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Study on the Mechanism of the Supersensitization of Some Allopolar Trinuclear Cyanine Dyes*

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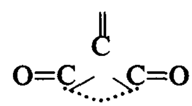
ABSTRACT

ESR studies have been made on the supersensitization of naphthothiacarbocyanine (NTCC) by some holopolar trinuclear cyanine dyes (TNC). It was found that some allopolar trinuclear cyanine dyes containing an acidic nucleus



(existing in holopolar form) can supersensitize NTCC very well; there is good correlation between ΔI_{ESR} and increase in the ΔS value. These results support the general conclusion that a positive hole produced by the sensitizer is trapped by the supersensitizer.

1 INTRODUCTION

It is well known that a supersensitizing combination of a meso-ethyl substituted naphthothiacarbocyanine and an allopolar trinuclear cyanine dye are widely used in aerial photography and colour films.

The sensitizing dye and supersensitizer are adsorbed onto the surface of silver halide grains. After exposure to light, a Frenkel exciton or dye positive hole and photoelectron are produced. The role of the supersensitizer, i.e. allopolar trinuclear cyanine, is either to promote the ionization of the Frenkel exciton, or to trap the positive hole of the sensitizing dye, with the formation of a positive hole of the super-

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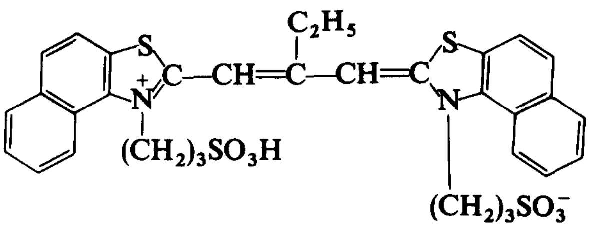
sensitizer. Thus, the recombination of a photoelectron injected to the conduction band of silver halide and of the positive hole of sensitizer is prohibited. This has already been demonstrated by Dember photovoltage measurements.[1] Since the positive holes of both the sensitizer and supersensitizer are semioxidized free-radical cations, the presence of these positive holes must give rise to an ESR signal after light exposure. In this paper, the intensities of the ESR signals of a meso-ethyl naphthothiacarbocyanine dye NTCC (dye A), with or without supersensitizer TNC, are measured. The light-induced ESR signals and their photographic sensitivities are studied and correlated.

2 EXPERIMENTAL

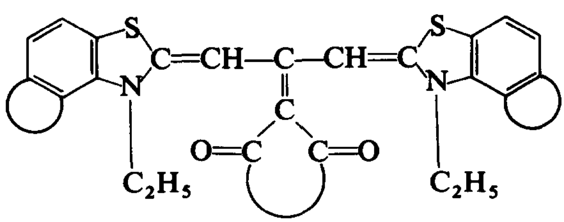
2.1 Sensitizing dyes and supersensitizer used

The sensitizing dye used in this study was the meso-ethyl naphthothiacarbocyanine dye A (NTCC):



This dye has λ_{max} at 575 nm and its sensitizing maximum (S_{max}) at 670 nm.

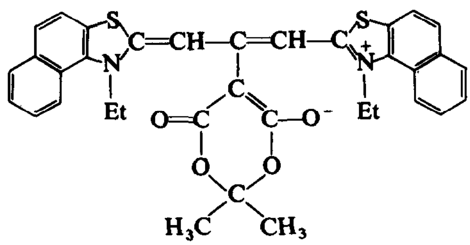
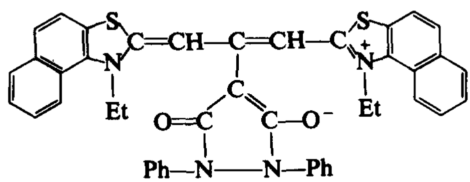
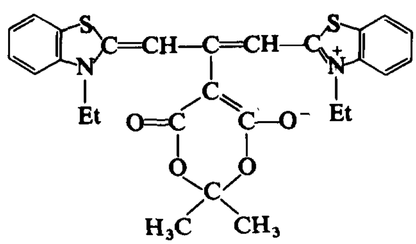
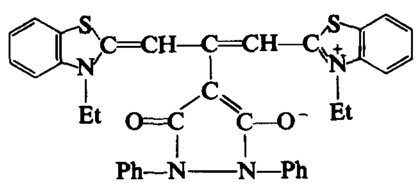
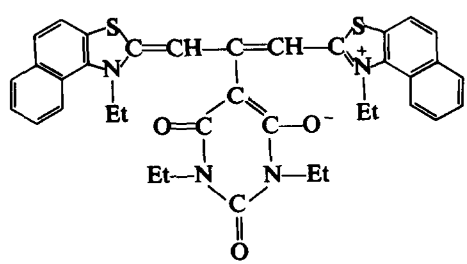
The general formula of the allopolar trinuclear cyanine dyes (TNC) used as supersensitizers to the above meso-ethyl naphthothiacarbocyanine is as follows:



