

Investigation on the electronic state of photodegradation processes in optical sensor compounds

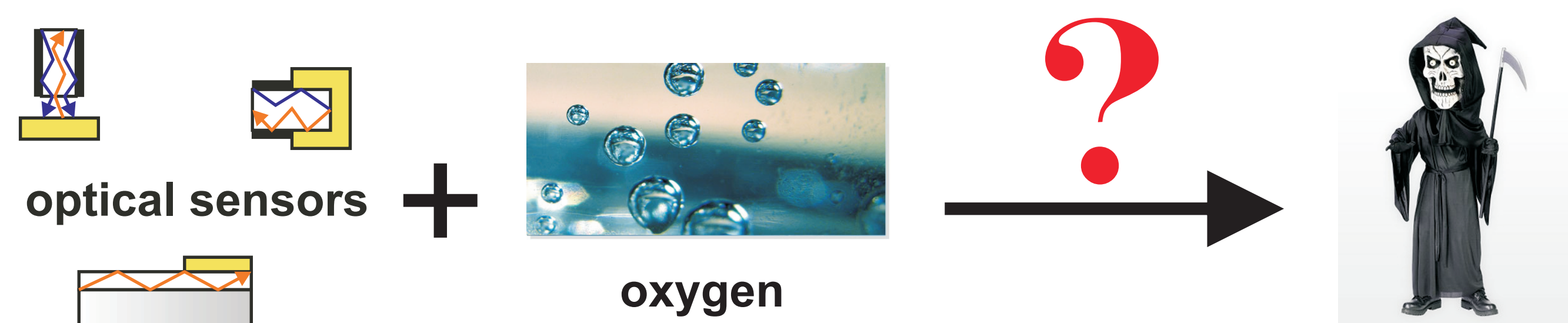
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Background

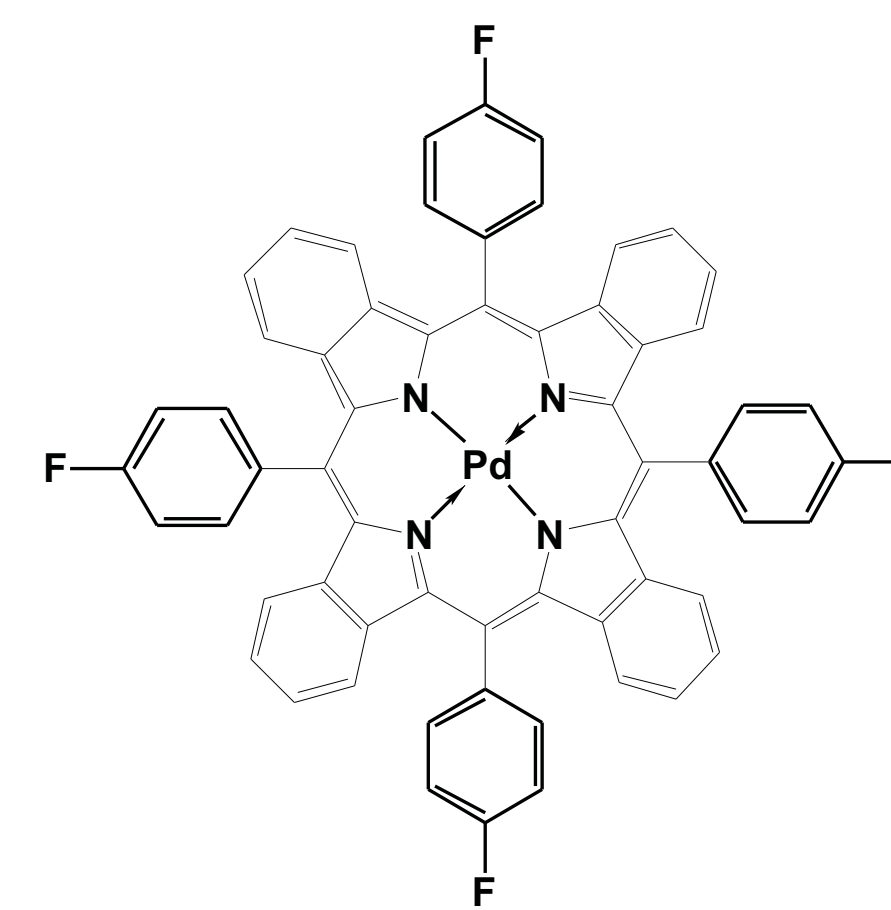
Optical sensors consist of several compounds (dyes immobilised in polymers) which are sensitive to reactions with singlet oxygen evolving from luminescence quenching processes in the sensor layer. Today, photodegradation mechanisms in optical sensors are poorly understood. It is of essential interest - especially for sensors consisting of multiple dye systems - to determine the reaction mechanisms of photochemical sensor dyes and singlet oxygen to prevent photodegradation processes in optical sensors.



