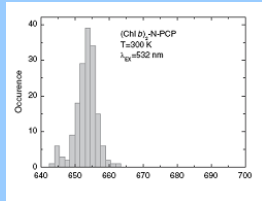
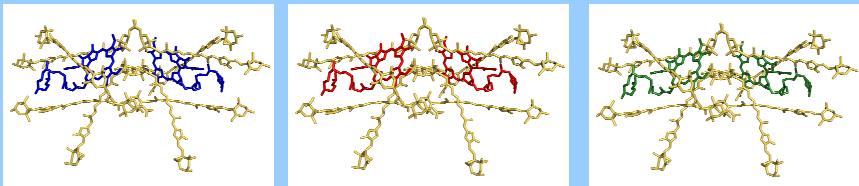


T.H.P. Brotsudarmo, SM, *et al.*,
Photosynth. Res. 95 (2008) 247

SL 2008/2009



Pojedyncze kompleksy

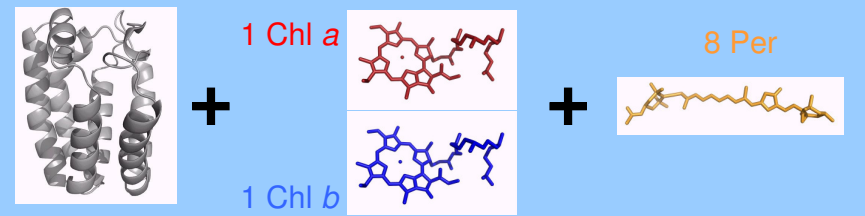


S. Wörmke, SM, *et al.*, *J. Fluor.* **18** (2008) 611

SL 2008/2009



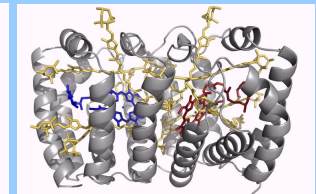
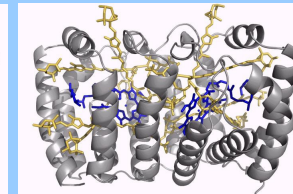
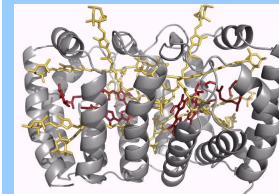
Układy dwuchlorofilowe



Chl a-N-PCP

Chl b-N-PCP

Chl a/Chl b-N-PCP



T.H.P. Brotsudarmo, SM, *et al.*, *Photosynth. Res.* **95** (2008) 247

SL 2008/2009

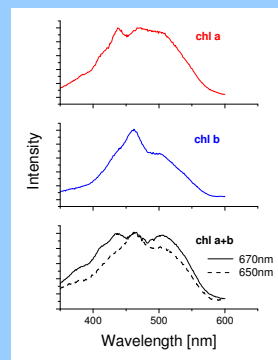
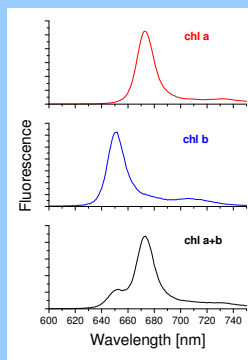
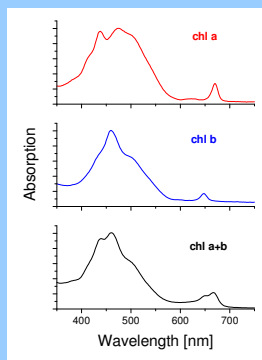


Układy dwuchlorofilowe

absorpcja

fluorescencja

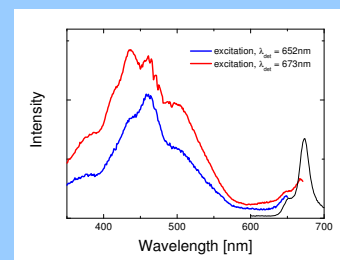
widmo wzbudzenia



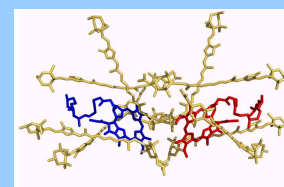
SL 2008/2009



Widmo wzbudzenia



excitation spectra show energy transfer between Chl a and Chl b



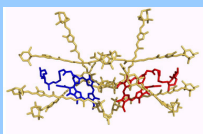
Förster description

$$k_T(r) = \frac{9000(\ln 10)\kappa^2\Phi_D}{128\pi^5 N_A n^4 \tau_D R^6} \int_0^\infty F_D(\lambda)\epsilon(\lambda)\lambda^4 d\lambda$$