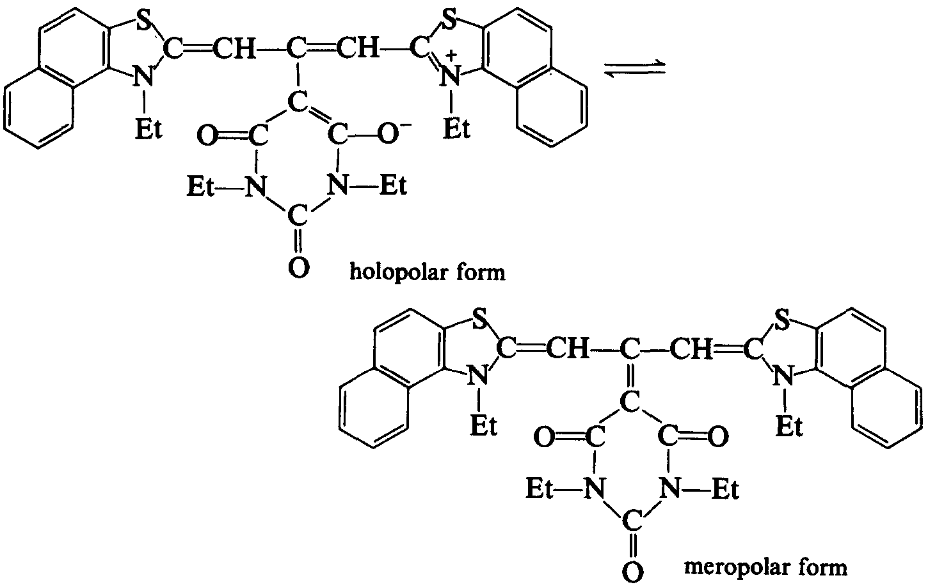
The formulae of the trinuclear cyanine dyes (TNC) are shown in Table 1.

A totally planar structure such as TNC-5 is too crowded and can exist in two distinct configurations, viz. one with complete charge separation

TABLE 1
Structure of TNC Dyes Used in This Investigation

Dye	*Structures of dye*
TNC-1	
TNC-2	
TNC-3	
TNC-4	
TNC-5	

(holopolar form) and the other with at least one non-ionized form (meropolar form).



holopolar form

meropolar form

In the holopolar form, the acidic nucleus is twisted out of the plane of the trimethine cyanine dye. This isomer predominates in methanol solution and has λ_{max} similar to that of the meso-substituted carbocyanine dye. In the meropolar form, one basic nucleus is twisted out of the plane of the dimethine merocyanine dye. This isomer type exists predominantly in cyclohexane–lutidine solution, and has λ_{max} similar to that of a dimethine merocyanine.

When allopolar trinuclear cyanines are adsorbed onto Ag(BrI) grains, the sensitization maxima are similar to those of meso-substituted carbocyanines. It is usually assumed, therefore, that in the adsorbed state, the dye exists predominantly in the holopolar form. This phenomenon is called allopolar isomerism.

