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Supporting Information

for

Catalytic Photooxidation of 4-Methoxybenzyl alcohol with a Flavin Zinc(II) cyclen complex

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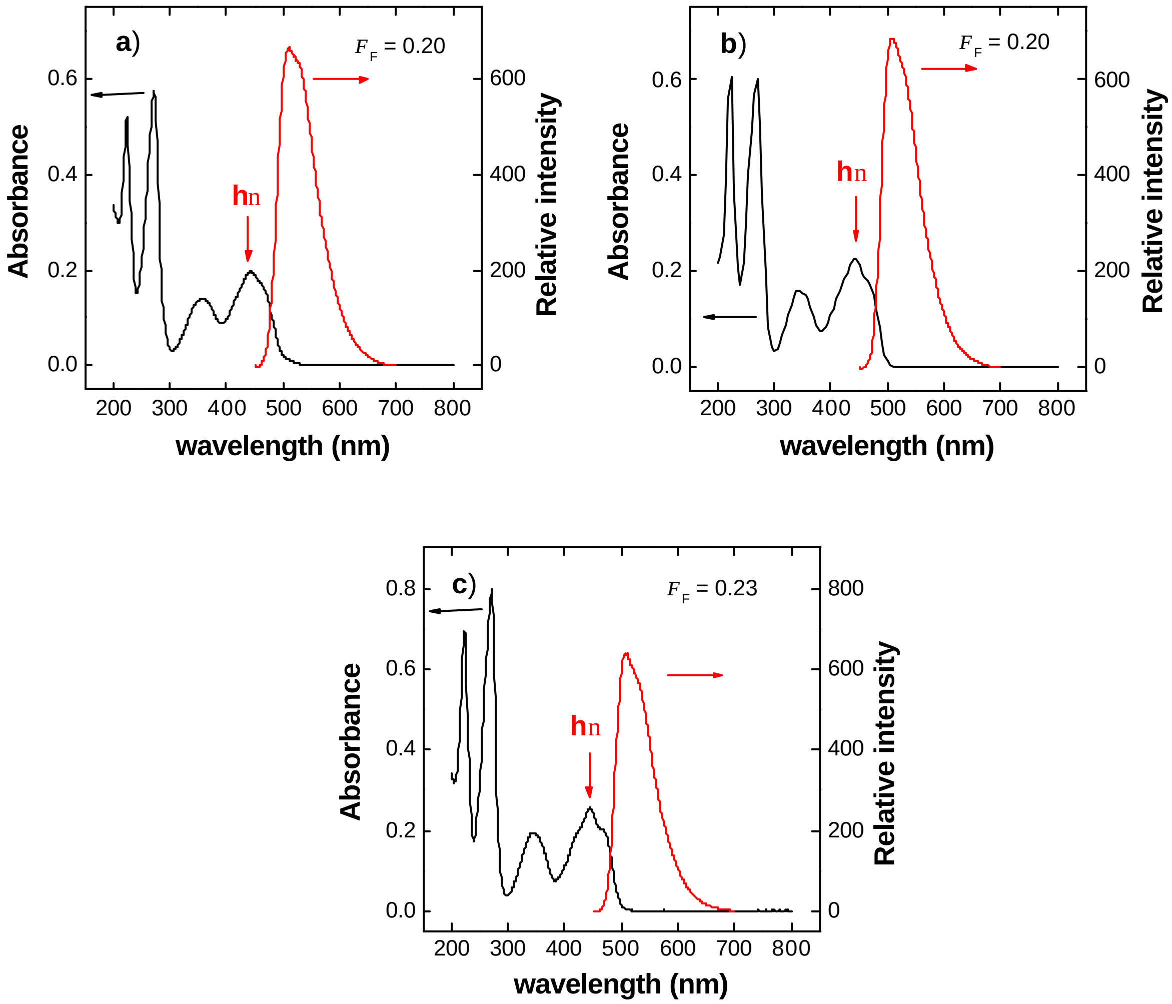
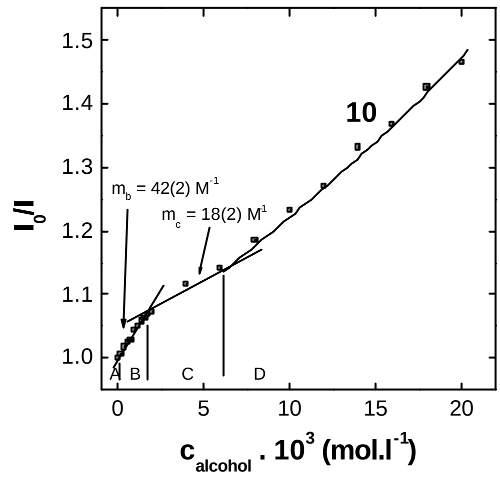
S1. **<u>UV absorption and fluorescence</u>** (λ_{ex} = 444 nm) spectra of **10** (a), **4** (b) and **5** (c) in acetonitrile. (a) c = 2 x 10^{-5} mol L^{-1}; (b) and (c) c = 2 x 10^{-5} mol L^{-1} and c = 1 x 10^{-5} mol L^{-1} for UV and fluorescence measurements, respectively. Fluorescence quantum yields F_F were determined by a standard procedure at c = 5 x 10^{-6} mol L^{-1} using quinine bisulfate in 0.5 M H_2SO_4 as a standard.[1]



