

The Effects of Aggregation on the Redox Levels of Cyanine Dyes

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Abstract

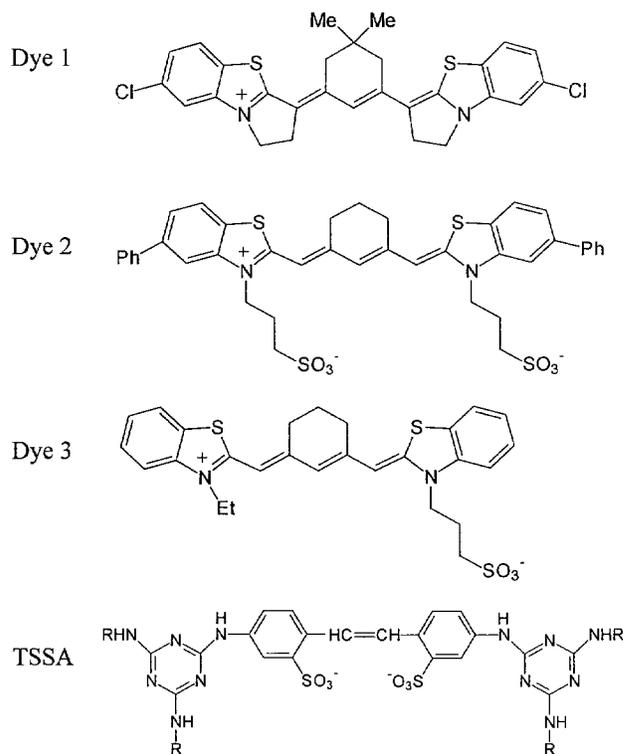
The effects of aggregation on the redox thermodynamics for a series of cyanine dyes are investigated. The adsorption of the dyes on a cubic silver bromide emulsion can be controlled to selectively yield the monomer or the J-, H-, or an H-herringbone aggregate. The adsorbed monomer and aggregate dyes can be reversibly oxidized with metalcyanide redox buffer solutions. The oxidation potential of the adsorbed dye is obtained from a Nernstian plot of redox-solution potential E vs $\log [\text{oxidized dye}]/[\text{dye}]$. The results indicate that the one-electron oxidation potential of the monomer to be lower than that of the aggregate by ca. 70 mV. The energies of the singlet excited-states of the various dye aggregates vary by 0.6 eV.

Introduction

The aggregation of a dye at the silver halide grain surface can dramatically affect the energetics and spectroscopy of the dye relative to its monomeric form.¹ The extent to which aggregation affects the redox thermodynamics of a cyanine dye can now be measured using a redox-titration technique.² In this paper the effects of aggregation on dye redox potential are examined for a family of thiadicarbocyanine dyes that form J-, H-, or herringbone aggregates when adsorbed to cubic silver bromide emulsion grains.

Experimental

The emulsion used consisted of 0.16 μm cubic AgBr crystals. The structures of the thiadicarbocyanine dyes 1-3 are shown below. To adsorb the dyes in the monomeric state the emulsion was pretreated with a triazinylstilbenesulfonic acid (TSSA) at a level (4.7×10^{-4} mol TSSA/mol Ag) that corresponds to ca. 80% of the saturation coverage for this AgBr emulsion. Dye was subsequently added to the treated emulsion at 40°C from a methanol solution at a concentration (ca. 2.0×10^{-4} mol dye/mol Ag) corresponding to a maximum surface coverage of ca. 15% of full monolayer coverage. Preferential dye adsorption in the aggregated state was achieved by addition of dye to the emulsion, with no TSSA, at 70°C. The dye-sensitized emulsions were equilibrated for 20 min at the temperature of dye addition and subsequently diluted with additional gelatin



solution. A gelatin hardening agent was added, and the emulsion was coated onto a transparent film base and dried.

Redox-mediator solutions were prepared in 0.02 M H_3PO_4 using various ratios $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}/\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ or $\text{Mo}^{\text{IV}}(\text{CN})_8^{4-}/\text{Mo}^{\text{V}}(\text{CN})_8^{3-}$. Iron cyanide solutions of varying potential E_{soln} were made by mixing equimolar solutions of ferri- and ferrocyanide prepared from their respective potassium salts. Solutions of molybdicyanide were prepared by electrolysis of molybdicyanide at a Pt gauze electrode by controlled potential coulometry. A constant total concentration of metal complex of 5 mM was maintained in all experiments. Potentiometric measurements of redox mediator solutions were made with the PAR Model 273 potentiostat and a glassy carbon disk electrode. Potentials E_{soln} could be varied between 0.25 V and 0.68 V, and were measured at $22 \pm 1^\circ\text{C}$ versus a KCl-saturated Ag/AgCl reference electrode.