SL 2008/2009

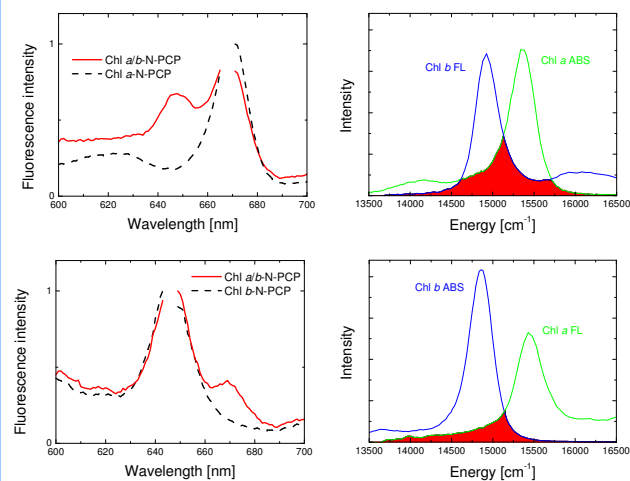


Widmo wzbudzenia



detekcja Chl a

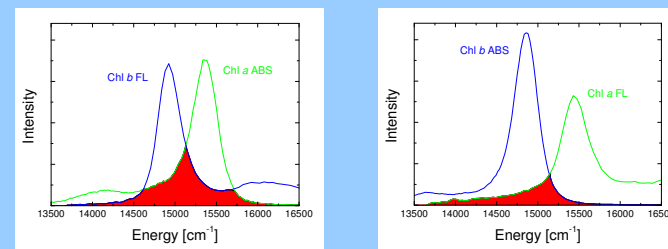
detekcja Chl b



SL 2008/2009



Przekaz energii



$$k_T(r) = \frac{9000(\ln 10)\kappa^2\Phi_D}{128\pi^5 N_A n^4 \tau_D R^6} \int_0^\infty F_D(\lambda)\epsilon(\lambda)\lambda^4 d\lambda$$

Förster transfer times

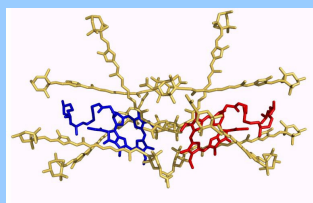
$$k_{AB}^F = 47 \text{ (ps)}^{-1}$$

$$k_{BA}^F = 31 \text{ (ps)}^{-1}$$

SL 2008/2009



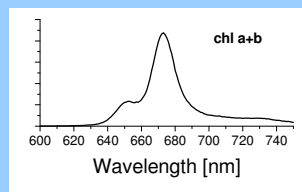
Rozkład obsadzeń



energy transfer between Chl a and Chl b takes place in both directions with comparable efficiency

intensity ratio between Chl a and Chl b:

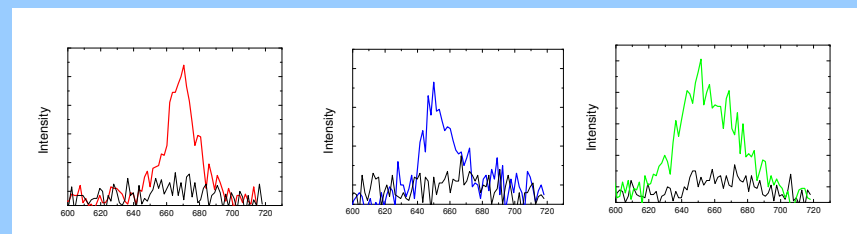
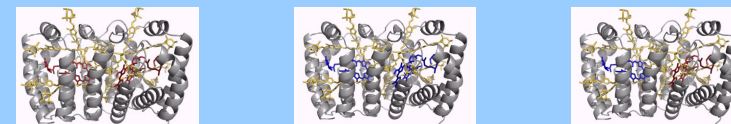
equilibrium: 0.51
Monte Carlo: 0.64



SL 2008/2009



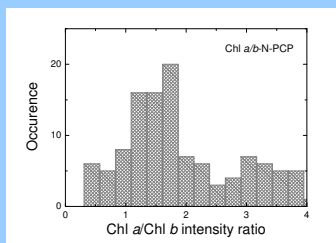
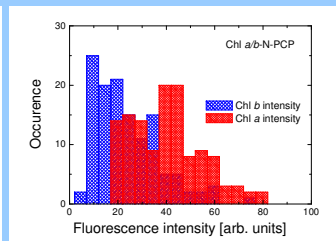
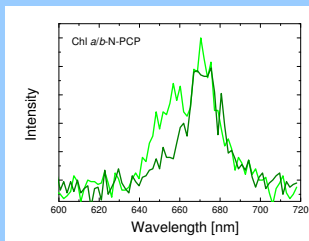
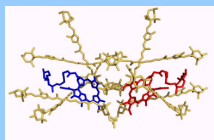
Pojedyncze kompleksy



SL 2008/2009



Pojedyncze kompleksy



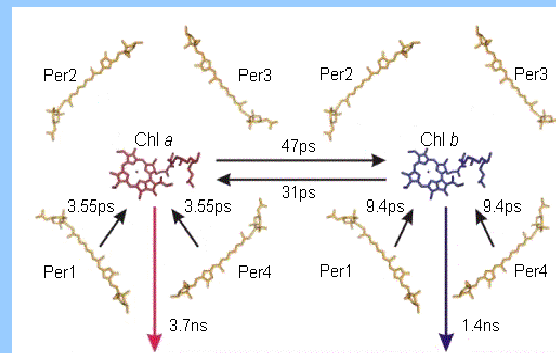
intensity ratio between
Chl a and Chl b:
1.9

