Journal of Photochemistry, *24* (1984) 285 - 292

TRIPLET STATE PROPERTIES OF CROCONATE DYES IN HOMOGENEOUS AND POLYMER-CONTAINING SOLUTIONS

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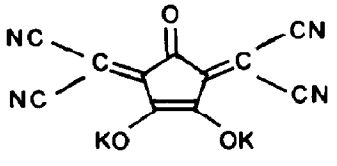
(Received August 2, 1983)

Summary

The effect of polymer microencagement on the lowest triplet excited state of croconate violet and croconate blue, members of a family of oxocarbon condensation derivatives which possess excellent electrocatalytic and photoelectrochemical dye sensitizing properties, has been investigated. These dyes, when surrounded by a poly(4-vinylpyridine) (PVP) matrix, displayed red-shifted $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_n$ absorption maxima. The triplet lifetimes for these dyes were 69 μs and 24 μs respectively in neat ethanol, and 134 μs and 36 μs respectively in ethanol containing 0.01 M PVP. The specific rates of triplet energy transfer from a triplet sensitizer to the dyes were lower in the polymer-containing solutions.

1. Introduction

Croconate blue (1) and croconate violet (2), condensation derivatives of the five-membered oxocarbon croconic acid, are intriguing materials worthy of evaluation for potential use in solar energy conversion:



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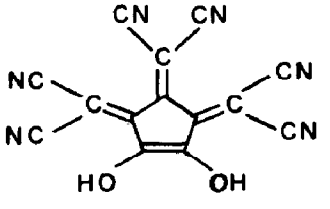

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These dyes display strong absorption in the visible region as well as some excellent semiconductor properties [1]. When loaded into polymer films on conductive n-type SnO_2 electrodes, they also exhibit interesting electrocatalytic properties [2], and excitation of these composite electrodes in the absorption band of the dye has led to novel photoelectrochemical sensitiza-

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tion [3]. Because of these interesting features, a thorough study of their photochemical properties is in order.

Our initial photophysical study revealed that an order-of-magnitude enhancement of the fluorescence yield of 1 can be achieved by microencaging the dye in a polymer matrix [4]. We now report on our characterization of the triplet states of these dyes in neat ethanol and in ethanolic solutions of poly(4-vinylpyridine) (PVP).

2. Experimental details

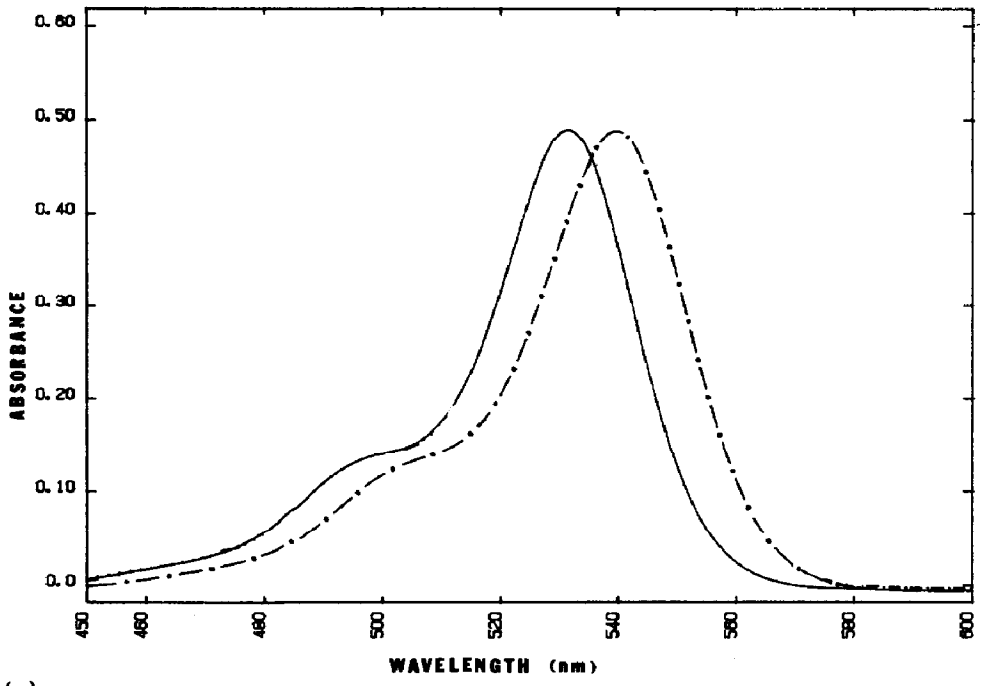
2.1. Materials

The synthesis and purification of the croconate dyes have been reported earlier [5]. PVP obtained from Polysciences Inc. was used as supplied. 9,10-dibromoanthracene (DBA) was sublimed twice. The ethanol was USP reagent grade. Unless otherwise stated, all solutions were deoxygenated by purging with nitrogen for 15 - 20 min. All other chemicals were analytical reagent grade.

