

Enhanced Charge Separation from Mixed J-Aggregate Excitons in Supersensitizing Dye Combinations: Photoelectrochemical and Fluorescence Studies

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Abstract

A specific type of supersensitizing dye combination, comprising both spectrally and structurally analogous anionic cyanine dyes but with considerably different oxidation potentials, gives rise to a unique mixed J-aggregate in which the excited state (molecular exciton) is shared by the two kinds cyanine dyes. Such unique mixed J-aggregates can be prepared either in a well-ordered 2D format on Au(111) (as metal electrode) with an intermediate aminoalkanethiolate spacer, or in some 3D format in aqueous solution containing excess inorganic salt. In this paper, a highly enhanced intra-aggregate charge separation from these mixed J-aggregate excitons is highlighted with high-efficiency photocurrent generation at the J-aggregate-coated Au electrode in a redox solution (photoelectrochemical study) along with a mixing-induced strong fluorescence quenching for the aqueous solution samples (fluorescence study).

Introduction

The spectral sensitivity of a dye in photographic emulsion is sometimes super-additively increased on addition of a second substance or dye. This technologically important phenomenon is known as supersensitization, which has been the focus of numerous studies in the past for better understanding and controlling spectral sensitization of silver halides.¹ The supersensitization mechanism depends on specific sensitizer-supersensitizer combinations, and in some cases more than two effects may simultaneously operate. In many cases of supersensitization by dyes, however, the effect seems to have been understood well either by exciton trapping or hole trapping model.¹

Some super-additive effects of dye mixing, closely related to the supersensitization, could also be found in whatever other processes involving photo-excited dyes. The corresponding experimental information can be of significant use to back illuminate some important aspects of supersensitization from a different angle. A particularly interesting example is the photocurrent generation with a J-

aggregate-coated model electrode (see Fig.1 for its structure) in a redox solution, where the electron transfer from the photoexcited J-aggregates to the redox species in solution plays the decisive role.

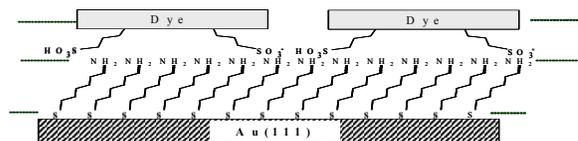


Fig. 1 Structure of J-aggregate-coated Au electrode with intermediate molecular spacer of aminoalkanethiolate

In this paper, a super-additive dye mixing effect in such photoelectrochemical J-aggregate systems is highlighted for special dye combinations that allow the excited state (exciton) to be delocalized over both kinds of dye units. Occurrence of this 'shared excitonic' state can be easily noticed in the absorption spectra, as it produces a singly-peaked sharp J-band in between the two individual J-bands. This strongly contrasts with the more general effect of dye mixing, causing both of the two separate J-bands to be significantly broadened and blue shifted (never merged into a single J-band).

Obviously, for this shared excitonic state to be predominant, the two dyes mixed with each other must have analogous molecular structures so as to co-aggregate well in some common J-aggregate framework. They also have to have similar monomer transition energies (HOMO-LUMO energy gap) for efficient delocalization of the shared excitonic state. There is no such restrictions for the individual HOMO (or LUMO) levels, however; a significant HOMO-HOMO (or LUMO-LUMO) energy gap between the two dyes rather playing an essential role for the super-additive effect. The dyes we specifically studied in this work are shown in Fig.2, where any of the four combinations indicated by straight line connections is effective.

An important point relating to the supersensitization mechanisms is that exciton trapping should have minor

relevance for the super-additive effect involving such a strongly shared excitonic state. The hole trapping mechanism may be partly relevant, but not yet representative enough, because the super-additive effect here is mutual, both dyes acting as an effective enhancer for the other. The effect in the present case, therefore, is best described in terms of 'enhanced intra-aggregate charge separation' from the shared excitonic state.

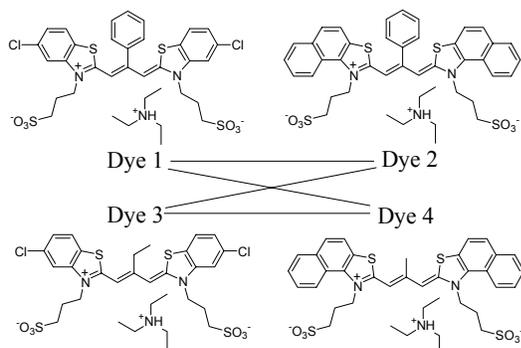


Fig.2 combinations of dyes that produce super-additive effect.