SL 2008/2009



Ścieżki przekazu energii

energy transfer pathways



Per – to – Chl energy transfer (T. Polivka, *et al.*, Photosyn. Res. 2005)

$$k_{\text{Per-Chl a}} = (3.55 \text{ ps})^{-1}$$
$$k_{\text{Per-Chl b}} = (9.4 \text{ ps})^{-1}$$

excitation distribution:
equilibrium: 1.3
Monte Carlo: 1.7
experiment: 1.9

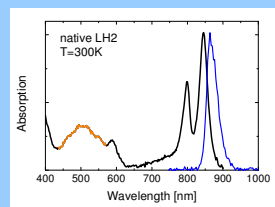
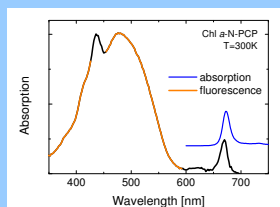
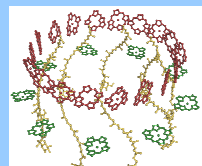
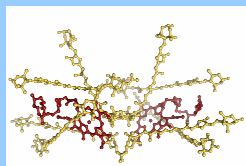
SM, S. Wörmke, *et al.*, Biophys. J. **93** (2007) 3249

SL 2008/2009



Pytanie

czy istnieją sposoby wpływania na własności optyczne układów fotosyntetycznych?



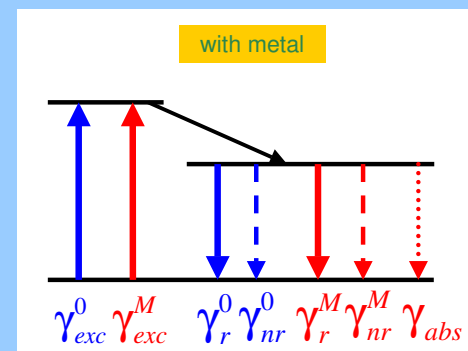
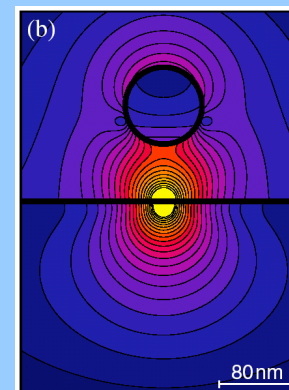
SL 2008/2009



Zasadnicza idea

P. Arger, *et al.* Phys. Rev. Lett. 2006

the presence of metal nanostructure in the vicinity of an emitting dipole strongly affects the optical properties of a fluorophore



SL 2008/2009



Zasadnicza idea

PRL 96, 113002 (2006)

PHYSICAL REVIEW LETTERS

week ending
24 MARCH 2006

Enhancement and Quenching of Single-Molecule Fluorescence

Pascal Anger, Palash Bharadwaj, and Lukas Novotny*

The Institute of Optics and Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627, USA[†]
(Received 23 November 2005; published 21 March 2006)

We present an experimental and theoretical study of the fluorescence rate of a single molecule as a function of its distance to a laser-irradiated gold nanoparticle. The local field enhancement leads to an increased excitation rate whereas nonradiative energy transfer to the particle leads to a decrease of the quantum yield (quenching). Because of these competing effects, previous experiments showed either fluorescence enhancement or fluorescence quenching. By varying the distance between molecule and particle we show the first experimental measurement demonstrating the continuous transition from fluorescence enhancement to fluorescence quenching. This transition cannot be explained by treating the particle as a polarizable sphere in the dipole approximation.

SL 2008/2009



Teoria

quantum yield

$$q = \gamma_r / (\gamma_r + \gamma_{nr} + \gamma_{abs}) = \frac{\gamma_r / \gamma_r^0}{\gamma_r / \gamma_r^0 + \gamma_{abs} / \gamma_r^0 + (1 - q^0) / q^0}$$

$$\frac{\gamma_{abs}}{\gamma_r^0} = \frac{3}{16} \operatorname{Im} \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 1} \frac{1}{k_2^3 z^3} \frac{(p_x^2 + p_y^2 + 2p_z^2)}{|\mathbf{p}|^2}$$

radiative decay

$$\frac{\gamma_r}{\gamma_r^0} = \frac{|\mathbf{p} + \mathbf{p}_{induced}|^2}{|\mathbf{p}|^2} = \left| \mathbf{n}_p + k_2^2 \frac{1}{\varepsilon_0} \bar{\alpha}_p(\omega_2) \bar{\mathbf{G}}(\mathbf{r}_p, \mathbf{r}_o; \omega_2) \mathbf{n}_p \right|^2$$

$$\frac{\gamma_r}{\gamma_r^0} = \left| 1 + 2 \frac{a^3}{(a+z)^3} \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 2} \right|^2$$

excitation rate

$$\gamma_{exc} \propto |\mathbf{p} \cdot [\mathbf{E}_o(\mathbf{r}_o, \omega_1) + \mathbf{E}_s(\mathbf{r}_o, \omega_1)]|^2$$

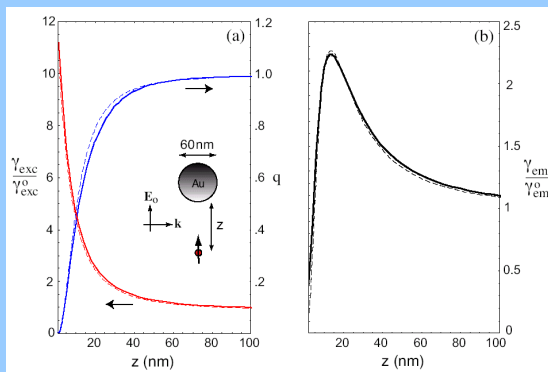
$$\frac{\gamma_{exc}}{\gamma_{exc}^0} = \frac{|\mathbf{n}_p \cdot [\mathbf{1} + k_1^2 \bar{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_p; \omega_1) \bar{\alpha}(\omega_1) / \varepsilon_0] \mathbf{n}_{E_o}|^2}{|\mathbf{n}_p \cdot \mathbf{n}_{E_o}|^2} = \left| 1 + 2 \frac{a^3}{(a+z)^3} \frac{\varepsilon(\omega_2) - 1}{\varepsilon(\omega_2) + 2} \right|^2$$