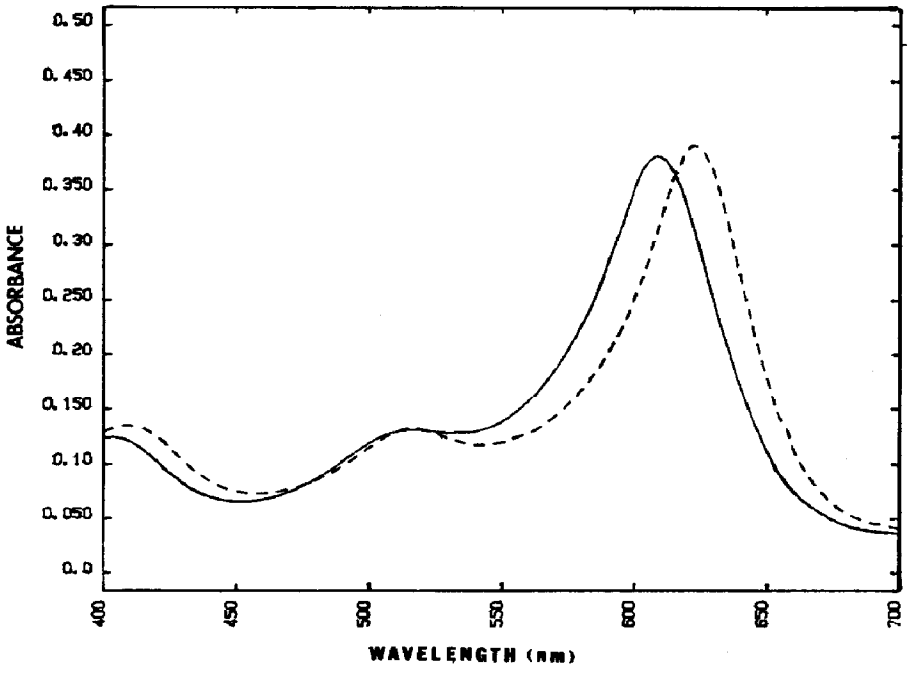
2.2. Absorption and fluorescence spectra

The absorption spectra were recorded using a Hewlett–Packard 8450 spectrophotometer and the emission spectra were recorded using a Spex Fluorolog spectrofluorometer. The flash photolysis experiments were performed at the Center for Fast Kinetics Research, University of Texas at Austin, and the details of the experimental set-up and the techniques for transient measurement can be found elsewhere [6, 7]. The excitation source for the flash photolysis measurements was either a 275 mJ 532 nm (second-harmonic) pulse for direct excitation or a 150 mJ 355 nm (third-harmonic) pulse for triplet sensitization from a Quantel YG-481 *Q*-switched neodymium–yttrium aluminum garnet (Nd–YAG) laser (mean full width at half-maximum, 10 ns). Decay of the dye triplets was followed either by triplet–triplet (T–T) absorption or by the recovery of the bleached dye in the S_0–S_1 absorption band. A nitrogen atmosphere was maintained in the sample cell during the flash photolysis experiments. The PVP concentration is expressed as the concentration of pendent absorptive functional groups employed.

The absorption spectra of dyes 1 and 2 are shown in Fig. 1. Their strong absorption ($\epsilon = 10^4\ M^{-1}\ cm^{-1}$ for 1) in the visible region suggests their use as credible sensitizers in photoelectrochemical cells. The presence of PVP in ethanolic solution shifts the absorption maxima of 1 and 2 to the red. The existence of isosbestic points at various polymer concentrations suggests the importance of hydrophobic bonding. Folding of the polymer chain creates a microcage in which the dye is enclosed by the non-polar environment created by the folded hydrocarbon backbone in the apparently homogeneous solution [8]. Since significant protonation of the pendent pyridine group cannot be expected in neutral ethanol, the possibility of electrostatic interaction between the dye and PVP is unlikely. Analogous hydrophobic interactions are commonly observed in micellar systems [7].



