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The concentration dependence of the normalized photostability of 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597) methanol solutions

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Abstract

The concentration invariance of *normalized photostability,*the accumulated energy needed for a 50% reduction in dye concentration in units of GJ mole^{-1}, is investigated for 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597) methanol solutions. Normalized photostability is purported to be concentration invariant. Result from this investigation, however, demonstrated increasing normalized photostabilities for decreasing concentrations, rendering normalized photostability inapplicable to PM-597 photodegradation.

Keywords: Laser dye; Normalized photostability; Photodegradation; Photooxidation; Pyrromethene difluoroborate complex; Singlet oxygen

1. Introduction

Pyrromethene dyes have been used extensively in liquid and solid-state dye lasers due to low intersystem crossing rates and low triplet–triplet absorption resulting in high fluorescence quantum yields [1]. Pyrromethene-based dye lasers provide tunable laser light from the near infrared to the near ultraviolet region.

Dye laser operation lifetimes are limited by dye photostability. Pyrromethene dye photostability is governed by a singlet oxygen mediated type II photooxidation described by Eqs. (1)–(7), where D is the pyrromethene difluoroborate laser dye and $(+h\nu)$ denotes radiative and nonradiative relaxation [2–5].

$$D + h\nu \xrightarrow{k_1} {}^1D^* \tag{1}$$

$$ {}^1D^* \xrightarrow{k_2} D(+h\nu) \tag{2}$$

$$ {}^1D^* \xrightarrow{k_3} {}^3D \tag{3}$$

$$ {}^3D + {}^3O_2 \xrightarrow{k_4} D + {}^1O_2 \tag{4}$$

$$ {}^1O_2 + D \xrightarrow{k_5} \text{products} \tag{5}$$

$$ {}^1O_2 + D \xrightarrow{k_6} {}^3O_2 + D \tag{6}$$

$$ {}^1O_2 \xrightarrow{k_7} {}^3O_2(+h\nu) \tag{7}$$

To characterize pyrromethene dye laser photostability Rahn and coworkers developed the concept of *normalized photostability* as a universal measure of photostability independent of dye concentration and laser power [1,2,6]. Other researchers have applied this concept to rhodamine and perylene laser dyes [7,8]. Normalized photostability is a particular value of the *normalized input energy,* "the total accumulated pump energy on the laser cavity per mole of dye molecules contributing to laser action" in units of GJ mole^{-1} [2]. A previous investigation of optically thick samples (samples with complete absorption of the laser energy) in which the decrease of the pyrromethene dye fluorescence was measured with accumulated laser pulses as a function of concentration demonstrated higher dye half-lives for lower concentration [3]. This is contrary to normalized photostability, which predicts lower dye half-lives for lower concentrations for optically thick samples. In that study, however, the experimental arrangement was, such that fluorescence was not proportional to concentration, precluding accurate kinetic modeling. In

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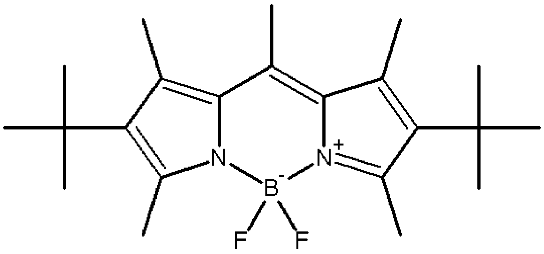

Fig. 1. 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597).

this study the concentration dependence of pyrromethene dye photodegradation is determined via absorbance measurements in order to evaluate the concentration invariance of normalized photostability. The dye selected for study is 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597) shown in Fig. 1. This was preferred over the commonly used 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-difluoroborate complex (PM-567) due to it's higher absorption coefficient at 532 nm resulting in faster photodegradation suitable for practical irradiation times.

2. Experimental

1,3,5,7,8-Pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex was purchased from Exciton and used without further purification. Several PM-597/methanol solutions ranging from 3.26×10^{-6} to 1.92×10^{-5} M were prepared from ultimar grade methanol (Aldrich). Quartz cuvettes (1 cm) containing 1.0 ml of PM-597 solution were irradiated by the second harmonic of a Nd:YAG laser (10 Hz, 103 mJ cm^{-2} per pulse). Absorbance spectra were recorded following irradiation of the samples for given time intervals and measured with a diode array ultraviolet–visible spectrophotometer.

