Monitoring photocatalytic radical formation processes by fluorescence correlation spectroscopy and time-correlated single-photon counting

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Rhodamine dye-based photo-induced redox catalytic processes hold great promise as efficient and cheap alternatives to existing transition metal-based photocatalytic compounds.[1,2,3] Recent examples show that consecutive photo-induced electron transfer processes (conPET) overcome the energetic limit of using the energy of only a single photon in photoredox catalysis, and enable controlled bond activation through light-color regulation of redox potentials.[4,5]

However, it is often not clear which excited states of the photocatalysts are involved in such reactions and how different solvents, reductants, or the environment, e.g. the pH-value, impact the dynamics of these systems. For this reason, we employ fluorescence correlation spectroscopy (FCS) in combination with time-correlated single-photon counting (TCSPC) in order to explore the fundamental details of such photoredox catalytic processes, as well as to characterize the efficiencies of the individual steps which are crucial in those photocatalytic cycles.[6] Here, we focus on the mechanisms that contribute to the photocatalytically driven formation of the radical anion state of rhodamine 6G (Rh-6G).

The combined application of FCS and TCSPC allows us to track the formation of the Rh-6G radical anion state back to the simultaneous depletion of the excited singlet or triplet state. To do this, we characterize in a first step the radical formation process for the two reductants N,N-diisopropylethylamine (DIPEA) and ascorbic acid (AA) in water and dimethyl sulfoxide (DMSO). In a second step, we control the pH value in aqueous reaction solutions and monitor the radical formation process of Rh-6G at different pH values.

Figure 1a illustrates the underlying mechanisms in a Jablonski diagram, depicting the states and transitions involved. By monitoring the blinking behavior of diffusing molecules in confocal fluorescence microscopy (Fig. 1b), we are able to draw conclusions on the population and the transitions between the respective states. The following parameters are extracted in a single experiment: (i) pulsed excitation enables measurement of the photoluminescence (PL) lifetime, τ_{PL}, of the first excited state, S_1; (ii) fitting the FCS-curve gives the average time the molecule spends in the singlet manifold, τ_{on}, as well as (iii) the average time the molecule resides in a dark-state, τ_{off}. This dark state may be a triplet state, T_1, or a radical state. Under ambient conditions, the triplet and the radical state can be easily distinguished by their different lifetimes.

With this approach, we observe the formation of photocatalytically formed radical states by simultaneously employing FCS and TCSPC. Different excited states, i.e. molecular singlets

and triplets, play a dominant role in populating the radical states, depending on the reductant used and the environment. As an example of environmental change, the pH value has a negative impact on the photophysical properties in strongly basic regimes, resulting in a shortening of τ_{PL}, but shows a beneficial effect on the radical anion accumulation in the acidic regime, when AA is added as the reductant. Finally, we outline the possibility to investigate the complete conPET process by additionally exciting the radical anion state and utilizing the techniques presented here.
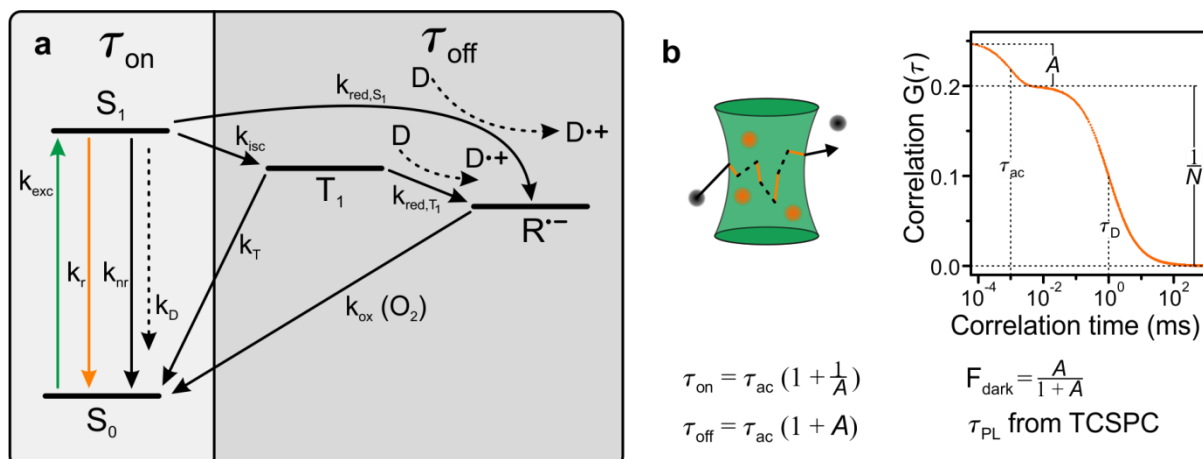

Figure 1. (a) Jablonski diagram representing the states and transitions in a photoredox cycle (S_0: singlet ground state, S_1: singlet excited state, T_1: triplet ground state, R•− : radical anion state, D: electron donor, D•+: oxidized electron donor, k_{exc}: excitation rate, k_r radiative decay rate, k_{nr}: non-radiative decay rate, k_D: additional non-radiative decay rate at high electron donor concentrations, k_{isc}: intersystem crossing rate, k_T: triplet depletion rate, $k_{red,S1}$: reduction rate from singlet to radical anion, $k_{red,T1}$: reduction rate from triplet to radical anion, $k_{ox}(O_2)$: oxygen-induced back-oxidation rate from radical anion to singlet ground state) (b) Schematic depiction of fluorescence correlation spectroscopy (FCS). From the correlation data, the on-time, τ_{on}, the off-time, τ_{off}, and the dark-state fraction, F_{dark}, are extracted. The photoluminescence lifetime, τ_{PL}, is measured by pulsed excitation and time-correlated single-photon counting (TCSPC)

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