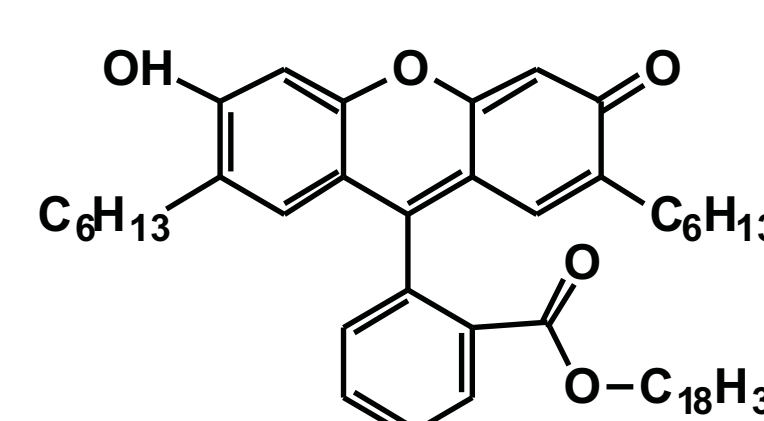
Here we present our initial investigations on the electronic state of two compounds in photodegradation reactions with singlet oxygen using a method that has the potential of being applied to various other important luminescent systems in sensor chemistry.

The obtained absorption spectra clearly indicate that both the ground state and the excited state account for photodegradation, the decisive factor for the dominating electronic state being the excited state lifetime of the dye.