P. Anger, *et al.* Phys. Rev. Lett. (2006)

SL 2008/2009



Teoria

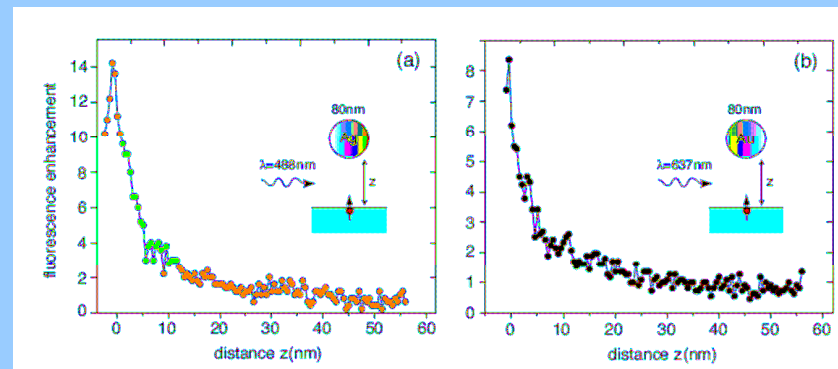


$$\frac{\gamma_{em}}{\gamma_{em}^0} = \frac{\gamma_{exc}}{\gamma_{exc}^0} \frac{q}{q^0}$$

SL 2008/2009



Zasadnicza idea

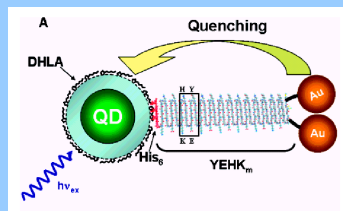


SL 2008/2009

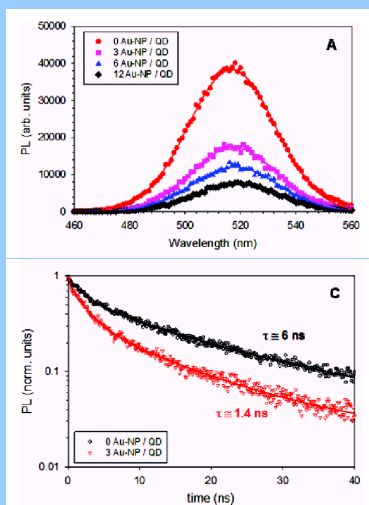


Tłumienie emisji

T. Pons, *et al.* Nano Lett. 2007



energy transfer from NC to NP leads to decrease of the fluorescence and faster decay of the emission

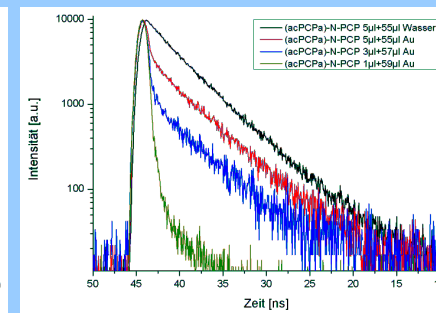
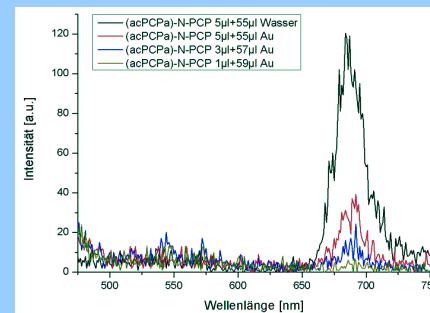


SL 2008/2009



PCP + Au NPs

(ac-Chl a)₂-N-PCP, emission @ 692 nm

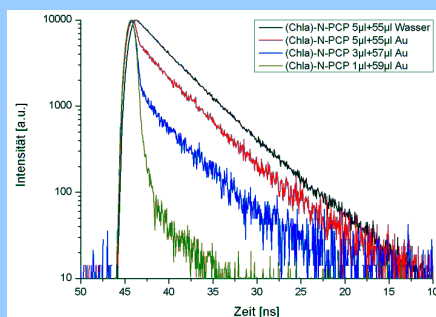
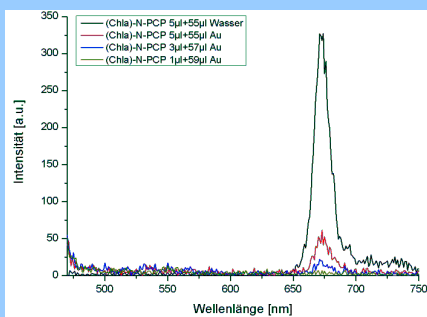