(a)



(b)

Fig. 1. Absorption spectra of croconate dyes: (a) 5×10^{-6} M **1** in ethanol (——, no PVP; — · —, with 10^{-2} M PVP); (b) 5×10^{-6} M **2** in ethanol (——, no PVP; — — —, with 10^{-2} M PVP).

TABLE 1

Absorption and emission characteristics of croconate dyes

	Data for 1			*Data for 2*	
	H_2O	*EtOH*	*0.01 M PVP–EtOH*	*EtOH*	*0.01 M PVP–EtOH*
λ_{max}^{abs} (nm)	530	538	542	605	620
$\epsilon_{\lambda_{max}}^{abs}$ (M^{-1} cm^{-1})	97000	100000	100000	90000	90000
$\lambda_{max}^{em}(S_0-S_1)$ (nm)	560	565	575	640 - 650	650 - 660
$\tau_{decay}(S_1-S_0)$ (ps)	<3	3	28	—	—
λ_{max}^{abs}(T–T) (nm)	≈585	≈590	≈600	—[a]	—[a]
$\epsilon_{\lambda_{max}}^{abs}$(T–T) ($M^{-1}$ cm^{-1})	20000	25000	22000	—[a]	—[a]
$\tau_{decay}(T_1-S_0)$ (μs)	32	69	134	24	36

[a] No detectable absorbance could be seen.

The absorption and emission characteristics of these dyes are summarized in Table 1. When PVP was added to the ethanolic solution of the dye, the emission maximum (fluorescence) was red shifted and the fluorescence quantum yield ϕ_f increased. Upon increasing the PVP concentration to 0.1 M, an enhancement of an order of magnitude in ϕ_f can be achieved [4]. For example, ϕ_f for croconate violet increased from 0.002 in neat ethanol to 0.017 in the presence of 0.1 M PVP. An increase in the singlet lifetime of the dye, parallel to the observed increase in the quantum yield of fluorescence, could also be observed. Such an enhancement in ϕ_f is attributed to the reduced radiationless decay caused by changes in the microviscosity of the region surrounding the dye molecule.

Upon exciting an aqueous solution of 1, a transient absorption (with a broad maximum at about 600 nm) could be observed. The decay of this transient coincided with the recovery of the dye and can be assigned to T_1-T_n absorptions by the dye triplet. However, the triplet yield obtained by direct excitation of the dye was too low (inefficient intersystem crossing) for effective monitoring. An indirect approach was then used.

2.3. Generation of dye triplets 1 and 2 by triplet sensitization

Pulsed irradiation of the solutions of 1 (20 μM) with the pulse from an Nd–YAG laser in the presence of 10^{-4} M DBA (E_T = 169 kJ mol^{-1}) [8] in unbuffered ethanol at 355 nm, conditions under which 98% of the incident light is absorbed by DBA, produced a transient absorption in the region of 600 nm identical with that seen with direct excitation of the dye. A typical transient spectrum is shown in Fig. 2. Assignment of the new band as the T_1-T_n absorption spectrum of croconate violet was based on several pieces of evidence: (1) the decay of the absorption of triplet DBA at 420 nm occurred simultaneously with the appearance of the new absorption at 600 nm and with the depletion of ground state 1 (as monitored by its S_0-S_1