The formation of such long-lived intermediate charge separated state is especially vital in the present case for two reasons. First, the rate of electron transfer from the J-aggregate to the redox species in solution is expected to be much smaller than that into the solid conduction band in the normal spectral sensitizing situation. Secondly, the J-aggregate is separated from the Au electrode surface only by 15 to 20 Å at most by the aminoalkanethiolate spacer (see Fig.1), which is approximately the maximum allowed spacing for effective electron tunneling between the Au electrode and the J-aggregate (this is necessary to sustain steady photocurrent). In this condition, however, the excited energy of the J-aggregate inevitably undergoes so rapid energy transfer to the Au electrode that the dye fluorescence signal is almost totally quenched. Then, the almost only possible way to cause substantial electron transfer from the photoexcited J-aggregate to the redox species in solution is through the formation of long-lived charge-separated states with a rate constant comparable to that of dye-to-metal energy transfer.

It should be also noted that although the intra-aggregate charge separation from the excited state contributes as an additional channel of fluorescence quenching, the extent of this contribution can not be inferred with the J-aggregate-coated electrode sample. This is because just dye-to-metal energy transfer alone already causes almost total fluorescence quenching as noted above. As samples for a complementary fluorescence study, therefore, we have chosen a series of mixed J-aggregates prepared in aqueous solution in the presence of excess NaCl. We verify that the enhanced intra-aggregate charge separation in this system indeed results in strong fluorescence quenching. A comparison of the corresponding fluorescence quantum

yields between the single-component and mixed J-aggregates then gives useful semi-quantitative information about the enhanced rate of intra-aggregate charge separation from the shared excitonic state.

Experimental

The ~200 nm thick Au(111) electrode was prepared by the DC Ar⁺ ion sputtering method² on freshly cleaved natural mica. It was immersed in 0.1 mM ethanolic solution of a series of aminoalkanethiols (in the form of hydrochloride salts) with different alkyl chain lengths (C₂, C₆, and C₁₁) at room temperature for ~5min to obtain a densely amino-functionalized Au(111) surface. Subsequent coadsorption of selected two kinds of dyes (see Fig.2) from typically 0.1 mM mixed dye solution in 1:1 water/ethanol solvent led to the formation of well-mixed 2D J-aggregates electrostatically bound to the amino-functionalized Au(111) surface (see Fig.1).³

The photoelectrochemical study (photocurrent measurement) was done in a potentiostat mode by using a three electrode cell with a malonate (0.7-1.5 M disodium malonate) buffered Fe²⁺/Fe³⁺ redox solution (0.2-0.4 M mixture of FeSO₄ and Fe₂(SO₄)₃). The corresponding redox potential was typically set at 0.37 V vs. Ag|AgCl. The total energy of the monochromatic irradiation used for the photocurrent generation was typically 1.2 mW, which was focused onto an area of ~0.07 cm² near the center of the J-aggregate-coated electrode.

The fluorescence measurement was done by using a home-built system for dilute aqueous J-aggregate solution containing 1.5 M NaCl (filled in a quartz cell with 1mm light path length). A dilute ethanolic solution of R6G was used as the reference for estimating the fluorescence quantum efficiency.

Results and Discussion

Of the four possible combinations shown in Fig.2, we focus here and below on the mixture of Dye 1 and Dye 2, because these dyes were found to exhibit most preferential J-aggregation with minor residual monomer absorption in aqueous NaCl solution used for the complementary fluorescence study.

Figure 3 shows a series of reflectance spectra taken for the J-aggregate-coated Au electrode with various Dye1/Dye2 mixing ratios. The light absorption by the J-aggregates appears as a dipped form of J-band (reduced reflectance) in these spectra. The position of the J-band systematically changed according to the mixing ratio in between the two single-component J-bands on the far left and right. This is what one expects for mixed J-aggregates that are characterized by the shared excitonic state.

In the malonate-buffered Fe²⁺/Fe³⁺ redox solution with the given typical concentration, ~1mW monochromatic

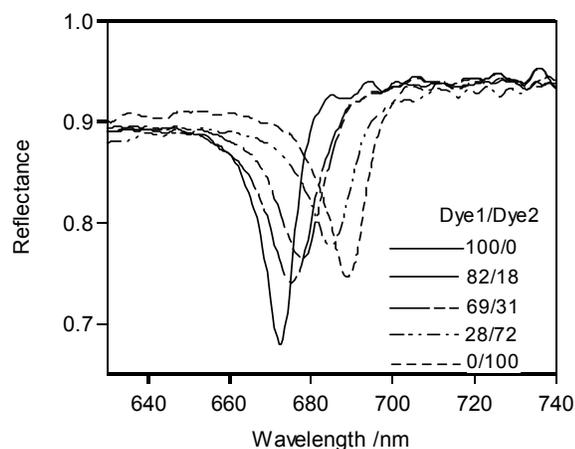


Fig.3 Reflectance spectra taken for J-aggregate-coated Au electrode with various Dye1/Dye2 mixing ratio.