2.2 Photographic tests[2]

The AgBr emulsion used was a positive emulsion containing 0·31 mol/kg of Ag. Methanolic solutions of dye and/or supersensitizer were added to the emulsion. The dye solution added was 1×10^{-5} mol/kg emulsion; the supersensitizer added was a saturated solution at 15°C, the quantity of supersensitizer added being one-fifth that of the sensitizer. D-72 was used as developer at 20°C for 6 min and F-5 used as fixing solution at 20°C for 5 min. A C-4 Sensitometer (USSR) and CMT Densitor (China) were used for the measurements.

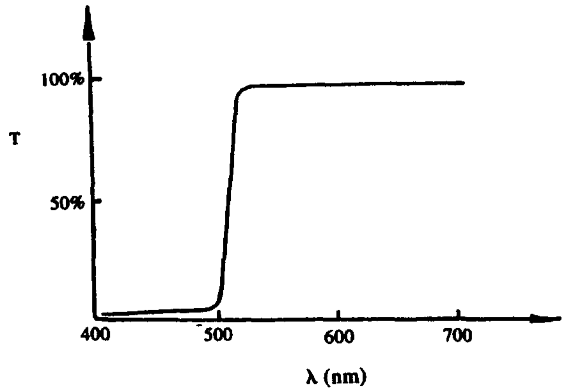


Fig. 1. Absorption spectrum of the filter.

2.3 Electron spin resonance measurements[3]

A Bruker ER 200D ESR spectrophotometer was used. The emulsion (15 g) was melted at 40°C, dye and supersensitizer added, the mixture de-foamed for 15 mins, coated on a film base and dried. The dried emulsion was put into a quartz tube and the ESR signals measured using an Electron Spin Resonance ER 200 D, with x-band and magnetic field modulation of 100 KHz and a 250 W Xenon lamp as light source; the light flux through a filter was focussed onto the sample. The absorption spectrum of the filter is shown in Fig. 1.

3 RESULTS AND DISCUSSION

The photographic properties of dye, and dye plus supersensitizer, are given in Table 2. The sensitizing ranges and sensitization maxima of dye A, the TNCs and their combinations are shown in Table 3.

The ESR measurements indicate the following:

(i) No ESR signal could be observed in the emulsion either in the absence of sensitizing dye, regardless of exposure to light, or in the presence of dye without exposure.

(ii) ESR signals of moderate strength could be observed with the dried emulsion adsorbed by the sensitizing dye A.

(iii) ESR signals of moderate strength could be observed with the dried emulsion adsorbed by TNC-1, TNC-2, and TNC-5 separately, but the ESR signal could not be observed with the dried emulsion adsorbed by TNC-3 or TNC-4.

TABLE 2
Photographic Properties of Dye and of Dye Plus Supersensitizer

Dye	*S*	ΔS
Dye A	11·7	—
Dye A + TNC-1	15·0	3·3
Dye A + TNC-2	15·1	3·4
Dye A + TNC-3	13·1	1·4
Dye A + TNC-4	12·8	1·1
Dye A + TNC-5	15·4	3·7

(iv) Intensified ESR signals could be observed with the dried emulsion when dye A + TNC-1, dye A + TNC-2, and dye A + TNC-5 were added, respectively.

The light-induced ESR signal of the emulsion with dye A is shown in Fig. 2 and ESR signals of TNC-1 and dye A+TNC-1 in Fig. 3.

The trinuclear cyanine dyes may be considered as being derived from the corresponding merocyanine dyes, in which a basic nucleus is connected through a conjugated chain to the acidic nucleus.The naphthothiazole nucleus is more basic than the benzothiazole nucleus. Thus, the π electrons are more readily delocalized from the N atom in the basic nucleus to the keto oxygen atom in the acidic nucleus, i.e. TNC-1, 2, and 5 may be expected to exist in holopolar forms. In the case of TNC-3 and 4, the benzothiazole nucleus is less basic than the naphthothiaozle nucleus; the π electrons are mainly located on the N atom of the more basic benzothiaozle nucleus, i.e. TNC-3 and 4 may be expected to exist in