SL 2008/2009



PCP + Au NPs

(Chl a)₂-N-PCP, emission @ 672 nm

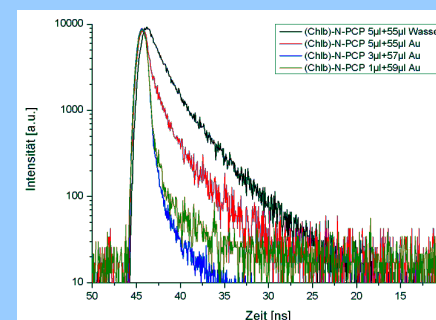
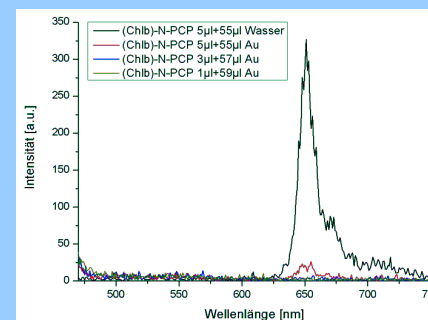


SL 2008/2009



PCP + Au NPs

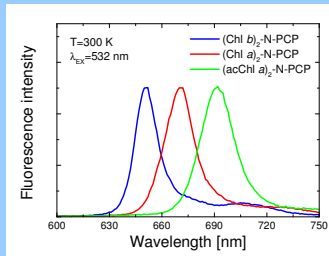
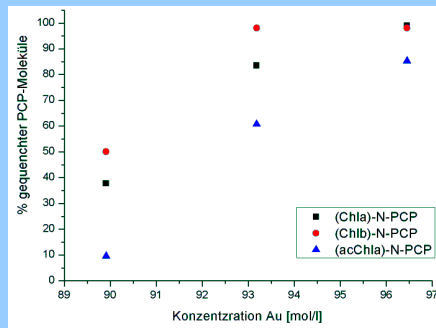
(Chl b)₂-N-PCP, emission @ 651 nm



SL 2008/2009



PCP + Au NPs

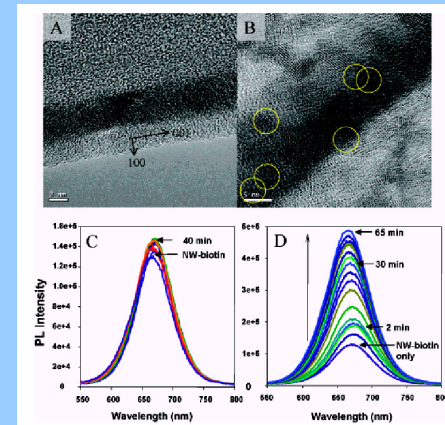
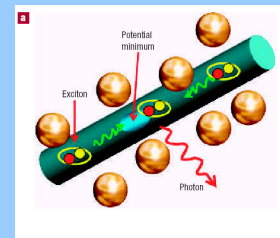


strongest quenching occurs for Chl *b* – reconstituted N-PCP due to largest overlap with the absorption of Au colloid



Wzmocnienie emisji

J. Lee, *et al.* Nano Lett. 2004, Nat. Materials 2007

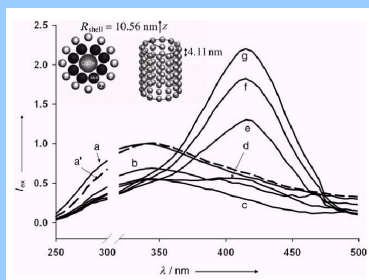


stimulation of photon emission by electromagnetic field generated through plasmons excited in Au NPs