3. Results and discussion

Fig. 2 shows the absorption spectra for the 1.28×10^{-5} M PM-597/methanol solution with a maximum at 522 nm that decreases for increasing laser pulses. For the region of the absorption spectra where $\lambda > 450$ nm the steady decrease of absorbance with increasing laser pulses suggests photobleaching in which there is minimal absorption in this spectral region by the photoproduct. This is consistent with a previous investigation of PM-597/methanol and PM-597/2-butanone solutions both showing a steady decrease of fluorescence with increasing 532 nm laser pulses [9]. Thus for the present experiment, photochemical reactions resulting from photoproduct absorption of 532 nm laser light need not be considered.

To obtain a measure of the relative photodegradation the normalized absorbance (A/A_0) at 522 nm versus accumulated laser pulses is plotted in Fig. 3.

It is apparent that solutions with higher PM-597 concentration have shorter absorbance half-lives. This is consistent with our previous PM-567 photodegradation investigation, in which higher photodegradation half-lives were observed for lower PM-567 concentrations via photoluminescence measurements [3]. To test the concept of normalized photostability for concentration invariance, the number of laser pulses is converted to normalized input energy,the accumulated laser pulses divided by moles of dye. The conversion

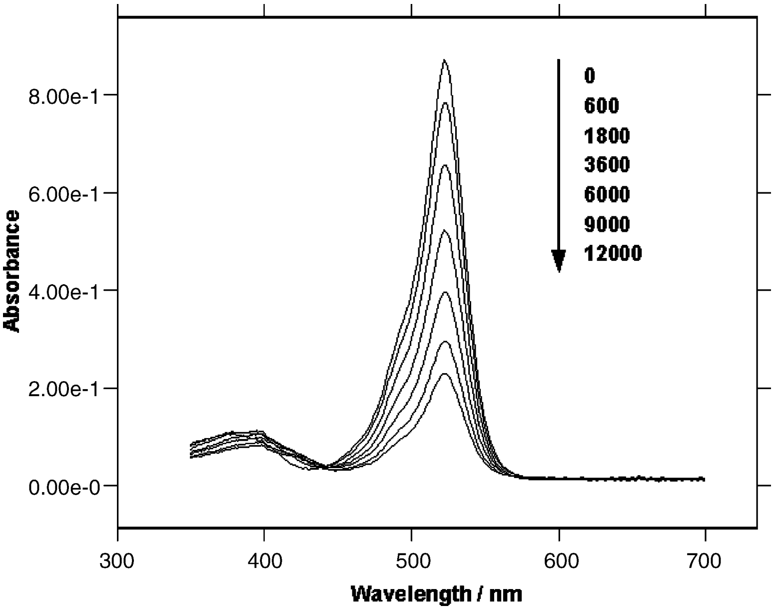

Fig. 2. Absorbance spectra of 1.28×10^{-5} M PM-597/methanol following 532 nm irradiation for a given number of laser pulses (103 mJ cm^{-2} per pulse) indicated by the numbers.

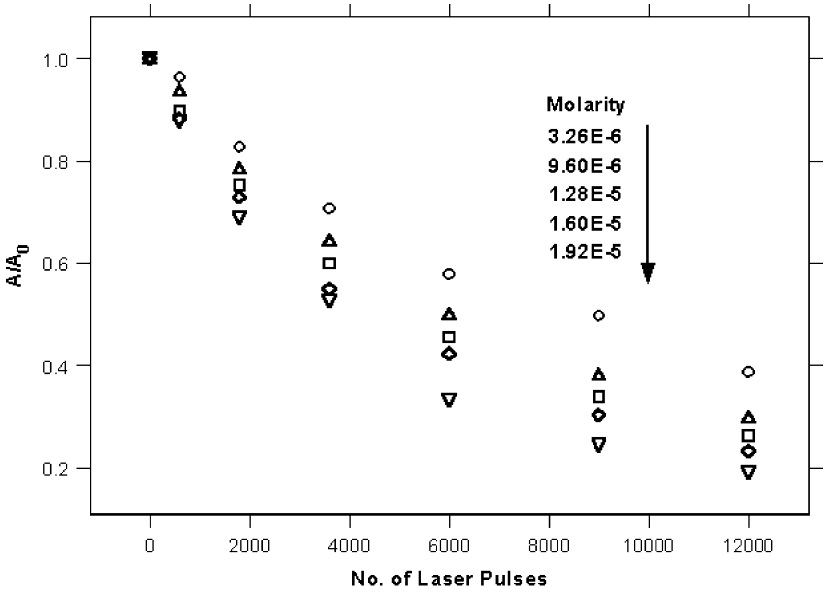

Fig. 3. Photodegradation concentration dependence via absorbance measurements at 522 nm. Dye concentrations: (○): 3.26 × 10^{-6} M, (△) 9.60 × 10^{-6} M, (□) 1.28 × 10^{-5} M, (◇) 1.60 × 10^{-5} M, (▽) 1.92 × 10^{-5} M.

