Antenna Dye Sensitization: Principles and Fluorescence Studies

R. L. Parton, T. L. Penner, W. J. Harrison, J. C. Deaton, and A. A. Muenter
Eastman Kodak Company,
Rochester, New York/USA

Abstract

Increased light absorption per microcrystal represents one approach for improving photographic sensitivity of silver halide emulsions. An implementation of this approach that has received recent attention is antenna dye sensitization, which functions by formation of multiple layers of sensitizing dye on a single microcrystal. In order for this method to be effective, the energy of light absorbed in the outer layer(s) must be efficiently transferred to the dye at the surface of the silver halide. The principles of antenna dye sensitization will be discussed in the context of examples from the Kodak Research & Development Laboratories. Fluorescence measurements on antenna dye sensitized silver halide emulsions will be presented and compared with photographic results.

Introduction

The efforts in recent years to maximize the sensitivity of camera speed photographic materials while retaining excellent image quality have led the silver halide research community to focus on the remaining sources of inefficiency in the formation of AgX-based images.[1] One of these inefficiencies is low visible light absorption per AgX microcrystal, a result of the usual limitation of a single monolayer of sensitizing dye on the crystal surface. The cyanine and merocyanine dyes used as spectral sensitizers are compounds with very high oscillator strength absorption bands, and the most useful dyes frequently form high extinction J-aggregates on the AgX surface. Nevertheless, the light absorption of such a J-aggregate monolayer on a single AgX microcrystal peaks at a value of approximately 15–20%, leaving ample room for improvement.

Although a useful overview of possible approaches for increasing light absorption per microcrystal was laid out by G. R. Bird in the 1970s,[2] there were numerous difficulties to overcome to make these approaches useful in actual multilayer color films. As the technology has evolved, two of these general approaches have been found to have potential practical utility: covalently linking a second, nonadsorbed chromophore to the primary adsorbed sensitizing dye and physisorbing a second dye on top of the primary adsorbed dye. In both cases, light absorbed by the outer dye (the antenna dye) must be effective in producing electrons in the conduction band of the silver halide. In principle, this can be accomplished by either energy or electron transfer from the antenna dye to the primary dye at the surface, with subsequent electron transfer from the primary dye to the AgX conduction band. In this paper, we will describe an implementation of antenna dye sensitization developed in the Kodak Research & Development Laboratories and present experiments supporting Förster energy transfer as the pathway for moving the excitation energy from the antenna dye to the primary dye.

Characteristics of Efficient Antenna Dye Sensitization

A primary requirement for antenna dye sensitization is that the antenna dye form a layer that is in close physical proximity to the primary adsorbed dye, yet does not displace it from the AgX surface. While this can be accomplished by using a covalent link from the primary dye to a nonadsorbing antenna dye, use of physisorption to produce the second dye layer is usually more tractable from a synthetic point of view. As demonstrated by the early work of Penner and Gilman,[3] Coulombic attraction between dyes with net positive and net negative charges can be used to produce multiple dye layers on AgX surfaces. The dispersion forces associated with the extended dye chromophores also contribute to the adsorption of the second dye on top of the primary adsorbed dye. To prevent having the antenna dye displace the primary dye from the surface or interfere with the surface structure of the primary dye, the adsorption of the antenna dye to the AgX should be significantly weaker than the adsorption of the primary dye.

We have also found that formation of a smetic liquid-crystalline phase by a dye in a gelatin environment is a useful diagnostic test for the likelihood that a dye will organize as a second layer over a primary dye. These smetic liquid crystals have ordered, two-dimensional layers of dye separated by an aqueous layer and generally exhibit a J-aggregate optical absorption.[4] Consequently, their formation is indicative of a propensity for the antenna dye to self-organize into an ordered structure as it adsorbs over the primary dye.