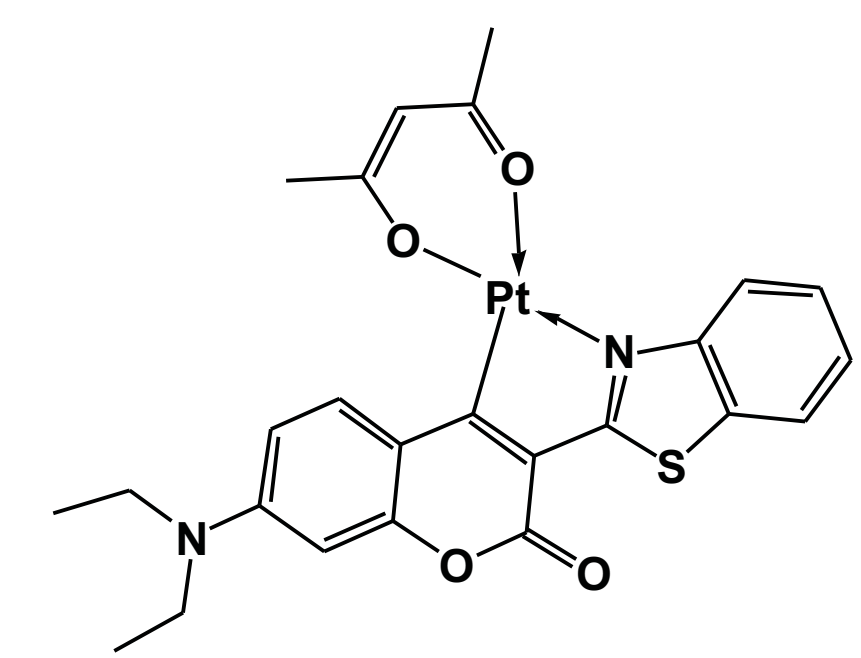
Compounds



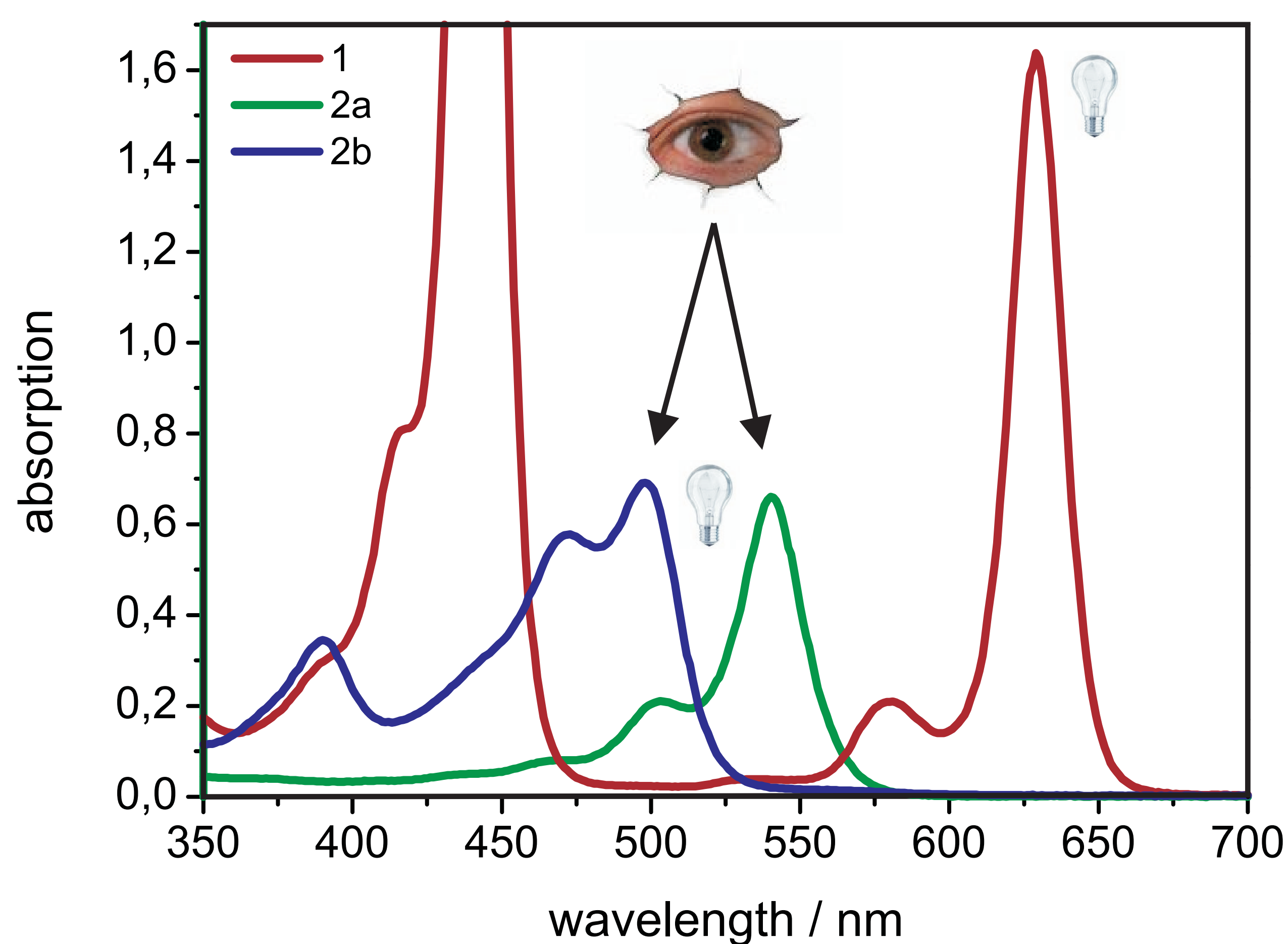
1
PdTPFBPF^[1]
Singlet oxygen generator
 $\lambda_{\max, \text{abs}} / \text{nm}$ ($\epsilon \cdot 10^{-3} / \text{M}^{-1} \text{cm}^{-1}$) =
443 (268); 579 (12.7); 629 (115)



