Holetrapping in Mixed Benzoxazolo-Benzimidazolo Carbocyanine Spectral Sensitized AgBrI (111) Tabular Microcrystals

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Abstract

The optical and photographic behaviour was investigated of J-aggregated benzoxazolo carbocyanine dyes (D1 and D2) in the presence of low surface concentrations of benzimidazolo carbocyanine dyes (S1 and S2). Diffuse reflectance spectra of the emulsions and the coatings (DRS) and photographic sensitivity on 405 nm and 535 nm were examined as a function of concentration of the super-sensitizing dye and the dye structure on primitive AgBrI (111) tabular crystals. In the absence of the supersensitizing dye a large degree of intrinsic aswell as spectral desensitization is detected for dye 1 and 2. The addition of 1 % of the supersensitizing dye (relative to the spectral sensitizer) increases sharply the intrinsic and spectral sensitivity without major changes in the optical absorption spectra of the emulsion. Our experiments confirm the importance of supersensitization through energy transfer mechanism but also that one has to take into account a decrease of recombination on trapped holes on the super-sensitizer after electron injection in the conduction band.

Introduction

One of the fundamental problems of spectral sensitization of AgX microcrystals is the effect of concentration dependent spectral desensitization in emulsions with high surface coverage of dyes. Several mechanisms have been proposed to explain these effects for instance the lowering of the efficiency of electron transfer by changes in the electron transfer kinetics, enhancement of fluorescence decay in J-aggregates (ref.1), enhancement of non-radiative decay channels in large J-aggregates (ref.2), enhancement of the recombination rate on trapped holes (ref.3), latent image regression through oxidation effects by holes (ref.4) and enhancement of the latent image dispersion by changes in the interstitial concentration in the microcrystal subsurface region. (ref.5)

Different ways exists to minimize the efficiency loss through concentration desensitization as partitioning the J-aggregate, enhancing electron transfer by energy transfer supersensitization , minimizing recombination by electron injection in the excited dye and restricting latent image dispersion by controlling the interstitial concentration in the surface layer.

In this study the effect of supersensitization is investigated in the blue and spectral region with optical and photographic methods with the goal of gaining insight in the role of recombination on trapped holes parallel to the gain in efficiency by electron-transfer supersenstization. A discussion related to the other mechanisms of concentration desensitization effects is presented.

Experimental

The dyes D1 , D2 and S1 and S2 were synthesized by the Research Laboratory of Agfa-Gevaert N.V.. The structures are given in figures 1 to 4. The structures S1 and S2 are symmetrical benzimidazolo dyes which are know to be efficient energy transfer supersensitizers with pseudo-isocyanine (ref.2). Dye D1 and D2 are J-aggregating benzoxazolo carbocyanine dyes. They are used in a 100 % surface coverage on a primitive AgBr0.99I0.01 tabular (111) emulsion with an equivalent spherical diameter of 0.68 micrometer and an aspect ratio of 6.5. The super-sensitizers are used in 1 % and 10 % concentration relative to the sensitizing dyes. The emulsion are spectral sensitized on 40 degrees Celsius pH 5.5 and pAg 8.6 and coated on a PET base. The DRS spectra of the liquid emulsion and the coated emulsion layers were recorded on a Shimadzu 2101 spectrometer.

The efficiency of latent image formation is evaluated by measuring the photographic sensitivity in the intrinsic optical absorption region (405 nm) and the spectral region of the J-aggregate (535 nm). A 0.01 sec exposure is used (Xe-lamp) followed by processing in a Agfa developer G150 (2 min. development time on 24 degrees Celsius) and fixer G333.