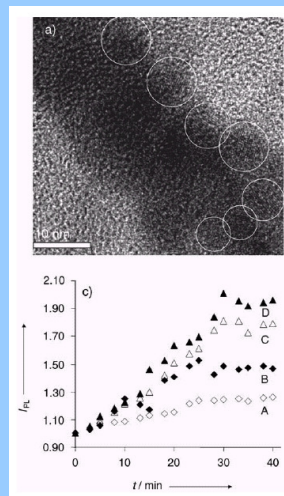


Wzmocnienie emisji

J. Lee, *et al.* Angew. Chemie Int. Ed. 2006

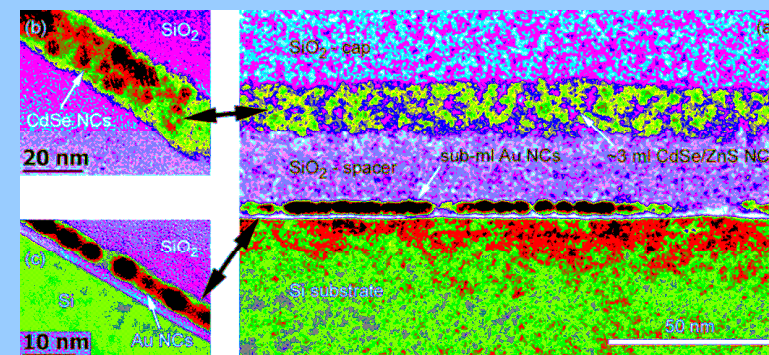


increase of NW absorption due to plasmonic excitations in Ag nanoparticles



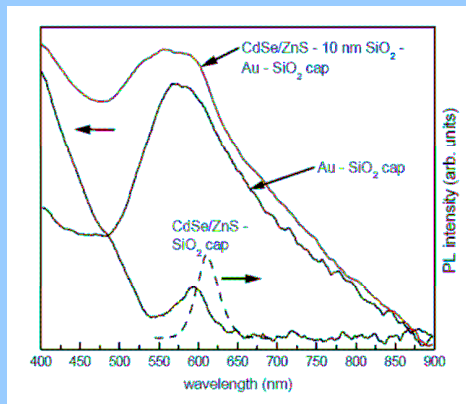
Wzmocnienie emisji

cząstki metaliczne + nanokryształy półprzewodnikowe





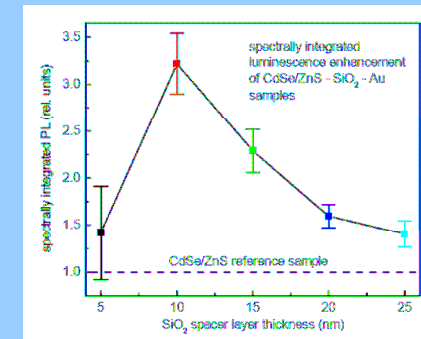
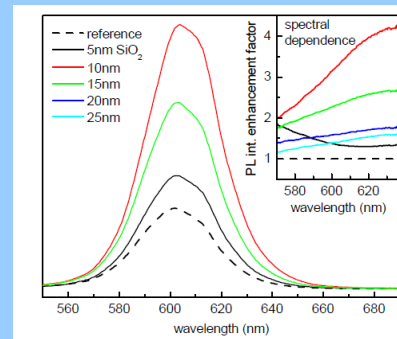
Własności optyczne



SL 2008/2009



Wzmocnienie emisji

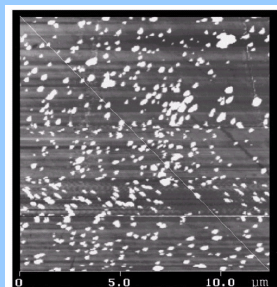


SL 2008/2009

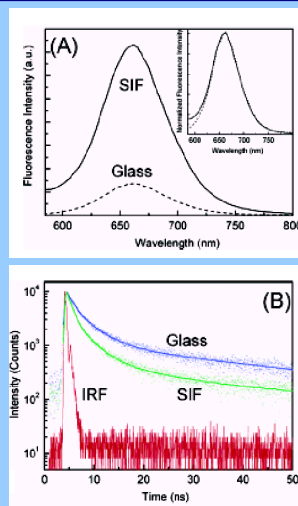


Wyspy srebrne (SIF)

J. Lakowicz, *et al.* Analytical Biochem. 2002
K. Ray, *et al.* J. Am. Chem. Soc. 2006



wzrost intensywności fluorescencji

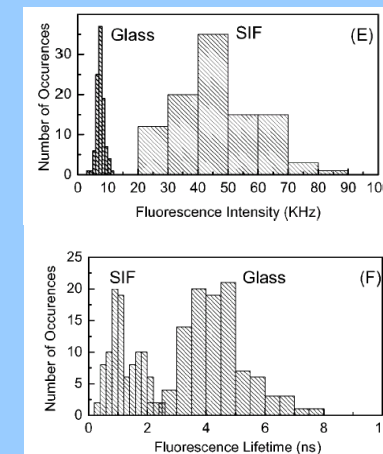
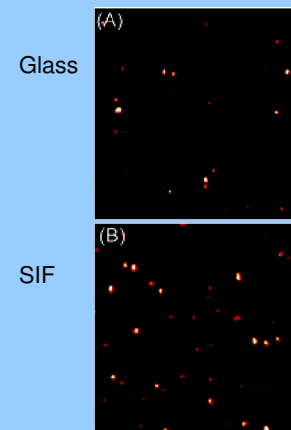


SL 2008/2009



Pojedyncze nanokryształy + SIF

K. Ray, *et al.* J. Am. Chem. Soc. 2006

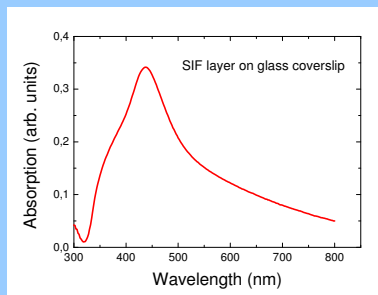
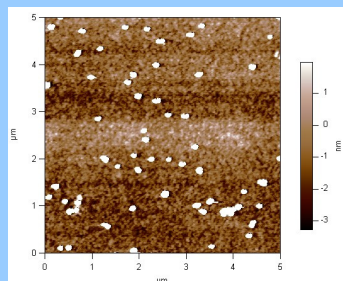


SL 2008/2009



Wyspy srebrne

AFM

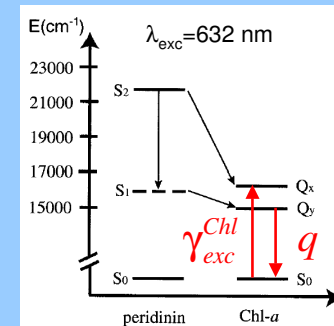
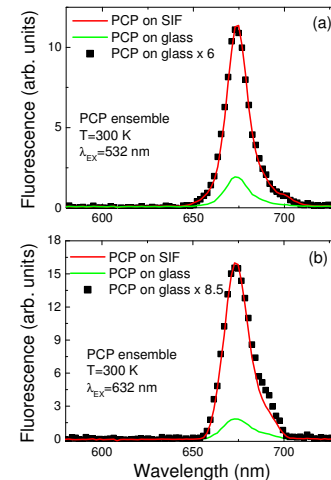


wyspy o średnicach od 70 do 140 nm
i wysokości około 30-40 nm

SL 2008/2009



PCP na wyspach srebrnych



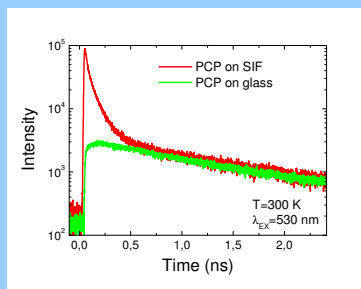
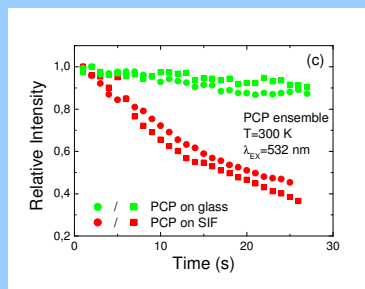
silny wzrost intensywności emisji
dla kompleksów PCP znajdujących się
się w pobliżu srebrnych wysp