Diffuse reflectance spectra were obtained using a Varian 2400 UV-vis-near-IR spectrophotometer fitted with a 4.5" dia. Halon coated integrating sphere. Film samples were equilibrated for 0.5 min in a stirred solution of the metal complex, and attached to the integrating sphere using a

0.25" thick disk of polished BaSO₄. Linear calibration curves (dye concentration vs 1/reflectance) were used to obtain surface concentration of dye or radical from the spectra.

Results and Discussion

Figure 1 shows the diffuse-reflectance spectra recorded coatings of a cubic AgBr emulsion that contains submonolayer amounts of adsorbed sensitizing dyes 1-3. The spectra indicate the formation of the J-aggregate, H-aggregate and herringbone-aggregate for dyes 1, 2, and 3, respectively. The J-aggregate band (842 nm) for dye 1 is narrowed and shifted bathochromically from the spectral band of dye 1 monomer (722 nm). The spectrum is consistent with a J-aggregate that is composed of planar, parallel dye molecules stacked plane-to-plane and end-to-end in a brickstone arrangement.³ Dye 2 absorbs as an H-aggregate (612 nm) that is blue-shifted from the monomer band (708 nm) and is consistent with the arrangement of the dye molecules in columns. The double-banded spectrum observed for dye 3 is a signature of a herringbone-like structure, i.e., a tilted columnar stacking of dye molecules with adjacent columns aligning at an oblique angle.⁴ The herringbone arrangement results in a two-stage exciton splitting; interactions within the one-dimensional H-aggregate column giving rise to an overall blue shift with respect to the monomer band, followed by a further split due to interactions between adjacent columns, resulting in a blue shift and red shift with respect to the H-aggregate band of each row. As a result, two blue-shifted bands are allowed in the system.⁵ The individual molecules in each aggregate type are adsorbed to the AgBr surface along their long molecular edges.

These cyanine dyes can also be adsorbed to the AgBr emulsion grains in a flat-on mode as monomers by the co-adsorption of the stilbene spacer molecule TSSA. The peak position of the respective monomer bands are indicated by the arrows (M) in Figure 1. The differences in the aggregation properties for this family of dyes are in contrast to the similarities in their solution properties. In acetonitrile solution, dyes 1-3 monomers exhibit similar oxidation potentials (0.50-0.55 V) and absorption wavelengths (648-671 nm).

The partial oxidation of the adsorbed dyes can be accomplished by treatment of the coatings with a redox solution of Fe^{III}(CN)₆⁻³ or Mo^V(CN)₈⁻³. Spectra recorded (Figure 2) after treatment with redox solution show a diminution of the spectral band of the dye and the appearance of a new band corresponding to a stable, mono-oxidized dye radical ion. For the J-aggregated dye the reflectance band for the dye shifts in the direction of the monomer band and becomes significantly broadened with increasing fractional degree of oxidation. The new band for the oxidized J-aggregate exhibits an unusually low extinction and is similar in wavelength (533 nm) to that for the oxidized dye monomer (553 nm). These data suggest oxidized sites in the J-aggregate have a monomer-like character, and as such appear to be localized on the spectroscopic time scale.