of laser pulses to normalized input energies was carried out via the following procedure. For a given PM-597 dye concentration the 532 nm absorbance was determined at all 12,000 laser pulses by interpolation from the measured values at 0, 600, 1800, 3600, 6000, 9000, and 12,000 pulses via the following fitting function

$$\frac{1}{A} = \frac{1}{A_0} + kt \qquad (8)$$

A represents the absorbance and k is a fitting constant proportional to the apparent dye photodegradation rate constant. The justification for the fitting function will be presented below. These 12,000 absorbance values are converted into absorbed energy for a given laser pulse by

$$E_i = (1 - 10^{-A})i\text{th pulse laser energy} \qquad (9)$$

E_i is the energy absorbed by the sample for the ith laser pulse. Converting the E_i array into a cumulative sum array and dividing by the moles of dye in the cuvette yields an array of normalized input energies. The resulting plot of absorbance versus normalized input energy is presented in Fig. 4.

The normalized absorbance versus normalized input energy plot mirrors the same trend observed in Fig. 3, namely lower photodegradation half-lives for higher dye concentrations. The *normalized photostabilities*, the half-lives of the A/A_0 versus normalized input energy plots, are tabulated in Table 1.

It is evident that higher concentrations correlate to lower normalized photostabilities. This concentration dependence of normalized photostability is contrary to the claim of concentration invariance by Rahn et al. [2]. This concentration dependence echoes the decrease of photodegradation half-lives with increasing dye concentration. These concentration dependent half-lives are consistent with dye photodegradation kinetics second order in dye concentration. The observed second order dye photodegradation rate is given by Eq. (10), where k_{app} is the apparent photodegradation rate constant.

Table 1
Normalized photostability concentration dependence

Concentration (moles L^{-1})	Normalized photostability (GJ mole^{-1})
3.26 × 10^{-6}	24.6
9.60 × 10^{-6}	13.2
1.28 × 10^{-5}	10.1
1.60 × 10^{-5}	8.02
1.92 × 10^{-5}	6.02

$$\frac{[D]_0}{[D]} = 1 + [D]_0 k_{\text{app}} t \qquad (10)$$

For all dye concentrations Eq. (10) adequately models dye photodegradation as shown by the least-squares fits of Fig. 5.

The rationale for a second order-fit results from the self-sensitized photooxidation mechanism (Eqs. (1)–(7)). Employing the steady state approximation for all intermediates ($[^1O_2]$, $[^1D^*]$, and $[^3D]$), the rate expression Eq. (11) is obtained for the dye.

$$\frac{d[D]}{dt} = -\frac{k_5 k_3 k_1 [D]^2}{(k_2 + k_3)\{(k_5 + k_6)[D] + k_7\}} \qquad (11)$$

However $(k_5 + k_6)[D] << k_7$, [4,10] so this simplifies to Eq. (12)[1]

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[1] Unpublished preliminary work in our laboratory has shown approximate $(k_5 + k_6)$ values for pyrromethene laser dyes in methanol ranging from ~1 × 10^6 to 2 × 10^8 $M^{-1}\,s^{-1}$. For PM-597 concentration ≤1.92 × 10^{-5} M results in $(k_5 + k_6)[D] \leq 3.84 \times 10^3\,s^{-1}$.