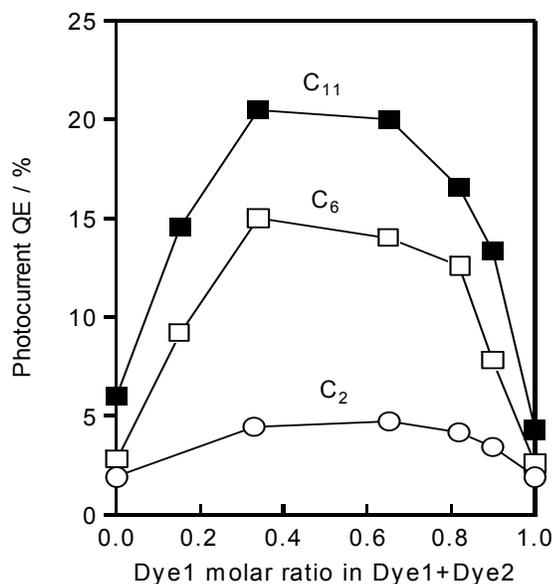


Fig.4 Photocurrent quantum efficiencies as functions of Dye1 molar ratio in the mixed J-aggregate, for three different series of samples with varied spacer chain lengths.

irradiation of the J-aggregate-coated Au electrode produced a cathodic photocurrent of the order of 1 to 10 μ A depending on the dye mixing ratio and on the chain length of the intermediate aminoalkanethiolate spacer. Figure 4 shows the corresponding photocurrent quantum yield (QE) plotted as a function of dye mixing ratio for three different series of samples with C₂, C₆, and C₁₁ spacers. The large increase of QE as a whole with increased length of alkyl chain spacer immediately testifies to the large effect of dye-to-metal energy transfer that becomes increasingly more serious as the spacer thickness decreases. The dependence on the dye mixing ratio is analogous at every spacer thickness, producing a broad but prominent maximum in the intermediate mixing ratios with 4–5 times enhancement

in photocurrent QE as compared to the single-component J-aggregates. This confirms a remarkable enhancement in the intra-aggregate charge separation from the shared excitonic state.

It should be noted here that even in the case of C₁₁ spacer, the fluorescence signal measured for the J-aggregate-coated electrode was almost totally quenched. This means that the dye-to-metal energy transfer is still very rapid, possibly with a picosecond time scale (see below). The maximum photocurrent QE of ~20 % obtained in this situation is quite remarkable. This is impossible without a highly efficient intra-aggregate charge separation in the mixed J-aggregate.

As shown in Fig.5, the mixed J-aggregate produced in aqueous solution also exhibits a singly-peaked J-band in the intermediate position between the single-component J-aggregates. Although the exact aggregate structure in solution is not very straightforward, the results indicate that a shared excitonic state similar to that in the electrode sample can be produced in aqueous solution as well.

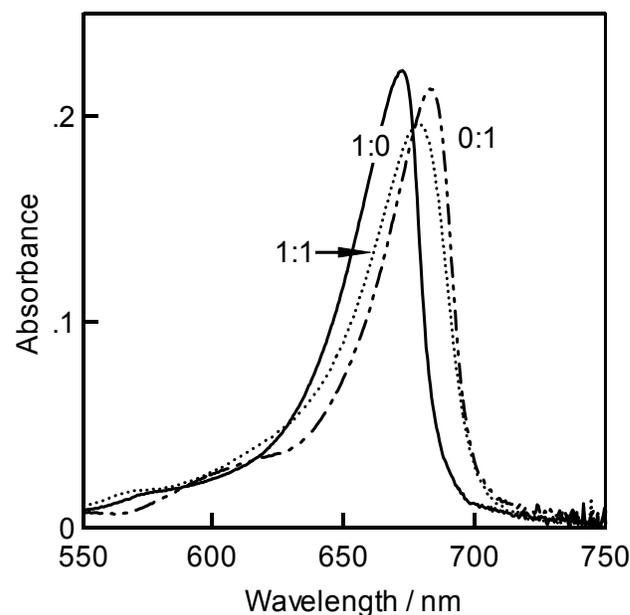


Fig.5 Absorption spectra taken for Dye1/Dye2 single-component and mixed J-aggregates prepared in aqueous solution of 1.5 M NaCl.