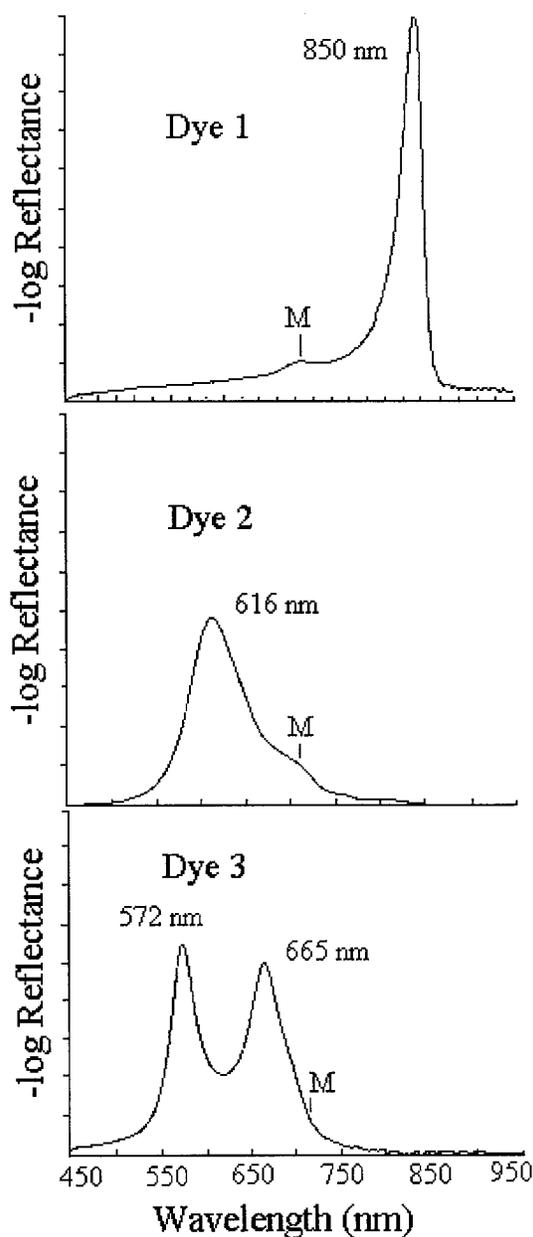


Figure 1: Reflectance spectra for emulsion coatings containing dyes 1-3.

Because the oxidized sites are localized, their formation leads to a dilution or a "partitioning" of the aggregate into smaller segments. This dilution effect results in the shifting and broadening of the aggregate spectrum. The band-broadening and wavelength shift that accompany the chemical oxidation of the J-aggregate are very similar to those obtained in experiments where the average physical size of a J-aggregate is varied in a statistical sense by dilution with a second dye chromophore.⁶ We propose that for the J-aggregate of dye 1, the formation of radical dications serves to partition the aggregate into smaller segments.² Thus the wavelength shift in Figure 2 is related to the fractional degree of oxidation.

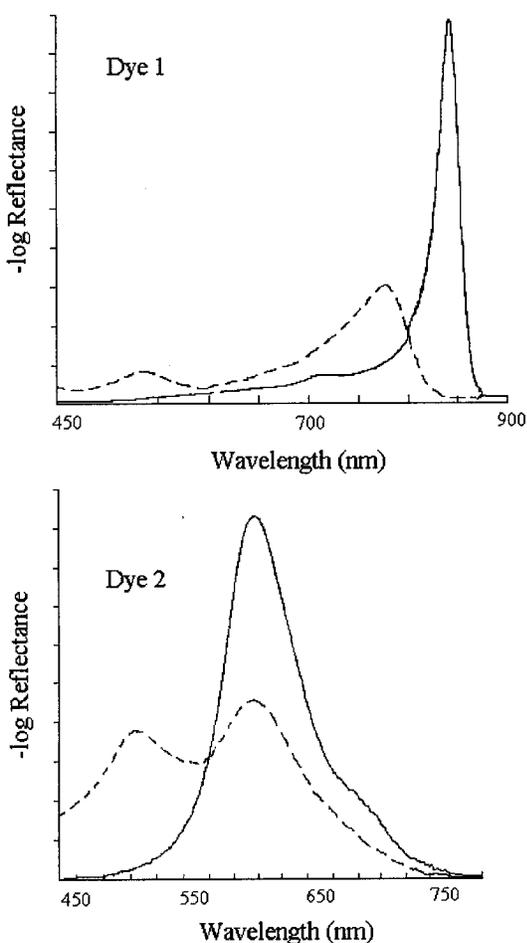


Figure 2: Reflectance spectra for coatings before (solid) and after (dashed) treatment with redox buffer solution.

In contrast, no shift in the dye band (614 nm) occurs during the oxidation of the H-aggregate. The spectral band for the oxidized H-aggregate (514 nm) is intense and spectrally distinct from that observed for the corresponding oxidized dye monomer (563 nm). These observations are consistent with delocalization of the oxidized site (i.e., dye-hole) within the H-aggregate column. Similar experiments conducted with AgBr films containing dye 3 show that the double-banded spectrum of the herringbone aggregate collapses into a single band during oxidation. The position of the single band (615 nm) is nearly identical to that of the (unoxidized) columnar aggregate of dye 2, indicating that the column-column interactions are minimized during the oxidation of the herringbone aggregate. The spectrum of the oxidized herringbone aggregate shows a new band (500 nm) which is similar to that observed for oxidized dye 2.