The efficiency of excitation transfer from the excited antenna dye donor to the primary dye acceptor depends on

the magnitude of the energy transfer rate, k_t, relative to the rates of the other processes that deactivate the excited state: fluorescence (with rate k_f) and nonradiative decay (with rate k_{nr}). For energy transfer via a Förster (dipole-dipole) mechanism this ratio is given by:[5]

$$\frac{k_t}{k_f + k_{nr}} = C \frac{\kappa^2}{r^6} \int_0^\infty F^D(\nu) \varepsilon^A(\nu) \frac{d\nu}{\nu^4} \qquad (1)$$

where r is the distance from the donor to the acceptor, κ is a factor depending on the relative orientation of the transition dipole in the donor vs the acceptor, $F^D(\nu)$ is the donor fluorescence intensity as a function of frequency, $\varepsilon^A(\nu)$ is the acceptor absorption coefficient as a function of frequency, and C is a constant containing a dependence on the refractive index of the environment. From this equation, it can be seen that the factors contributing to efficient energy transfer are:

a) minimum distance separating the donor and acceptor,

b) favorable orientation (i.e., parallel) of the transition dipoles of the donor and acceptor,

c) high fluorescence yield of the donor (implicit in the fluorescence integral in Eq. 1),

d) strong absorption in the acceptor, and

e) good overlap of the donor fluorescence with the acceptor absorption.

Additional requirements for the antenna dye donor are that it have a high extinction coefficient, so as to contribute as much additional light absorption as possible, and that it not interfere with the electron injection from the excited primary dye into the AgX substrate. To meet this latter requirement, back-electron transfer from the excited primary dye to the antenna dye must have low probability.

Tricyanopropene Dyes as Antenna Dyes

We have found that the general class of tricyanopropene (TCP) merocyanine dyes contains dyes that are particularly useful as antenna dyes, fulfilling all of the general requirements outlined above.[6] The general structure of this dye class, as well as some specific examples, are given in Table I. Dyes where R1 contains a positively charged nitrogen substituent have a center of localized positive charge that helps promote adsorption as a second layer on top of anionically charged cyanine primary sensitizers.

Dyes where the cyanine nucleus is a benzoxazole are useful as antenna dyes in green-sensitive layers, while dyes where the cyanine nucleus is benzothiazole or quinoline are useful in red-sensitive layers.

Figure 1 shows the increase in light absorption and photographic sensitivity obtained when Dye B is used as an antenna dye with a tabular grain emulsion sensitized with a combination of two anionic green-absorbing cyanine dyes as the primary dye layer. Figure 2 shows similar data obtained when Dye C is used as an antenna dye with a tabular grain emulsion sensitized with a combination of three anionic red-absorbing cyanine dyes as the primary dye layer. As the figures illustrate, in both cases, the TCP

Table I. Tricyanopropene merocyanine dyes
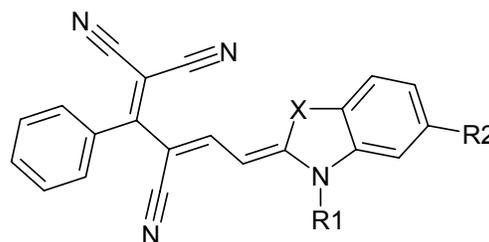
Dye	X	R1	R2
Dye A	O	$-(CH_2)_3N(Me)_3^+$	Ph
Dye B	O	$-(CH_2)_3N(Me)(CH_2CH_2OH)_2^+$	Ph
Dye C	CH-C(Ph)-	$-(CH_2)_4N(Me)_3^+$	H
Dye D	S	$-(CH_2)_5N(Me)_3^+$	Ph

