Supplementary information for paper

Riboflavin – understanding the dynamics and interactions of the triplet state

Marek Scholz,[a] Jan Moučka,[a] Jakub Pšenčík,[a] Jan Hála[a] and Roman Dědic,[a*]

DF of riboflavin quenched by sodium azide

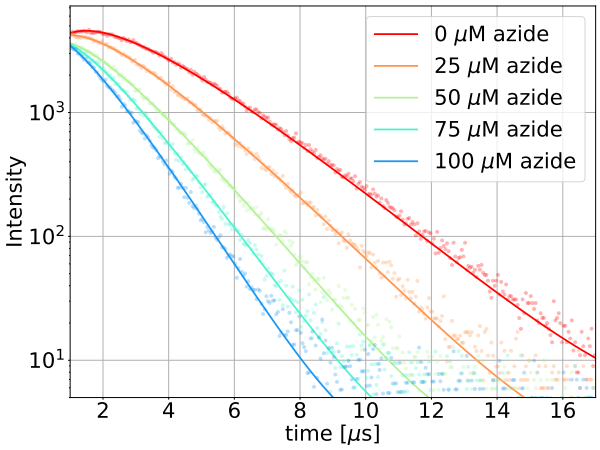

Fig. SI-1 Quenching of DF of riboflavin (50 μM) by sodium azide. The signal was fitted by a SOFDF kinetic model.

DF of riboflavin quenched by sodium azide

azide	$^1O_2$ lum.		DF
c [μM]	τ_Δ [μs]	τ_T [μs]	τ_T [μs]
0	3.7	3.3	3.5
25	3.6	2.6	2.7
50	3.5	2.0	2.1
75	3.3	1.7	1.8
100	3.2	1.4	1.5

Table SI-1 Lifetimes of riboflavin triplet (τ_T) and $^1O_2$ at increasing concentrations of sodium azide. The triplet lifetime was determined either by fitting the $^1O_2$ infrared luminiscence or by fitting the riboflavin's DF decay by a SOFDF kinetic model. The triplets lifetimes obtained from the DF decay are consistent with those from $^1O_2$ luminiscence. This further confirms that SOFDF mechanism is responsible for the formation of delayed fluorescence in our riboflavin samples.

Delayed fluorescence spectrum

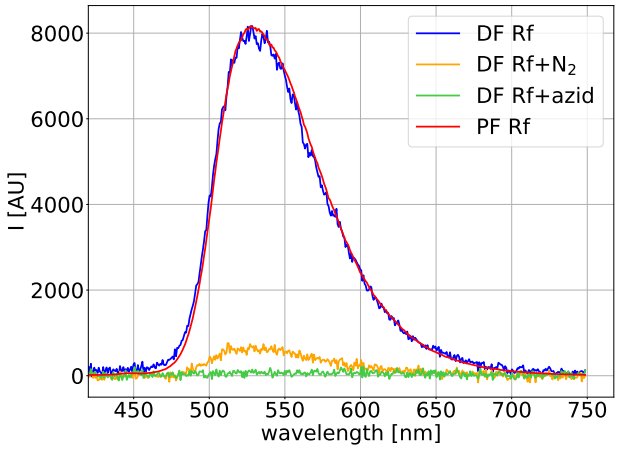

Fig. SI-2 Delayed fluorescence (DF) spectrum compared to prompt fluorescence (PF) spectrum of 50 μM riboflavin detected by setup no. 3. The PF was collected within the first 20 ns after the excitation laser pulse (445 nm), whereas the DF was collected in the 1 μs-5 μs time interval. The spectrum of DF and PF are almost identical. The DF is suppressed in the presence of sodium azide and in a nitrogen-saturated sample, which is consistent with the SOFDF mechanism.

[a] *Charles University, Facaulty of Mathemtics and Physics, Department of Chemical Physics and Optics, Prague, The Czech Republic.*
[*] *Tel. +420 95155 1234; E-mail: Roman.Dedic@matfyz.cuni.cz*

Singlet-singlet vs. triplet-triplet energy transfer

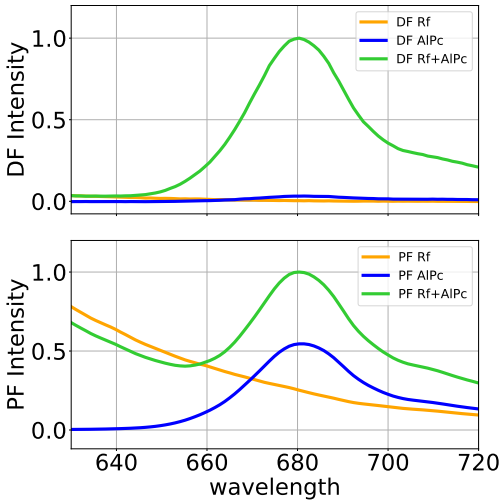

Fig. SI-3 Delayed fluorescence (DF) and prompt fluorescence (PF) of 1) Rf, 2) AlPc, 3) mixture of Rf + AlPc, all at 50 μM. The sample was excited at 445 nm (Rf absorption) and signal was detected in the red region (AlPc fluorescence) using setup no. 2. It can be clearly seen that the DF of AlPc is dramatically enhanced in the presence of riboflavin, whereas the PF of AlPc is enhanced only mildly. This indicates that the energy transfer from ^{3}Rf* to ^{3}AlPc happens on microsecond time-scales that are typical for the triplet-triplet energy transfer. In contrast, a singlet-singlet energy transfer that happens on nanosecond time-scales cannot account for the dramatic enhancement of AlPc DF.

Energy transfer from Rf to 10 μM AlPc

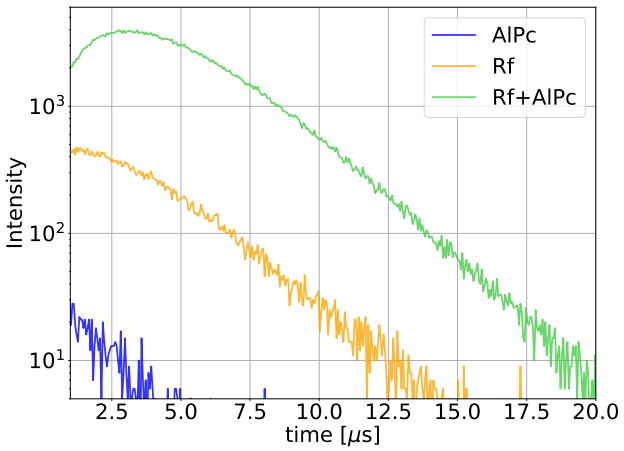

Fig. SI-4 The figure documents that the dramatic enhancement of AlPc delayed fluorescence in presence of riboflavin (50 uM) is clearly visible also at lower AlPc concentrations, here 10 uM. The sample was excited at 445 nm (Rf absorption) and signal was detected around 690 nm (AlPc fluorescence) using setup no. 1.