

Time Scales for Electron Transfer Reactions of J-Aggregates at AgBr Surfaces

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The experimental conditions have been found which allow the determination of picosecond time-resolved fluorescence lifetimes from J-aggregates of cyanine dyes adsorbed on the surface of octahedral AgBr grains. Lifetimes were determined for J-aggregated cyanine dyes and compared with monomeric cyanine dyes. Electron transfer rate constants were extracted from these decay transients and were analyzed in terms of the appropriate models for electron transfer in heterogeneous systems.

For the study of the fluorescence lifetimes of monomeric cyanine dyes, it was found necessary to reduce the surface coverage of the AgBr to less than .001 and to employ a photon flux of less than $5 \times 10^{13}/\text{cm}^2\text{s}$. Each sample area was exposed to less than 3 s of illumination before translation of the laser beam to a new area.

For the aggregated dyes, a practical surface coverage for the dye of 30-40% was employed with a photon flux of $1.5 \times 10^{13}/\text{cm}^2\text{s}$. Only a few seconds of exposure were allowed for each area sampled.²

The two best examples of these studies featured the monomeric dye 3,3' diethylthiarcyanine iodide (**M**) and the K^+ salt of the J-aggregating dye 9-ethyl, 5,5' dimethyl, 3,3'disulfopropylthiarcyanine (**J**). These were found to exhibit kinetic behavior that was distinctly different. At the low concentrations used for **M**, the results were found to be the same for both iodide and paratoluenesulfonate counterions.

Below 100 K, the fluorescence lifetime of **M** was found to be a constant 550 ps, and the dye appeared to suffer no photodegradation.¹ As the temperature of the sample was increased to 300 K the lifetime shortened to 55 ps. With the assumption that the 550 ps lifetime represents the decay parameters not related to electron transfer, an activation energy of 90 meV can be extracted for electron transfer to the AgBr. The pre-exponential factor of this Arrhenius analysis was found to be $3 \times 10^{11} \text{ s}^{-1}$. One can analyze the electron transfer in terms of multiple acceptor levels³ at the surface and extract the electronic coupling constant of 26 cm^{-1} , a reorganization energy of .250 meV, and an energy level

difference of 65 meV for the electron transfer from the donor excited state to the lowest level of the AgBr conduction band. These results imply that the thermodynamic oxidation potential of the dye has shifted by less than 50 meV through adsorption on the AgBr surface site of this study.

For **J**, the electron transfer reaction did not shut down until the sensitized AgBr sample was cooled to below 40 K.¹ At liquid helium temperatures, it was possible to examine the spectral characteristics of the system at leisure as there appeared to be no deleterious photoreactions below this temperature. For analysis of the electron transfer characteristics of this system, the baseline for extraction of fluorescence lifetimes at elevated temperatures was taken to be the time resolved fluorescence of an overexposed spot on the sensitized AgBr sample. An Arrhenius plot of the temperature dependence of this difference yielded an activation energy of less than 30 meV, but the same pre-exponential factor as **M**, $3 \times 10^{11} \text{ s}^{-1}$.

In a manner similar the analysis for **M** for multiple acceptor states, the fluorescence data for **J** yielded an electron transfer integral of 5 cm^{-1} , a reorganization energy of 20 meV, and an energy of 20 meV for the uphill energy difference between the excited state and the acceptor level in the AgBr. This implies that the shift in oxidation potential of the dye in going from solution to adsorbed aggregate is about -200 meV.

The linewidth of the J-aggregate emission was found to be smaller than 3.5 nm and shifted to the blue by several nanometers as the dye on the surface was photo-oxidized. Evidently, energy transfer to the furthest red-shifted aggregate of the dye occurred prior to the electron transfer step with the smaller aggregates having a smaller rate constant for electron transfer.

The difference in reorganization energies for **M** and **J** lead to different predictions for the form of the energetic threshold for spectral sensitization of AgBr by cyanine dyes.⁴ With small reorganization energies of 20 meV for J-aggregates, a sharp threshold is expected for the sensitization yield of the dye as a function of the energy level of the

excited state. This is in line with observations on the relative quantum yield Φ_{rel} for latent image formation in silver halides where a steep rise in Φ_{rel} from .1 to 1.0 occurs within 100 meV.⁵ In contrast, the slower kinetics of the electron transfer from the monomer dye to AgBr and its larger, 250 meV reorganization energy should result in a 0.1-to-1.0 threshold which is several hundred meV broad.

References

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