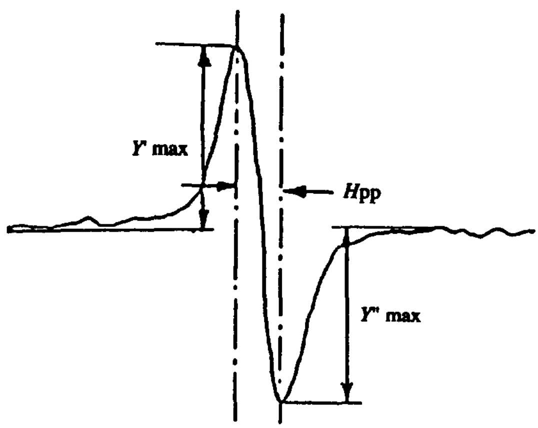


Fig. 2. Light-induced ESR signal of emulsion with dye A, where $y_{max} = y'_{max} + y''_{max}$, H_{pp} = width of ESR peak, and $I_{ESR} = H_{pp}^2 \times y_{max}$.

TABLE 3
The Sensitization Ranges and Sensitization Maxima of Dye-A, the TNCs, and Dye A + TNC

Dye	*Sensitization range (nm)*	S_{max}
Dye A	565–675	670
TNC-1	560–670	650
TNC-2	565–660	655
TNC-3	545–610	585
TNC-4	550–615	590
TNC-5	560–675	660
Dye A + TNC-1	560–695	680
Dye A + TNC-2	575–710	695
Dye A + TNC-5	570–695	680

the meropolar form. Thus, the ability of TNC-1, 2, and 5 to trap positive holes is stronger than that of TNC-3 and 4. Table 2 shows that the supersensitization effect of TNC-1, 2, and 5 is much better than that of TNC-3 and 4.

When the amount of supersensitizer used in combination with dye A is increased, both the intensity of the ESR signal $I_{ESR}(I_{ESR} = H^2_{pp} \times Y_{max})$,

Fig. 3. Light-induced ESR signal of emulsion with TNC-1 and dye A + TNC-1.

TABLE 4
ESR Signal and Photographic Sensitivity of Dye A, with Different Amounts of Supersensitizer TNC-1

Dye	I_{ESR}	ΔI_{ESR}	S	ΔS
1 Dye A + TNC-1 (0 ml)	2139·5	—	11·7	—
2 Dye A + TNC-1 (0·3 ml)	3134·9	1004·6	13·2	1·7
3 Dye A + TNC-1 (0·5 ml)	3297·7	1158·2	13·7	2·0
4 Dye A + TNC-1 (0·7 ml)	3610·4	1471·0	13·9	2·2
5 Dye A + TNC-1 (1·0 ml)	4064·9	1925·4	17·7	3·0
6 Dye A + TNC-1 (1·2 ml)	4386·5	2247·0	15·0	3·5

$I_{ESR} = H^2_{pp} \times Y_{max}$.

and the photographic sensitivity are increased simultaneously. The intensity of the ESR signal and the photographic sensitivity of dye A and different TNC supersensitizer combinations are shown in Tables 4, 5, and 6.

Plots of ΔS against ΔI_{ESR} for sensitizer A with different amounts of supersensitizer TNC-1, TNC-2, and TNC-5 are shown in Figs 4, 5, and 6.

Since the ESR signal results from the paramagnetic center of a light-induced dye, ΔI_{ESR} represents an increase in the number of positive holes when the supersensitizer is added. The total positive hole is increased at the expense of positive holes produced from the sensitizing dye. Thus, the recombination of photoelectrons in the conduction band and in the dye positive holes from the exposed adsorbed sensitizing dye is retarded. This result is in accord with the mechanism of supersenstization in which the supersensitizer acts as a positive hole trap for the sensitizing dye A:

$$\text{dye} + h\nu \rightarrow \text{dye}^*(\text{excited state})$$
$$\text{dye}^* \rightarrow \text{dye}^+(\text{positive hole}) + \text{e}(\text{electron in conduction band})$$
$$\text{dye}^+ + \text{e} \rightarrow \text{dye}(\text{recombination})$$
$$\text{SS} + \text{dye}^+ \rightarrow \text{SS}^+(\text{positive hole}) + \text{dye}$$