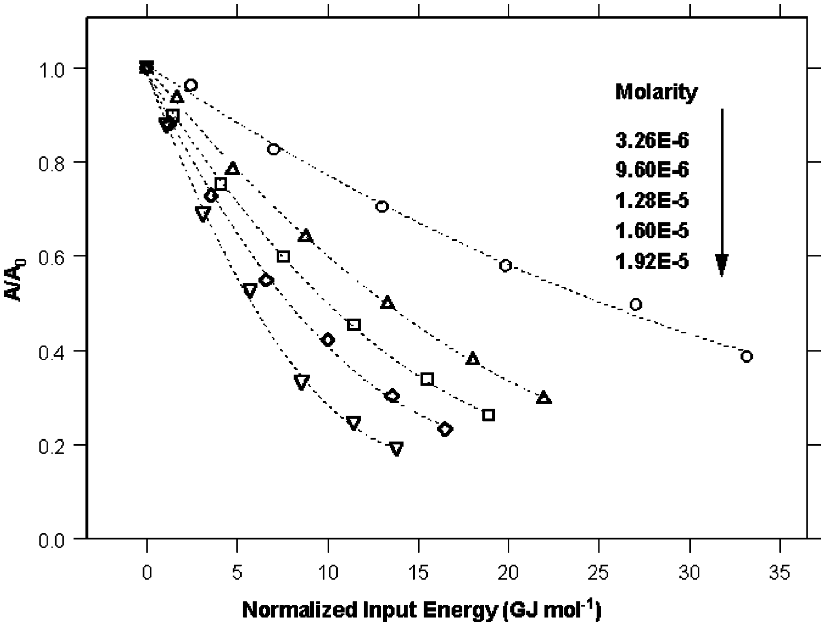

Fig. 4. Normalized input energy concentration dependence. The dashed lines represent second-order polynomial fits.

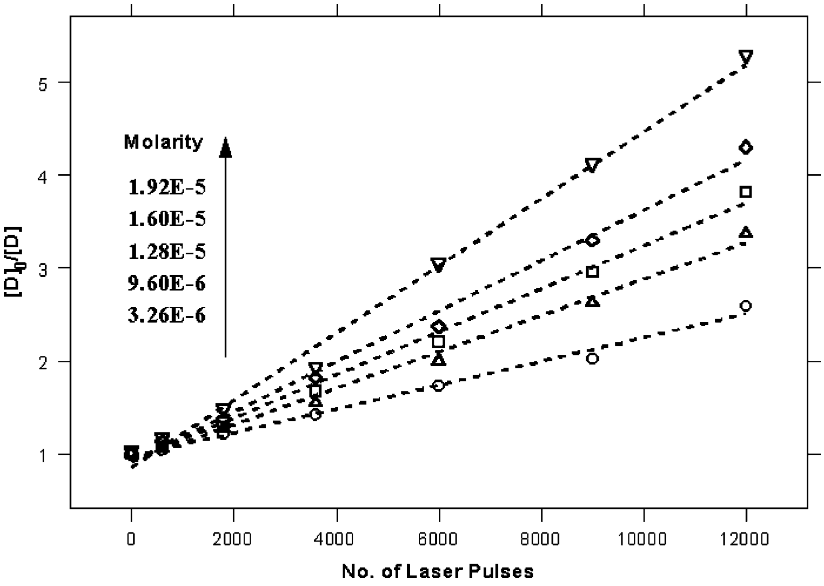

Fig. 5. Least-squares fit of PM-597 concentration vs. time according to $[D]_0/[D] = 1 + [D]_0kt$.

$$\frac{d[D]}{dt} = -\frac{k_5k_3k_1}{(k_2+k_3)k_7}[D]^2 = -k_{app}[D]^2 \qquad (12)$$

$$k_1 = \frac{\sigma I}{h\nu} \qquad (13)$$

I is the laser fluence in watts cm^{-2}, σ the dye absorption cross section, ν the frequency of laser light, and h the Planck's constant. Integration of this equation leads to

$$\frac{1}{[D]} = \frac{1}{[D]_0} + k_{app}t \qquad (14)$$

The half-life is given by

$$\tau_{1/2} = \frac{1}{[D]_0k_{app}} \qquad (15)$$

The inverse relationship between the photodegradation half-life and initial concentration predicted by Eq. (15) is illustrated in Fig. 5.

4. Conclusions

This investigation refutes the applicability of concentration invariant normalized photostability for the self-sensitized photooxidation of PM-597/methanol solutions with 532 nm laser light. Previous studies promoting the concentration invariance of normalized photostabilities of pyrromethene dyes failed to consider dye photooxidation kinetics, specifically the concentration dependent $^1O_2$ generation, which leads to second order dye photodegradation [1,2]. The observed second order dependence results in a decrease of $\tau_{\frac{1}{2}}$ with increasing concentration which manifests in the normalized photostability concentration dependence.

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