[1] D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107 – 1114.

S2. **Stern-Volmer plot** of the emission quenching of **10**, **4** and **5** by 4-methoxybenzyl alcohol (**11-OCH$_3$**) in acetonitrile. Excitation wavelength λ_{ex} = 444 nm; emission wavelength λ_{em} = 510 nm.



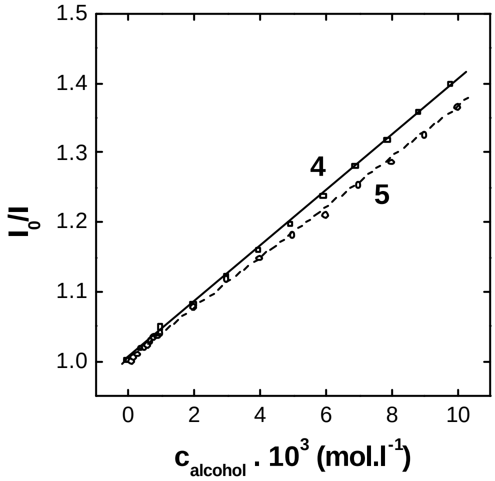
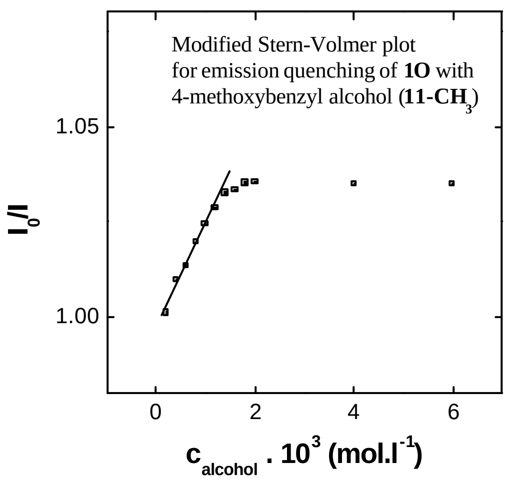


Table of **Stern-Volmer constants K_S** calculated as a slope of the I/I_0 vs concentration of quencher dependence[2] ($I_0/I = 1 + K_S[Q]$). In the case of **10**, slope of linear part B was taken as K_S value.

Flavin	K_S/L mol^{-1}
10	42
4	40
5	36

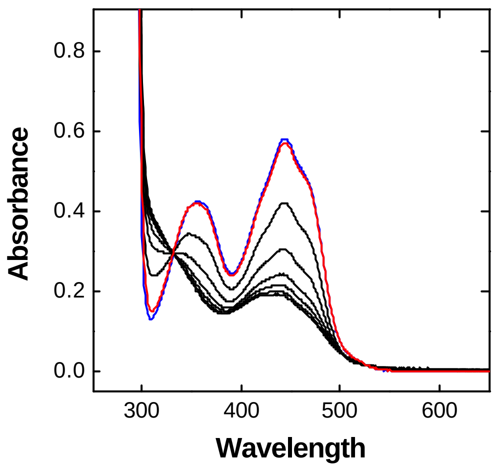
Binding constant K_b between flavin **10** with substrate binding site and 4-methoxybenzyl alcohol (**11-OCH$_3$**) was estimated from the Stern-Volmer plot according to a procedure published by Dürr[3] (see Figure above). Substraction of the slope of section C (m_c) from the slope of the section B (m_b) leads to a modified Stern-Volmer plot with the slope m_b' ($m_b' = m_b - m_c$) including only the effect of "intramolecular" quenching. From these modified Stern-Volmer data, the binding constant K_b = 24(4) L mol^{-1} was calculated as a slope of the dependence ($I_0/I = 1 + K_b[Q]$).