Dye	X	R2	E_R	E_{OX}
Dye A	O	Ph	-1.06	1.19
Dye C	CH-C(Ph)-	H	-0.93	1.05
Dye D	S	Ph	-0.98	1.12
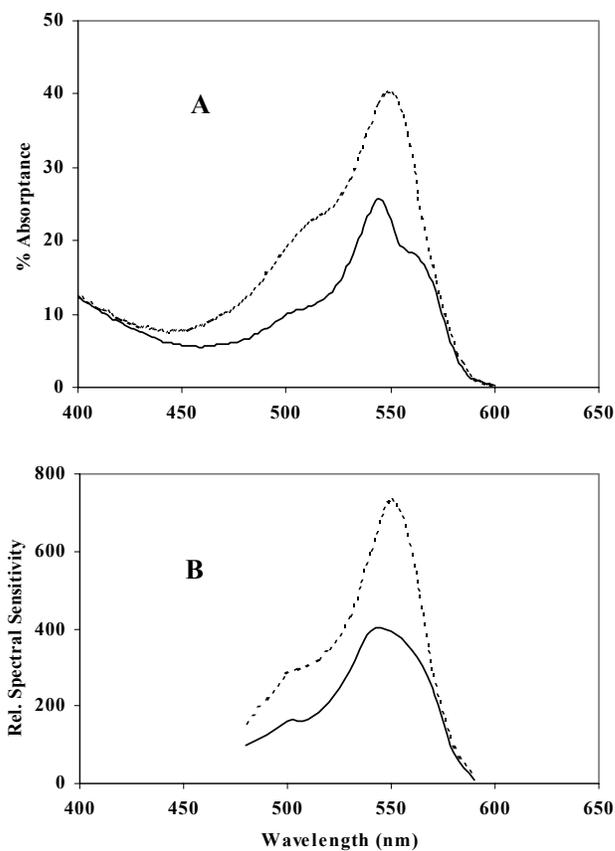
Figure 1. Absorptance (A) and spectral sensitivity (B) for coatings of a green-sensitized AgBrI tabular grain without (solid) and with (dotted) the addition of Dye B as an antenna dye.

disrupting or displacing this layer, and they provide significantly increased spectral sensitivity in the region where they absorb light.
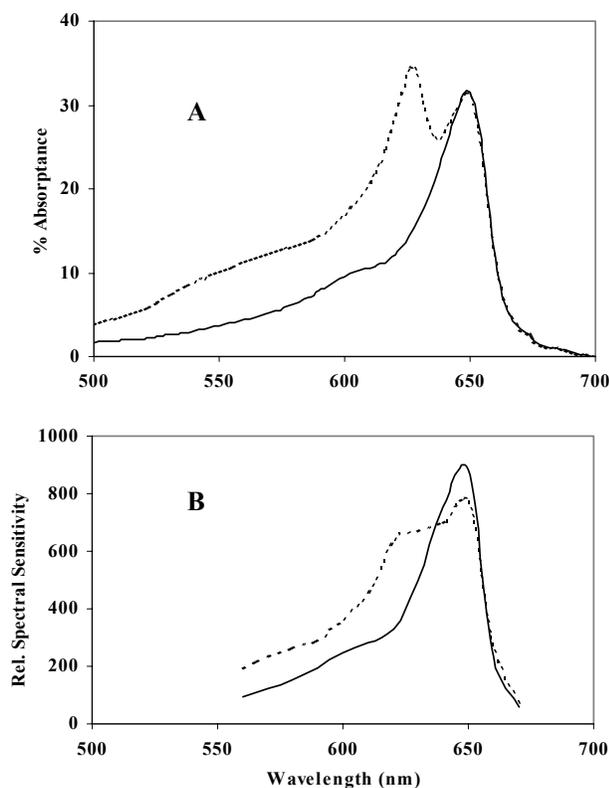
Figure 2. Absorptance (A) and spectral sensitivity (B) for coatings of a red-sensitized AgBrI tabular grain without (solid) and with (dotted) the addition of Dye C as an antenna dye.