TABLE 5
ESR Signal and Photographic Sensitivity of Dye A, with Different Amounts of Supersensitizer TNC-2

Dye	I_{ESR}	ΔI_{ESR}	S	ΔS
Dye A + TNC-1 (0 ml)	2139·5	—	11·7	—
A + TNC-2 (0·2 ml)	2458·7	319·2	12·2	0·5
A + TNC-2 (0·4 ml)	2917·4	777·9	12·7	1·0
A + TNC-2 (0·8 ml)	3326·0	1186·6	13·8	2·1
A + TNC-2 (1·0 ml)	3649·2	1509·7	14·4	2·7
A + TNC-2 (1·2 ml)	4501·6	2360·1	15·1	3·4

TABLE 6
ESR Signal and Photographic Sensitivity of Dye A, with Different Amounts of Supersensitizer TNC-5

Dye	I_{ESR}	ΔI_{ESR}	S	ΔS
Dye A	2 139·5	—	11·7	0·0
A + TNC-5 (0·2 ml)	2 853·9	714·4	12·8	1·1
A + TNC-5 (0·4 ml)	3 013·0	873·5	13·1	1·4
A + TNC-5 (0·6 ml)	3 359·0	1 217·5	13·4	1·7
A + TNC-5 (1·0 ml)	4 219·6	2 080·1	14·8	3·1
A + TNC-5 (1·2 ml)	4 780·0	2 640·5	15·4	3·7

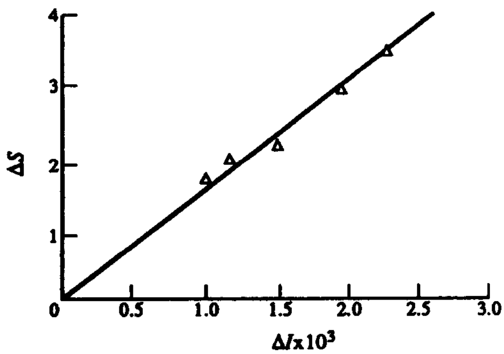


Fig. 4. Plots of ΔS against ΔI_{ESR} of dye A, with different amounts of supersensitizer TNC-1.

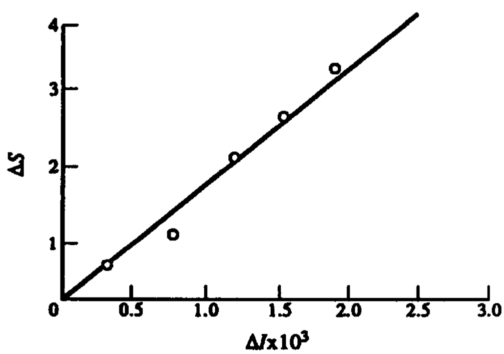


Fig. 5. Plots of ΔS against ΔI_{ESR} of dye A, with different amounts of supersensitizer TNC-2.

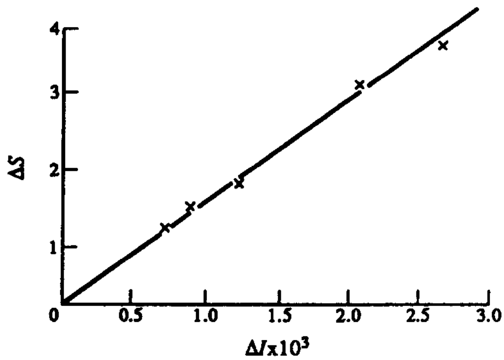


Fig. 6. Plots of ΔS against ΔI_{ESR} of dye A, with different amounts of supersensitizer TNC-5.

4 CONCLUSIONS

A correlation exists between the increase in the intensities of the ESR signals and photographic sensitivities. The function of the supersensitizer may be explained in terms of its ability to act as a dye positive hole trap, otherwise recombination of positive holes of the sensitizer and photoelectrons will occur and the photographic sensitivity will be decreased.

The supersensitizing effects of TNC-1, TNC-2, and TNC-5 are better than those of TNC-3 and TNC-4; so it is apparent, therefore, that some allopolar trinuclear cyanine dyes existing in the holopolar form can supersensitive NTCC very well.

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