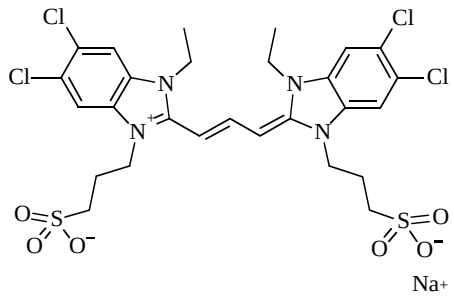

Figure 1: Supersensitizer S1

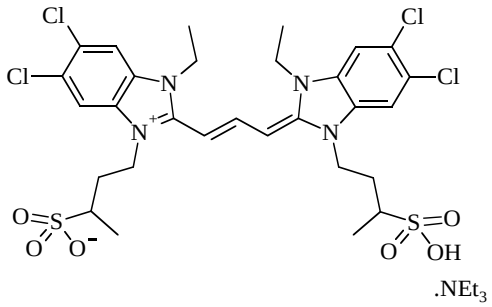

Figure 2: Supersensitizer S2

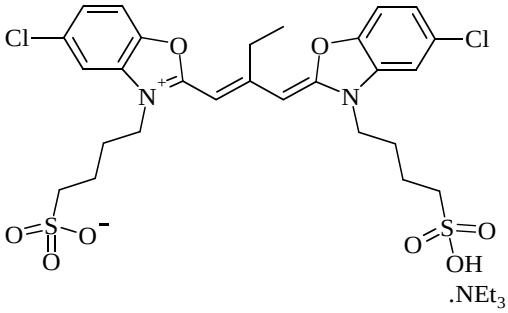

Figure 3: Dye D1

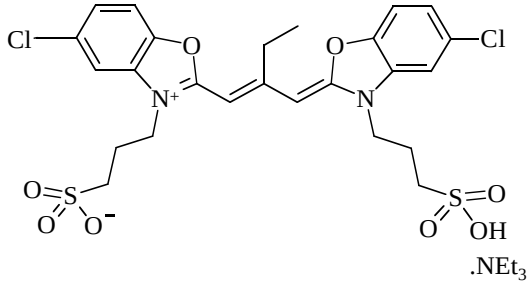

Figure 4: Dye D2

Results and Discussion

The optical spectra of the D1 and D2 in the emulsion melt show a J-aggregate of the dye in adsorbed state at the crystal surface at 550 nm and 546 nm with the presence of the dye monomer in solution which is normal for a 100 % surface coverage. The peak half width of D1 is 40 % smaller than of D2. D2 has also an hypsochromic assymetry near the J-aggregate absorption. The dyes S1 and S2 have a main absorption in the emulsion melt at 578 and 582 nm for the 1 % surface coverage These spectra show the features of a J-aggregated dye adsorbed on the crystal surface. The combination of the D1 and D2 with S1 and S2 has a minor influence on the absorption maximum, peak half-width and absorption amplitude for the 1 % addition. The 10 % addition of dyes S1 and S2 to the 100 % D1 and D2 gives a convolution of the absorption spectra. The simular features are present in the optical absorption spectra of the emulsion coatings.

Photographic results : EG&G - 10-2s + V405

Sensi	Dmin	Dmax	Gev.1 + 0,2 a/fog	Gev.2 80% of Dmax	Gev.3 + 0,1 a/fog	G.1 25-75%	AgNO3/m²
/	0.046	0.75	2.68	3.05	2.50	0.95	1.58
Dye 1	0,038	0,81	3,62	4,04	3,30	0,97	1,47
Dye 1+S 1 1%	0.049	0.70	+0.51	+0.35	+0.45	0.56	1.51
Dye 1+S 1 10%	0,052	0,76	+0.44	+0.38	+0.33	0,75	1,59
Dye 1+S 2 1%	0.033	0.93	+0.62	+0.39	+0.60	0.82	1.99
Dye 1+S 2 10%	0.036	0.78	+0.51	+0.41	+0.45	0.76	1.41
/	0,032	0,58	2,85	3,11	2,70	0,87	1,58
Dye 1	0,029	0,59	3,62	3,93	3,41	0,74	1,35

Table 1: Photograpic results of Dye 1

Photographic results: EG&G - 10-2s + U535

Sensi	Dmin	Dmax	Gev.1 + 0,2 a/fog	Gev.2 80% of Dmax	Gev.3 + 0,1 a/fog	G.1 25-75%	AgNO3/m²
/	0,039	0,05	***	***	***	***	1,58
Dye 1	0,036	0,71	2,68	3,07	2,47	0,84	1,47
Dye 1+S 1 1%	0,039	0,90	+0.58	+0.39	+0.67	0,91	1,51
Dye 1+S 1 10%	0,041	0,81	+0.41	+0.29	+0.45	0,80	1,59
Dye 1+S 2 1%	0,032	0,79	+0.5	+0.34	+0.6	0,76	1,99
Dye 1+S 2 10%	0,034	0,89	+0.49	+0.26	+0.52	0,81	1,41
/	0,027	0,03	***	***	***	***	1,58
Dye 1	0,027	0,61	2,77	3,10	2,55	0,75	1,35