[2] a) N. J. Turro, *Molecular Photochemistry*, W. A. Benjamin, Inc, New York **1967**; p. 94; b) K. K. Rohatgi-Mukherjee, *Fundamentals of Photochemistry*, Wiley Eastern Limited, Bombay **1978**, p. 171 – 175.

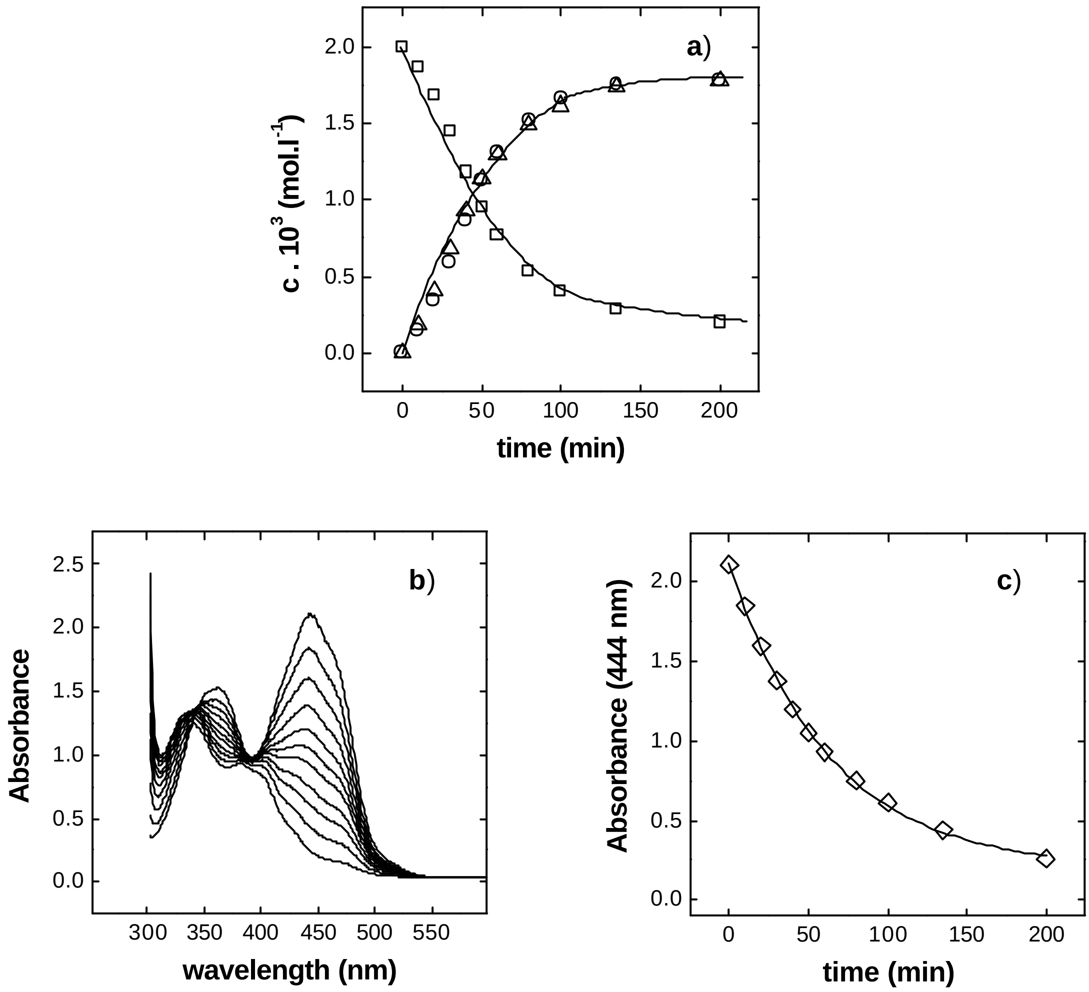
[3] S. Bossmann, M. Seiler, H. Dürr, *J. Phys. Org. Chem.* **1992**, *5*, 63 – 73.