SM, S. Wörmke, *et al.*,
Nano Lett. **8** (2008) 558

SL 2008/2009



PCP na wyspach srebrnych



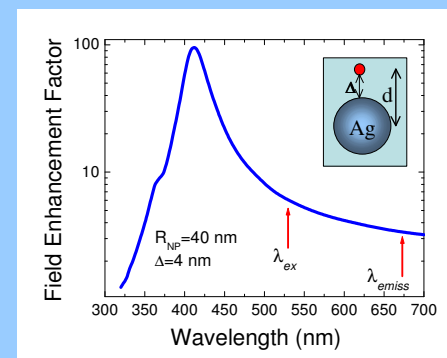
wzrost intensywności fluorescencji
spowodowany większą absorpcją światła
przez kompleks fotosyntetyczny

SM, S. Wörmke, *et al.*,
Nano Lett. **8** (2008) 558

SL 2008/2009



PCP na wyspach srebrnych



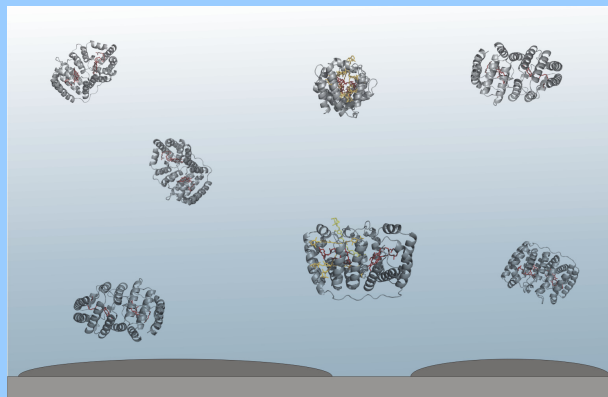
SM, S. Wörmke, *et al.*,
Nano Lett. **8** (2008) 558

SL 2008/2009



Pojedyncze kompleksy PCP

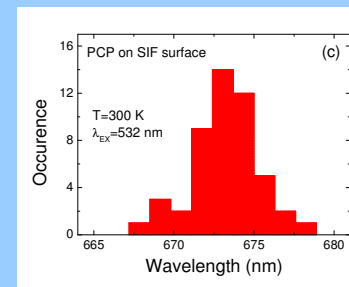
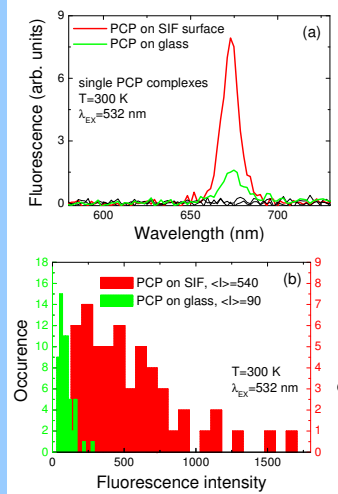
rozkład wielkości wysp srebrnych, odległości między wyspami i kompleksami PCP, a także ich wzajemnej orientacji



SL 2008/2009



Pojedyncze kompleksy PCP



wzmocnienie fluorescencji układu biologicznego pod wpływem oddziaływania z cząstką metalu

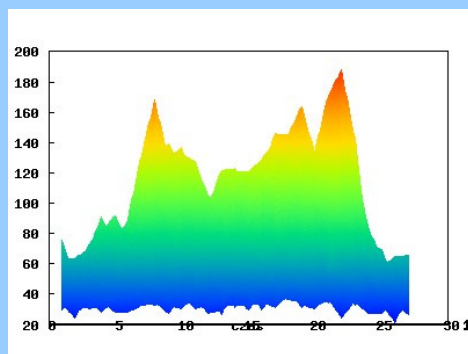
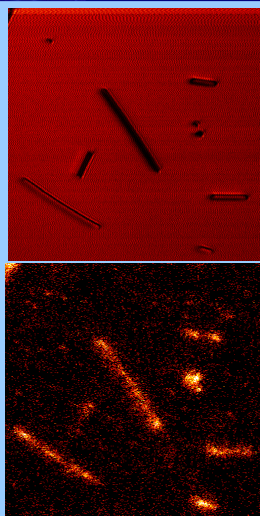
SM, S. Wörmke, *et al.*, Nano Lett. 8 (2008) 558

SL 2008/2009



Plany

nanodrut Ag + pojedyncze kompleksy PCP



SL 2008/2009



Przekaz energii

50

J. Phys. Chem. C 2007, 111, 50–56

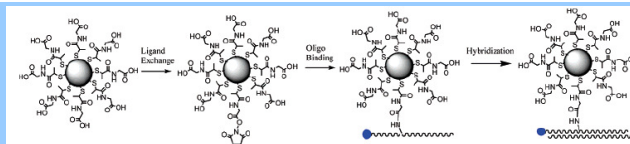
Enhanced Förster Resonance Energy Transfer (FRET) on a Single Metal Particle