Table 2: Photograpic results of Dye 1

Photographic results : EG&G - 10-2s + V405

Sensi	Dmin	Dmax	Gev.1 + 0,2 a/fog	Gev.2 80% of Dmax	Gev.3 + 0,1 a/fog	G.1 25-75%	AgNO3/m²
/	0,039	0,69	2,73	3,09	2,58	0,88	1,6
Dye 2	0,043	0,64	3,71	4,05	3,50	0,78	1,42
Dye 2+S 1 1%	0,041	0,84	+0.78	+0.52	+0.80	0,75	1,7
Dye 2+S 1 10%	0,049	0,70	+0.66	+0.54	+1.25	0,74	1,42
Dye 2+S 2 1%	0,039	0,87	+0.86	+0.49	+0.95	0,67	1,89
Dye 2+S 2 10%	0,046	0,78	+0.75	+0.53	+0.76	0,68	1,58
/	0,032	0,58	2,85	3,11	2,70	0,87	1,58
Dye 2	0,036	0,57	3,45	3,83	3,15	0,53	1,34

Table 3: Photograpic results of Dye 2

Photographic results : EG&G - 10-2s + U535

Sensi	Dmin	Dmax	Gev.1 + 0,2 a/fog	Gev.2 80% of Dmax	Gev.3 + 0,1 a/fog	G.1 25-75%	AgNO3/m²
/	0,03	0,03	***	***	***	***	1,6
Dye 2	0,035	0,68	2,70	3,09	2,48	0,78	1,42
Dye 2+S 1 1%	0,035	0,86	+0.70	+0.46	+0.68	0,75	1,7
Dye 2+S 1 10%	0,04	0,74	+0.60	+0.54	+0.58	0,80	1,42
Dye 2+S 2 1%	0,031	0,72	+0.60	+0.43	+0.63	0,62	1,89
Dye 2+S 2 10%	0,033	0,70	+0.64	+0.54	+0.63	0,67	1,58
/	0,027	0,03	***	***	***	***	1,58
Dye 2	0,03	0,72	2,52	3,00	2,25	0,75	1,34

Table 4: Photograpic results of Dye 2

The photographic results are presented in table 1 to 4 for the different dye combinations and concentrations. Table

1 gives the optical response after illumination on 405 nm. Three sensitivities values are given : Gev.1 is the sensitivity 0.2 above Dmin, Gev.2 is the sensitivity point on 80 % of Dmax in the shoulder of the sensitometric curve and Gev.3 is the sensitivity point 0.1 above Dmin.

Dye D1 blue desensitization is for the 100 % surface coverage 0.97 logIt . The effect of S1 and S2 on the blue and spectral sensitivity of D1 can be seen from the tables 1 and 2.

Dye D2 blue desensitization is for the 100 % surface coverage 0.97logIt wich is comparable to D1. However the effect of S1 and S2 on the blue and spectral sensitivity of D2 is much higher as can be seen from the tables 3 and 4 compared with tables 1 and 2.

The speed enhancement by the supersensitizer is for the intrinsic as for the spectral exposure of the same magnitude although small differences exist between the D1 and D2 supersensitized emulsions. The intrinsic sensitivities are 0.05 to 0.15 logIt higher than the spectral sensitivities which is for D2 very clear.

Dielectric loss measurements on the D1 and D2, S1 and S2 combinations show no increase of the ionic conductivity compared to the D1 and D2 dyed reference emulsions with the 100 % surface coverage.

From these data we conclude that as the optical absorption does not change upon adsorption of dyes S1 and S2 with dyes D and as the ionic conductivity is not changing, the supersenstizing action in this case is not due to enhancement of the optical absorption or partitioning of the J-aggregate neither due to latent image dispersion. As the effect of supersensitization is already occuring on 1 % surface concentration electron transfer enhancement by energy transfer is possible. However this does not explain the dramatic blue sensitivity increase by S1 and S2. Therefore we conclude that a large part of the supersentizing effect with the benzoxazolo-benzimidazolo dye combination is due to a reduced recombination on the dye hole which must be positioned on the benzimidazolo carbocyanine dye. A part of the supersensitizing action can also be due to the enhancement of electron transfer by energy transfer supersensitization.

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