We then measured the fluorescence signals from a series of mixed J-aggregates in solution, with an R6G dye solution as a reference for determination of the fluorescence QE. The fluorescence spectra taken for various mixing ratios are presented in Fig. 6. The single-component J-aggregate of Dye 1 gave the strongest fluorescence, and that of Dye 2 easily measurable moderate signal. In the case of mixed J-aggregates, however, the fluorescence signal was strongly quenched as expected, even by minor mixing of Dye 2 (~10 %) with Dye 1.

The estimated fluorescence QE for the single-component Dye 1 J-aggregate in solution was ~5%. Fig.6 shows that the fluorescence QE of the mixed J-aggregate

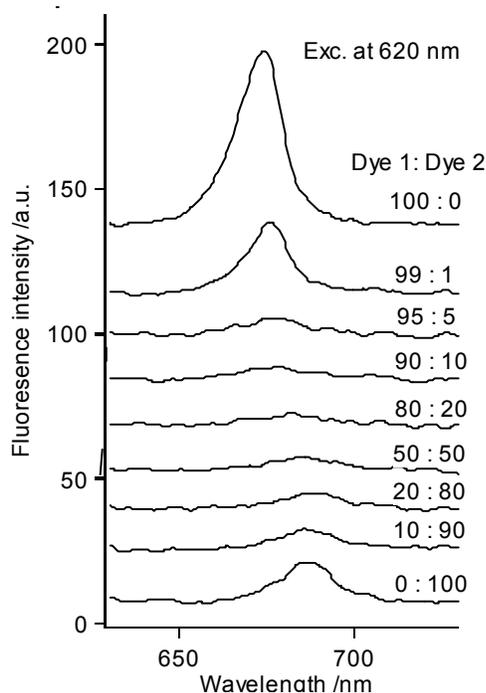


Fig.6 Series of fluorescence spectra taken for mixed Dye1/Dye2 J-aggregates in solution.

drops by factor of ~ 20 to $\sim 0.25\%$. These values can then be used to infer a crude time scale of the enhanced intra-aggregate charge separation. Specifically, the radiative lifetime of Dye 1 J-aggregate is expected to be of the order of 1 ns. The $\sim 5\%$ fluorescence QE then points to a non-radiative decay time constant of ~ 50 ps. Under the assumption that the enhanced intra-aggregate charge separation introduces an additional nonradiative channel, its time constant that fits the $\sim 0.25\%$ QE should be less than 3 ps. Though crude, this rationalizes the large photocurrent QE achieved with the J-aggregate-coated Au electrode in competition with the rapid dye-to-metal energy transfer.

Figure 7 shows a schematic energy level diagram for the intra-aggregate charge separation in the Dye1/Dye2 mixed J-aggregate. In the initial excited state, the exciton is shared by Dye 1 and Dye 2 [denoted by (Dye1/Dye2)*]. This state undergoes a rapid transition into the charge-separated state, where the electron and hole are localized at Dye 1 and Dye 2 sites, respectively. Occurrence of this charge separated state is consistent with the relative positions of the HOMO and LUMO levels of the two dyes.⁴

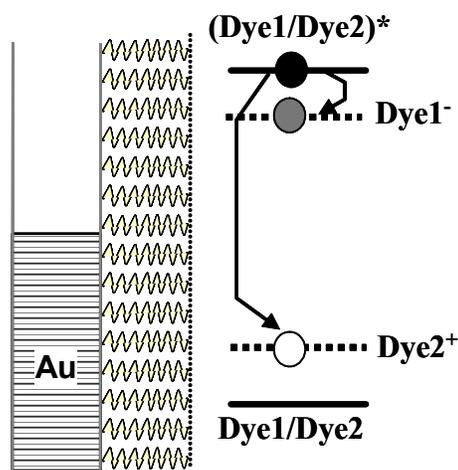


Fig.7 Energy level diagram for intra-aggregate charge separation from shared excitonic state of the mixed J-aggregate.

Conclusion

In summary, mixed J-aggregates comprising structurally and spectrally analogous cyanine dyes are distinguished by the formation of shared molecular excitonic state that gives rise to a singly-peaked J-band in between the single-component J-bands. With a certain HOMO-HOMO (or LUMO-LUMO) gap between the two dyes, this shared excitonic state can undergo a vary rapid intra-aggregate charge separation with a time constant of several ps, thereby producing a highly efficient photocurrent generation in a redox solution.

References

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