The oxidation reactions for each monomer and aggregate dye are fully reversible. The adsorbed, oxidized dyes can be quantitatively reduced by treatment of the AgBr film samples with an ascorbic acid solution. The fact that reflectance spectra taken before and after a redox cycling experiment are

identical indicates that the molecular packing in the aggregate is not disrupted during oxidation. For each dye 1-3 the fraction of dye oxidized can be accurately varied by simple adjustment of the electrochemical potential of the redox solution. Given the assumption that the equilibrium state of each AgBr/dye grain in the coating is determined by the electrochemical potential E_{soln} of the surrounding chemical redox solution, the potential E_{ox} for the oxidation of adsorbed dye could be determined using the Nernst equation:

$$E_{\text{soln}} = E_{\text{ox}} + RT/nF \ln [\text{oxidized dye}]/[\text{dye}]$$

where the ratio $[\text{oxidized dye}]/[\text{dye}]$ is obtained from the reflectance spectral data. Redox data for the monomeric and aggregated forms of these dyes are listed in Table 1. The results indicate that the oxidation potential of the dye aggregate is more positive by ca. 70 mV than that of the corresponding monomer. An estimate for the energy of the dye excited state E^* can be obtained by subtracting the energy for optical excitation of the monomer and aggregate from their respective oxidation potential values. Calculated in this manner, this excited state level will correlate with the ability of the photoexcited dye to inject electrons into the silver halide conduction band. Differences in the calculated excited-state energies E^* for the various aggregates are as large as 0.6 eV.

Table 1. Oxidation potentials for adsorbed dyes.

Dye no.	Agg'n State	λ_{max} (nm)	E_{ox} (vs Ag/AgCl)	E^*
1	M	722	0.355	-1.363
1	J	842	0.429	-1.044
2	M	708	-	-
2	H	612	-	-
3	M	704	0.424	-1.337
3	H(hb)	572,665	0.496	-1.672

Several important conclusions can be drawn from the data of Table 1. First, the fact that the monomer form of the dye is slightly easier to oxidize than the aggregate suggests that, in dye systems containing monomer/aggregate mixtures, the monomer may act as a shallow hole-trap for the aggregate. Accordingly, if the monomer is adsorbed adjacent to, or within an effective electron transfer range of the aggregate, monomer dye can supersensitize the aggregate by improving electron-hole separation, either through a mechanism involving electron transfer from the monomer to a photoexcited aggregate, or from the monomer to photo-oxidized aggregate molecules. This "hole-trapping" mode of sensitization efficiency improvement has been previously described as self-supersensitization and has been postulated to be operative for the J-aggregates of certain carbocyanine dyes.⁷ Second, the energetic consequences of aggregation are seen to have a much larger impact on the dye excited state

E* as compared to the change reflected in the ground state levels. These aggregation-induced changes in redox potential can result in dramatic differences in thermodynamics of spectral sensitization for the various dyes. The energy of the conduction band edge for silver bromide is estimated to be at ca. -1.3 V on this scale of reference. The excited state levels of the monomeric forms of dyes 1-3 are calculated to be approximately isoenergetic with the AgBr conduction band edge. The H-herringbone aggregate of dye 3 is predicted to have E* positioned well above the AgBr band edge. The H-aggregate of dye 2 is estimated to have potentials similar to those of dye 3. Electron injection from the excited monomers and H-aggregates into the conduction band is thermodynamically favorable in these cases. In contrast, the excited state energy of the J-aggregate (dye 1) is found to be significantly below the conduction band edge, and electron injection is thermodynamically unfavorable. The results of

photoexposure experiments conducted with AgBr emulsions containing dyes 1-3 are consistent with these predictions.

References

1. A. H. Herz, *Adv. Colloid Interface Sci.*, **8**, 237 (1977).
2. J. Lenhard and B. Hein, *J. Phys. Chem.*, **100**, 17487 (1996).
3. V. Czikkely, H. Forsterling, and H. Kuhn, *Chem. Phys. Lett.*, **6**, 11 (1970).
4. C. Reich, *Photogr. Sci. Eng.*, **18**, 335 (1974).
5. K. Saito, K. Ikegami, K., S. Kiroda, Y. Tabe, and M. Sugi, *J. Appl. Phys.*, **71**, 1401 (1992).
6. A. A. Muentner, D. V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano, and S. Mukamel, *J. Phys. Chem.*, **96**: 2783 (1992).
7. W. West and P. B. Gilman Jr., *Photogr. Sci. Eng.*, **18**, 418, (1974).