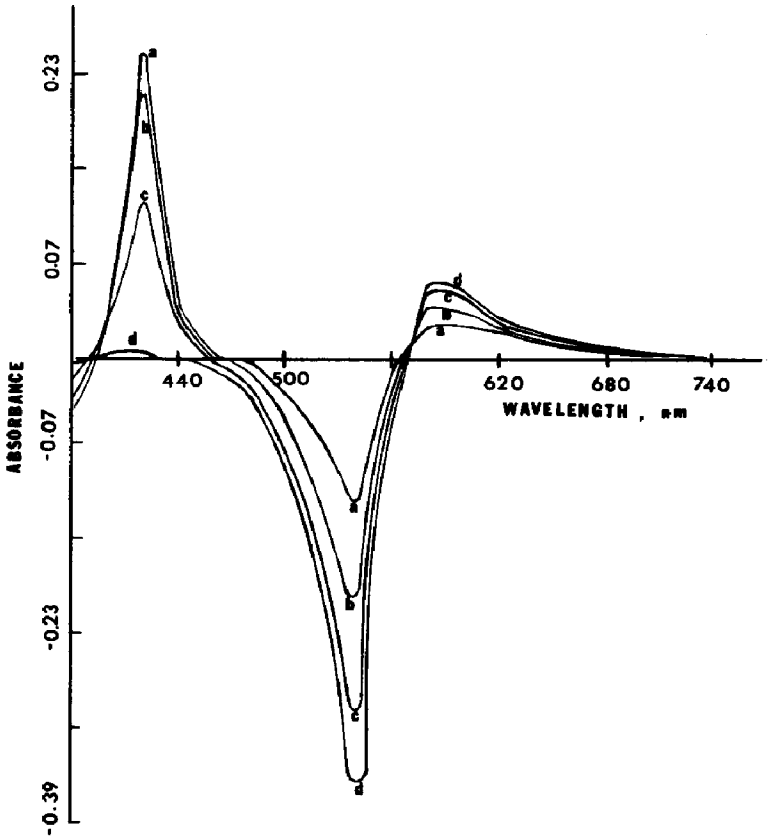


Fig. 2. Transient absorption on pulse excitation (355 nm) of a solution containing 10^{-4} M DBA and 2×10^{-5} M 1 in ethanol: curve a, 0.8 μs; curve b, 2.0 μs; curve c, 5.4 μs; curve d, 18.9 μs.

absorption band); (2) the rate of decay of the absorption assigned to the triplet of 1 and the recovery of 1 were identical, showing that the transient absorbance at 600 nm originated from ground state 1; (3) oxygen, which is a typical triplet quencher, removed the transient efficiently. These observations were parallel to those reported earlier for the sensitization of an oxazine dye by triplet DBA [8].

No transient absorbance attributable to 2 could be seen when parallel sensitization was attempted. However, ground state bleaching of 2 paralleled the disappearance of triplet DBA (Fig. 3). The T–T absorption of 2 overlaps its S_0–S_1 absorption band, making it difficult to see any direct triplet absorption. The lifetime of triplet 2, as measured by the rate of recovery of the bleached dye, was of the same order as that of triplet 1 generated under identical conditions.

The extinction coefficient of the absorption for triplet 1 (Table 1) was measured by determining the triplet concentration by fractional bleaching of the S_0–S_1 absorption band (at wavelengths of 500 - 530 nm) and by assuming that T–T absorption was negligible at this wavelength. The wavelengths

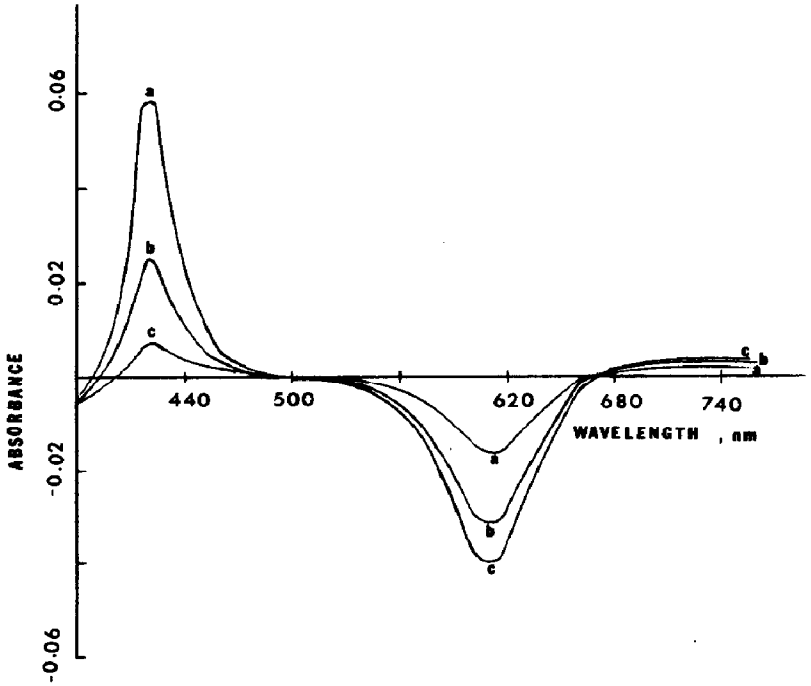


Fig. 3. Transient absorption on pulse excitation (355 nm) of a solution containing 10^{-4} M DBA and 2×10^{-5} M **2** in ethanol: curve a, 0.5 μs; curve b, 2.0 μs; curve c, 3.5 μs.

monitored for the decay kinetics of the transients were 420 nm for triplet DBA, 500 and 590 nm for triplet **1** and 600 nm for triplet **2**.