S3. <u>Experiments under argon</u>. Irradiation of acetonitrile solution of 4-methoxybenzyl alcohol (**11-OCH$_3$**, c = 1 x 10^{-1} mol L^{-1}) in the presence of **10** (c = 5 x 10^{-5} mol L^{-1}) under argon atmosphere: The UV spectrum of the reaction mixture before irradiation (blue color), after 30 s, 60 s, 90 s, 120 s, 150 s and 180 s of irradiation with visible light (λ > 420 nm) (black color) and after exposing the mixture to oxygen (red color). At first, flavin oxidizes the alcohol is being reduced, then the reduced flavin is reoxidized by oxygen and hydrogen peroxide was formed (c_{H2O2} = 4.7 x 10^{-5} mol l^{-1}).



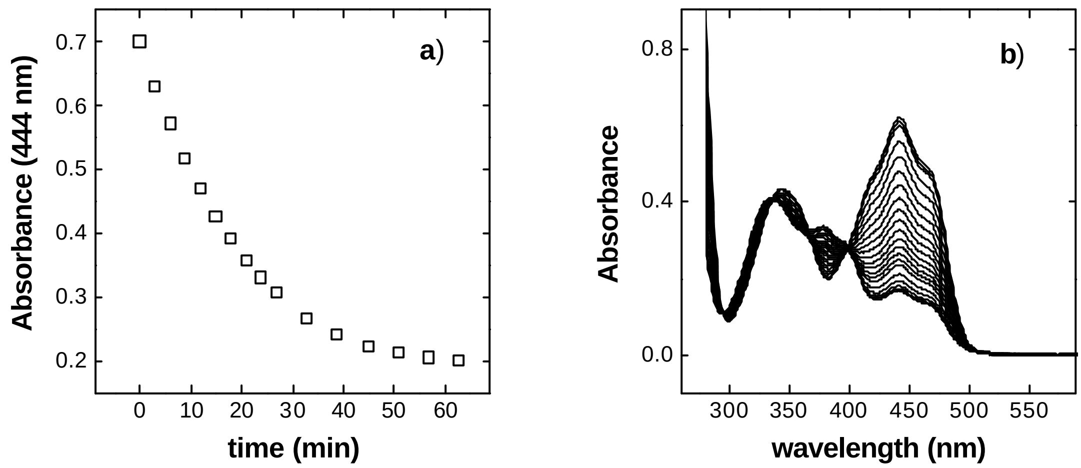
After 60 min irradiation of the solution of 4-methoxybenzyl alcohol (**11-OCH$_3$**, c = 2 x 10^{-3} mol L^{-1}) and **10** (c = 2 x 10^{-4} mol L^{-1}) under argon atmosphere in acetonitrile and in water, the corresponding amount of 4-methoxybenzaldehyde (**12-OCH$_3$**): c = 1.9 x 10^{-4} mol L^{-1} was determined by HPLC.

S4. **Kinetic of the photooxidation of 4-methoxybenzyl alcohol** (**11-OCH$_3$**, *c* = 2 x 10^{-3} mol.L^{-1}) in oxygen saturated acetonitrile in the presence of a catalytic amount of **10** (*c* = 2 x 10^{-4} mol L^{-1}). The concentration of 4-methoxybenzyl alcohol (a,?), 4-methoxybenzaldehyde (a, △) and hydrogen peroxide (a,?), spectra of the reaction mixture (b) and value of flavin absorbance at 444 nm (c).



S5. **<u>Photodecomposition of flavin 4</u>** was monitored in oxygen-saturated acetonitrile solution in the absence of alcohol (see figure below). The rate of decomposition k_{obs} = 0.046 min^{-1} was faster than in the presence of alcohol with k_{obs} = 0.016 min^{-1} (calculated from absorbance *vs* time plot). This indicates that photodecomposition of flavin represents side reactions during photooxidation of alcohols mediated by flavins.
Unfortunately, the analysis of the reaction mixture by NMR and HPLC-MS technique after irradiation of flavin **10** and **4** in acetonitrile revealed a complex mixture of compounds which prevents structure assignment. From aromatic signals in the ^{1}H NMR we could conclude that compounds with and without intact flavin moiety are present in the solution after irradiation. Probably several mechanisms[4] (dealkylation of position 10-, opening of the ring) contribute to the decomposition process.

Absorbance at 444 nm (a) and UV spectra (b) of a flavin **4** solution ($c = 5 \times 10^{-5}$ $mol.l^{-1}$) in acetonitrile during its irradiation with visible light (λ > 420 nm).



[4] P. F. Heelis, The Photochemistry of Flavins *in Chemistry and Biochemistry of Flavoenzymes,* (Franz Müller, Ed.), Vol I, CRC Press, **1991**, p. 172.