2a
DHFOE^[2]
Singlet oxygen acceptor
 $\lambda_{\max, \text{abs}} / \text{nm}$ ($\epsilon \cdot 10^{-3} / \text{M}^{-1} \text{cm}^{-1}$) =
457_{acid} (80); 515_{base} (98)

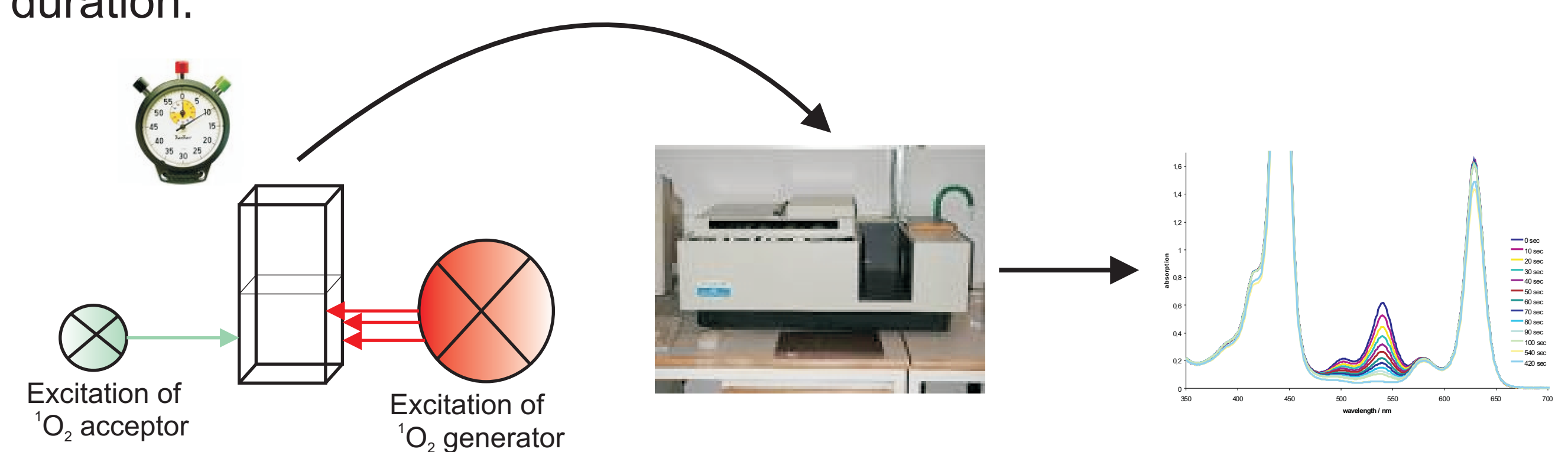


2b
c6Pt(acac)^[3]
Singlet oxygen acceptor
 $\lambda_{\max, \text{abs}} / \text{nm}$ ($\epsilon \cdot 10^{-3} / \text{M}^{-1} \text{cm}^{-1}$) =
300 (20); 388 (23); 469 (41); 496 (51)