The presence of PVP in the medium increased the triplet lifetimes of the dyes. For example, the triplet lifetime of **1** increased from 69 to 134 μs upon addition of 10^{-2} M PVP to the ethanol solution. As in analogous perturbations observed with singlet lifetimes [4], the microcage of polymer surrounding the dye apparently stabilized the triplet state.

T–T energy transfer was studied by measuring the rate k_q of quenching by appropriate energy acceptors. The pseudo-first-order decay of triplet DBA was monitored (420 nm) at various dye concentrations. Any contribution from T–T annihilation was corrected by analyzing the data as competing pseudo-first-order and second-order processes. The specific rate of pseudo-first-order decay increased linearly with increased dye concentration:

$$k_d = k_i + k_q[\text{dye}] \qquad (1)$$

where k_d represents the observed rate of triplet decay, k_i represents the intrinsic rate constant for decay of the dye triplet state, and k_q represents the rate constant for triplet self-quenching. Values for k_q determined from the plots of the decay rate *versus* dye concentration (4.5×10^9 M^{-1} s^{-1} for **1** and 3×10^9 M^{-1} s^{-1} for **2**) were close to the diffusion-controlled rates (Table 2). The high rate constants for energy transfer from triplet DBA to the croconate dyes indicate that the triplet energies of these dyes must be less

TABLE 2

Sensitization of triplet croconate dyes with 9,10-dibromoanthracene in ethanol

Dye[a]	[PVP] (M)	*Specific rate k_q of quenching of sensitizer*[a] ($\times 10^9$ M^{-1} s^{-1})	*Specific rate k_i of intrinsic decay* ($\times 10^4$ s^{-1})
—	0	—	6.6[b]
—	0.01	—	6.5[b]
1	0	4.5	1.45
1	0.01	2.0	7.5
1	0.01[c]	6.5	2.2
2	0	3.0	4.1
2	0.01	0.94	2.8

[a] In 10^{-4} M DBA.
[b] Refers to DBA.
[c] In the presence of 0.2 M H_3PO_4.

than that of the sensitizer (169 kJ mol^{-1}), *i.e.* the energy transfer is exothermic.

Values of k_q were reduced by a factor of 2 - 3 in the presence of 10^{-2} M PVP. Alteration of the energetics of the excited states of the dye caused by hydrophobic interactions with the polymer is a probable explanation for this effect. However, the segmental diffusion of the polymer chain (to which the dye molecules are physically attached) could well contribute to the observed decrease in the effective diffusion of the dye in ethanol solution.

Unlike the triplet croconate dyes, neither the lifetime nor the T–T absorption spectrum of DBA itself was affected by the presence of PVP in neat ethanol. We conclude therefore that hydrophobic interactions between DBA and PVP are minimal.

Experiments were also performed to evaluate the importance of ground state quenching of the triplet states of the dyes. Ground state quenching involving up to 50% electron transfer efficiency has been reported for oxazine and thiazine dyes [8, 9]. With our dyes, very little variation in the specific rate of pseudo-first-order decay of dye triplets was seen upon increasing the ground state dye concentration. Our analytical method allows us, in fact, to establish an upper limit of 10^7 M^{-1} s^{-1} for the rate constant for such quenching. Apparently, polymer microencagement also protects excited states from diffusional or aggregational self-quenching.

Some irreversible changes (5% - 10%) in these dyes could be seen after flash excitation, but no product isolation has been attempted. As previously reported [1], these dyes are sensitive to hydrolysis, the rate of which is enhanced during steady state irradiation. However, the presence of polymer in the ethanolic solution retarded these irreversible changes, again highlighting the protection afforded to excited states by the encaging polymer.

3. Conclusions

Both singlet and triplet excited states of highly absorptive croconate dyes are stabilized by microencagement by a dissolved polymer. Further studies of the spectroscopic properties of molecules in a polymer matrix may lead to improved dye stability in a number of important applications.

Acknowledgment

This research was supported by the U.S. Department of Energy, Division of Chemical Sciences, Fundamental Interactions Branch. The use of the equipment at the Center for Fast Kinetics Research, a facility supported by the National Institutes of Health and by the University of Texas at Austin, is greatly appreciated. We sincerely thank Dr. A. J. Fatiadi for samples of the croconate dyes. M.A.F. is grateful for support as an Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar.

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