Jian Zhang, Yi Fu, and Joseph R. Lakowicz*

Center for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland School of Medicine, 725 West Lombard Street, Baltimore, Maryland 21201

Received: May 1, 2006; In Final Form: October 13, 2006

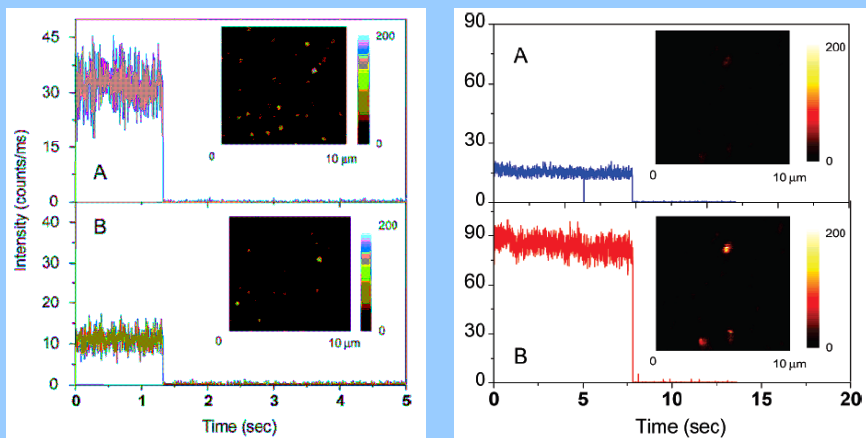
We examined the effect of a metallic silver particle on Förster resonance energy transfer (FRET) between a nearby donor–acceptor pair. A donor-labeled oligonucleotide was chemically bound to a single silver particle, and then an acceptor-labeled complementary oligonucleotide was conjugated by hybridization. The photophysical behavior of FRET between the donor–acceptor pair on the metal particle was investigated using both ensemble emission spectra and single-molecule fluorescence detections. Both the emission intensities and lifetimes indicated an enhanced FRET efficiency due to the metal particle. This interaction led to an increase in the Förster distance for energy transfer from 8.3 to 13 nm. The rate constant of FRET near the silver particle was 21 times faster than that of unbound donor–acceptor pairs. These results suggest the use of metal-enhanced FRET for measuring proximity of large biomolecules or for energy-transfer-based assays.



SL 2008/2009



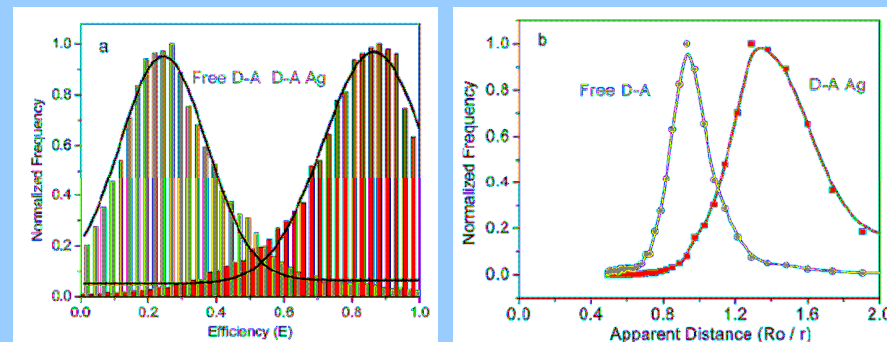
Przekaz energii



SL 2008/2009



Przekaz energii

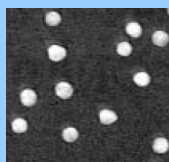


SL 2008/2009

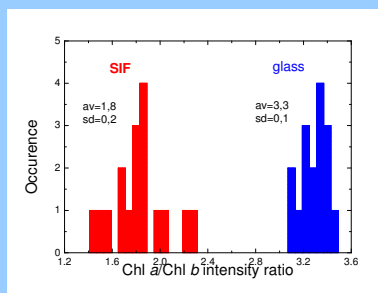
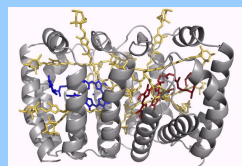


Przekaz energii

cząstki metaliczne



hetero-Chl
PCP



SL 2008/2009

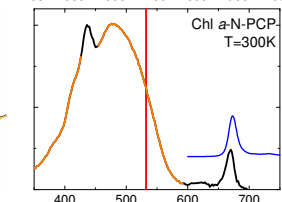
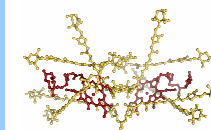
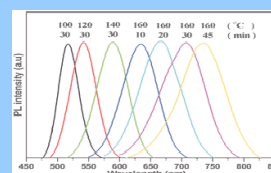
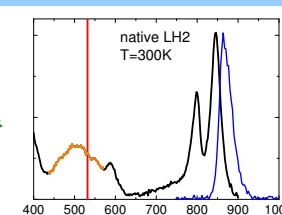
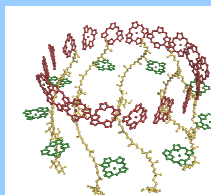


Inne sposoby

nanokryształy



kompleksy fotosyntetyczne



SL 2008/2009