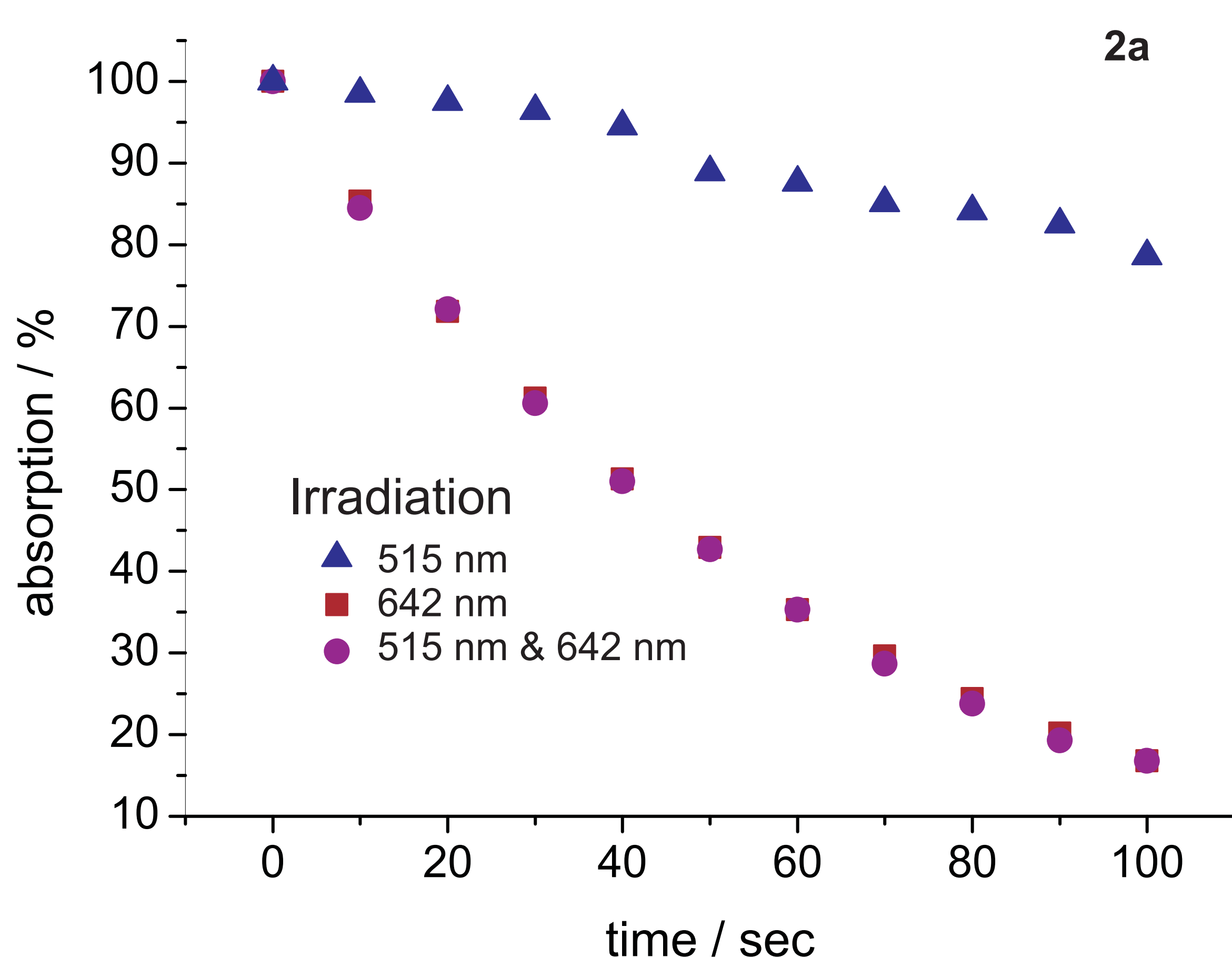
Method

The photochemical system in use consists of two components, one serving as a singlet oxygen generator (1), the other being the dye of interest (2). By irradiating both dyes simultaneously, we assure the presence of a singlet oxygen surplus, mainly produced by the „generator“ dye in the solution. The absorption maximum of the investigated dye band is plotted vs. irradiation duration.