In the presence of the antenna dye, the overall relative quantum efficiency (RQE) of spectral sensitization, $\Phi_T(\lambda)$, at wavelength λ can be expressed as:

$$\Phi_T(\lambda) = \Phi_p(\lambda)\frac{A_p(\lambda)}{A_T(\lambda)} + \Phi_{tr}(\lambda)\Phi_p(\lambda)\frac{A_a(\lambda)}{A_T(\lambda)} \qquad (2)$$

where $\Phi_p(\lambda)$ is the RQE of the primary dye sensitization at wavelength λ in the presence of the layering dye, $A_p(\lambda)$ is the absorptance of the primary dyes, $A_a(\lambda)$ is the absorptance of the antenna dye, $A_T(\lambda)$ is the absorptance of the combination of the antenna dye with the primary dyes, and $\Phi_{tr}(\lambda)$ is the quantum efficiency of excitation transfer from the antenna dye to the primary dyes. Using this equation and the data in Figs. 1 and 2, it is possible to determine that the efficiency of excitation transfer from Dye B to the green primary dyes averages about 95% and is about 80% from Dye C to the red primary dyes.

Evidence for Förster Energy Transfer

While the efficiency of excitation transfer for the two examples presented above is consistent with a Förster energy-transfer mechanism, it is also the case that electron transfer from the antenna dye to the primary dye could be quite efficient if the energy levels of the antenna dye are designed to make this process favorable. In fact, the early work of Penner and Gilman on layers of cyanine dyes of opposite charge suggested electron transfer as a primary mechanism.[3] In the case of the TCP antenna dyes, however, there is a significant body of evidence supporting Förster energy transfer.

One important observation is the correlation that we have observed between photographic effectiveness and relatively high fluorescence quantum yield for the J-aggregated antenna dye in gelatin.[7] In the course of developing the TCP antenna dyes, a number of examples have been synthesized and their J-aggregate fluorescence measured. As in shown in Fig. 3 for a representative group of quinoline TCP dyes on a red-sensitized tabular emulsion, the data obtained indicates that dyes with low J-aggregate fluorescence yields do not make effective antenna dyes
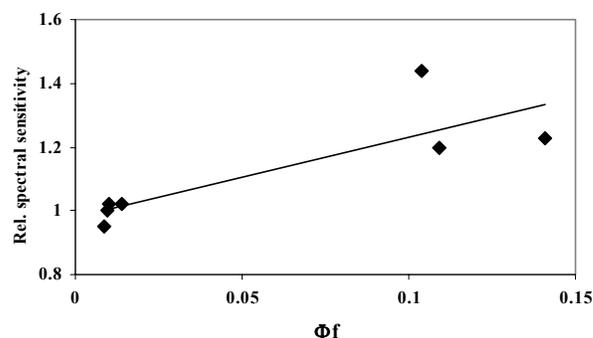
Figure 3. Relative spectral sensitivity for a series of quinoline TCP dyes as antenna dyes on a red-sensitized AgBrI tabular emulsion. Normalized to 1.0 for emulsion with no antenna dye.

Electrochemical data for the monomeric dyes can be used to estimate the energy levels of these TCP dyes relative to the primary dyes, and data for some representative examples are included in Table I. For electron transfer from the antenna dye to the primary dye to be energetically favorable, the reduction potential E_R of the antenna dye should be more negative than the primary dye. For the benzoxazole TCP dye, the E_R value of –1.06 V is less negative than the estimated –1.15 V value for E_R of the benzoxazole benzothiazole carbocyanine that is the longer wavelength component of the primary dye combination used for the green sensitizations shown here. For the quinoline TCP dye, the E_R value of –0.93 V is also less negative than the –1.07 value for the benzothiazole carbocyanine that is the major component of the red sensitization illustrated above. Although there are always questions about how well these monomeric redox potentials predict the relative potentials for the adsorbed J-aggregated dyes, it seems unlikely that electron transfer from the antenna dyes to the primary dyes is an energetically favored

process. The conclusion that the effective E_R for the aggregated quinoline TCP dye is in the range of –0.9 V is supported by the fact that this dye is a marginal spectral sensitizer when adsorbed directly to an AgBrI tabular grain, giving a spectral sensitization efficiency that is no better than 5% of that for a good J-aggregated cyanine dye sensitization. Previous work has shown that spectral sensitizing efficiencies generally decrease as E_R values become less negative than –1.0 V.[8,9] This poor spectral sensitizing efficiency of the directly adsorbed quinoline dye also is evidence that the good sensitization provided when this dye is used as an antenna dye must be the result of energy transfer to the primary dye.