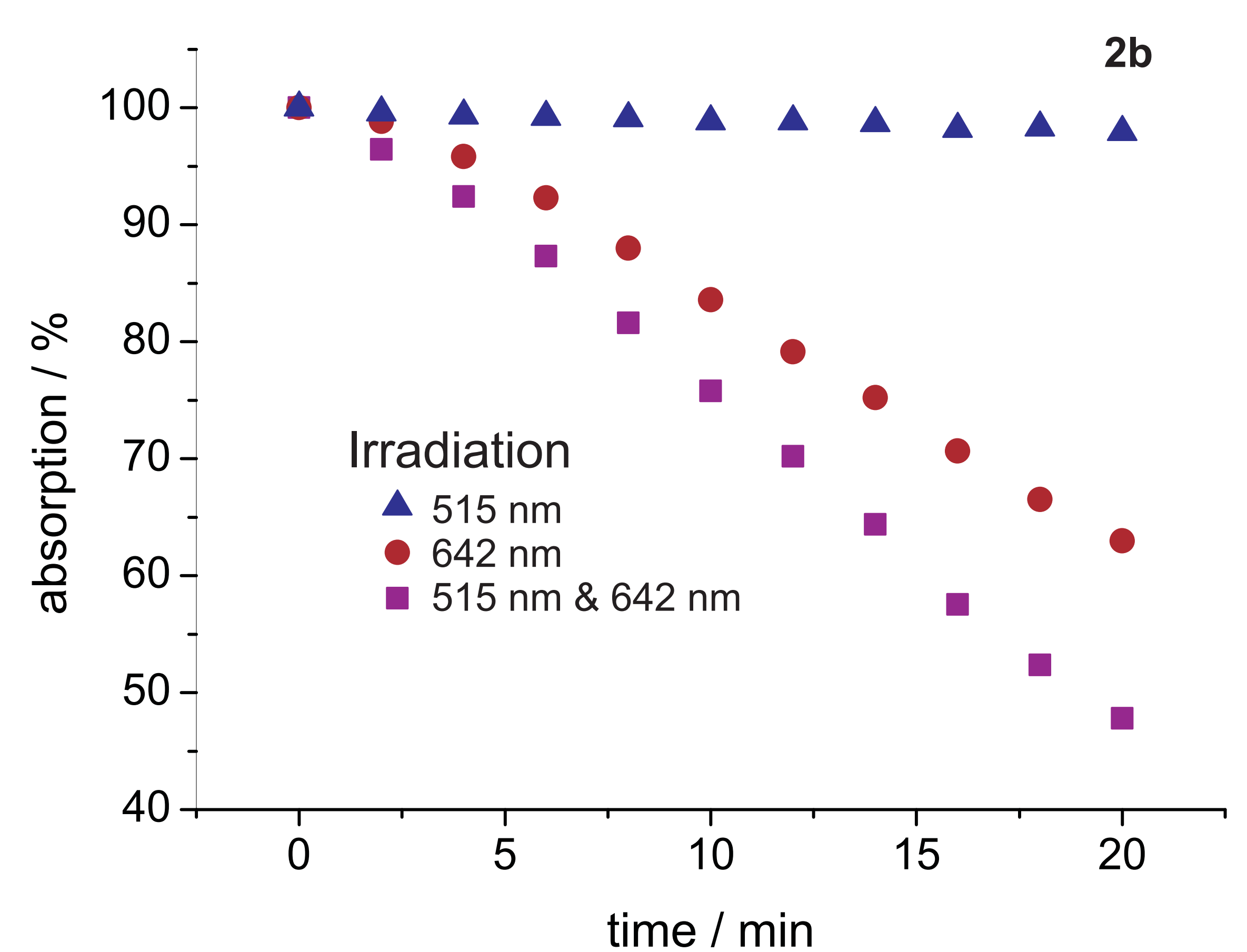
The concentration and ϵ of 1 in the solution are significantly (2-3x) higher than the concentration and ϵ of 2a or 2b respectively to assure a singlet oxygen surplus upon irradiation of 1. Moreover, the irradiation light source for 1 is operated at higher (10x) power with respect to the irradiation light source for 2. To achieve oxygen saturation in the solution, the cuvette is shaken before measurement and before irradiation.

Results



Obviously, both electronic states of the dye contribute to photodegradation upon reaction with singlet oxygen. **2a** is a fluorescent dye ($\tau = 3.98 \text{ ns}$), **2b** phosphoresces ($\tau = 54.1 \mu\text{s}$). The excited state contribution to the photodegradation reaction can only be observed in **2b**.

Therefore, the decisive factor of the dominating electronic state in photodegradation is the luminescence lifetime.



Outlook

The method will be used to characterise several interesting sensor dyes. A method to determine the electronic state of photodegradation reactions with singlet oxygen in sensor films is being developed.

References & Acknowledgements

- ^[1] S.M. Borisov et al., *J. Photochem. a. Photobiol. A*, **2009**, 201, 128-135
^[2] B.M. Weidgans et al., *Analyst* **2004**, 129, 645-650
^[3] J. Brooks et al., *Inorg. Chem.* **2002**, 41, 3055-3066

Acknowledgements to:
Freche Materie