The importance of the Förster energy transfer mechanism for these TCP dyes is also supported by the photographic data obtained when the red-absorbing quinoline TCP dye C is adsorbed as an outer layer on the green sensitization of Fig 1. In this case, because the fluorescence of Dye C has no overlap with the absorption of the primary dyes, one would expect little or no red sensitivity for this combination. Indeed, the spectral sensitivity curves for this combination show only a very inefficient response in the red (which is probably due to some directly adsorbed antenna dye), and energy transfer from the green dyes to the inefficient red dye significantly diminishes the green response of the primary dyes.

Studies of the fluorescence of the TCP dyes when adsorbed on an emulsion substrate also give data that are consistent with what would be expected from a Förster energy transfer mechanism. Figure 4 compares the fluorescence of coatings containing Dye C in two different configurations: adsorbed as the outer layer on a tabular-grain emulsion sensitized with a blue-absorbing cyanine J-aggregate, and adsorbed as the outer layer on the same emulsion sensitized with the red-adsorbing cyanine dye combination used for the photographic data in Fig. 2.
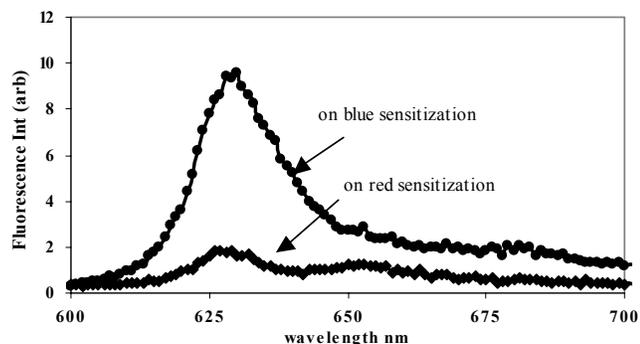
Figure 4. Fluorescence of Dye C adsorbed on a blue-sensitized tabular grain emulsion and adsorbed on a red-sensitized tabular emulsion.

As can be seen in this figure, Dye C is highly fluorescent when used with a blue-absorbing cyanine because there is no overlap of this fluorescence with the absorption of the underlying cyanine dye. However, when used with the red-absorbing cyanine dyes where there is

good overlap of the Dye C fluorescence with the cyanine dye absorption, the fluorescence yield of Dye C is reduced by 80%. This reduction is in good agreement with the calculated yield (80%) of excitation transfer from Dye C derived from the photographic data using Eq. 2. A similar analysis of Dye B indicates that the fluorescence yield of this dye is reduced by at least 95% when adsorbed to the green-absorbing cyanine dye combination in Fig. 1, a value which, again, is in good agreement with the yield of excitation transfer calculated from the photographic data.

Conclusions

Use of the tricyanopropene dyes as antenna dyes provides increases in light absorption that translate to usable increases in spectrally sensitized speed for AgX systems. Data from electrochemical and fluorescence measurements indicate that transfer of the excitation energy from these antenna dyes to the underlying primary dye sensitization takes place via a Förster energy transfer mechanism.

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Biography

Annabel Muenter received a B.S. in Chemistry from the University of Michigan in 1966 and a Ph. D. in Chemical Physics from Harvard University in 1972. She joined Eastman Kodak Company Research & Development Laboratories in late 1970 in the Phototheory Laboratory headed by Dr. T. H. James. During her career, she has combined spectroscopic and photographic studies to improve understanding of spectral sensitization mechanism. She has also applied spectral sensitization knowledge to practical photographic problems. Annabel is currently a Research Fellow in the Materials and Media Platform Center of Eastman Kodak Company. She is a Fellow and Senior Member of IS&T and serves as the Secretary for the International Committee for Imaging Science.