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Energy transfer and photodegradation of Perylene Red with DTTC and HITC acceptor dyes in PMMA

Chaevia Clendinen [a], Chaevien Clendinen [a], Wade N. Sisk [a,*], Hiromasa Nishikiori [b], Nobuaki Tanaka [b], Tsuneo Fuji [b]

[a] Chemistry Department, University of North Carolina at Charlotte, 9201 University City Blvd., Charlotte, NC 28223-0001, USA
[b] Department of Environmental Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

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Abstract

Energy transfer from Perylene Red to 1,1′,3,3,3′,3′-hexamethylindoletricarbocyanine iodide and 3,3′-diethylthiatricarbocyanine iodide in poly(methyl methacrylate) was investigated by monitoring the extent of fluorescence following irradiation with light of 532 nm. The measurements yielded information about the enhancement of HITC fluorescence induced by the dye, the energy transfer efficiency from the dye to HITC and the relative stability of the fluorescence of dye/HITC (DTTC)/PMMA films. The results of this study have important implications for near-IR emitting energy transfer dye lasers.

Keywords: Energy transfer; Perylene Red; Hexamethylindoletricarbocyanine iodide; Diethylthiatricarbocyanine iodide; Photodegradation; Infrared emission

1. Introduction

Infrared emitting laser dyes have been utilized in photonic devices for telecommunications; these devices exploit the dye's emission in the first transmission window of optical communication, 820–850 nm, where absorption losses of telecommunication fibers due to iron and water impurities are minimal [1]. An infrared emitting plastic waveguide utilizing the IR emitting colorant LDS821 was recently studied [2,3] and the colorant's infrared emission was enhanced by the addition of Perylene Orange in PMMA films following 532 nm irradiation [3]. It is believed that both radiative and nonradiative energy transfer from the dye to LDS821 occurred resulting in excitation of LDS821 as well as subsequent fluorescence ($\lambda_{max} = 750$ nm). This energy transfer and the 532 nm induced generation of infrared emission from dye/polymer films will be exploited in the present paper.

The cyanine dyes, 3,3′-diethylthiatricarbocyanine iodide (DTTC) and 1,1′,3,3,3′,3′-hexamethylindoletricarbocyanine iodide (HITC), shown in Fig. 1, quickly undergo vibrational relaxation to the $v = 0$ state of S_1 or isomerize to the spectroscopic twisted intramolecular charge-transfer state following visible irradiation [4].

The $S_1 \rightarrow S_0$ infrared emission of DTTC and HITC has better overlap with the first transmission window of optical communication in comparison to the infrared emission of LDS821. PMMA thin films containing Perylene Red (Fig. 2) and HITC (DTTC) fluorophore are expected to demonstrate significant energy transfer from the dye to HITC (DTTC) due to significant overlap of the absorption spectrum of HITC (DTTC) with the emission spectrum of Perylene Red as shown in Figs. 3 and 4. In the present paper, the efficiency of this energy transfer will be determined via measurements of Perylene Red fluorescence quenching and HITC (DTTC) fluorescence enhancement. Furthermore, relative dye photodegradation information will be obtained from the change in HITC (DTTC) fluorescence intensity with cumulative laser pulses for PMMA films containing the dyes.

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* Corresponding author. Tel.: +1 704 687 4433; fax: +1 704 687 3151.
E-mail address: wsisk@uncc.edu (W.N. Sisk).

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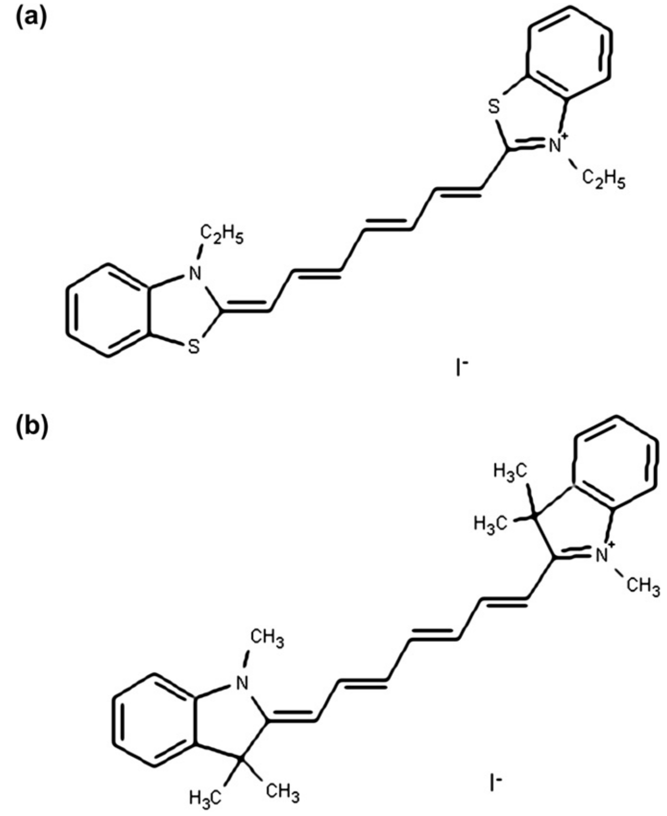

Fig. 1. (a) 3,3′-Diethylthiatricarbocyanine iodide (DTTC); (b) 1,1′,3,3,3′,3′-hexamethylindoletricarbocyanine iodide (HITC).

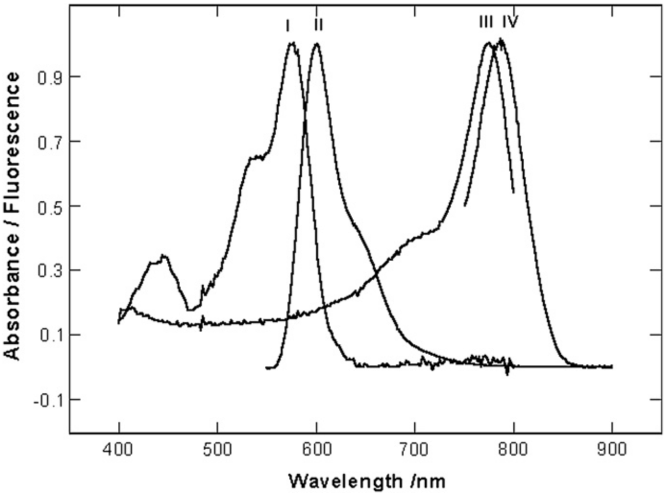

Fig. 3. I – Perylene Red absorbance; II – Perylene Red emission; III – DTTC absorbance; IV – DTTC emission (actually estimated from 7.14×10^{-3} M Perylene Red, 2.38×10^{-3} M DTTC).

2. Experimental

The laser dyes HITC, DTTC and Perylene Red were obtained from Exciton Inc. and were used without further purification. Poly(methyl methacrylate) (PMMA, average molar mass ~ 120,000) was obtained from Aldrich. Dye/PMMA/chloroform solutions were prepared by adding 20 ml of a dye/chloroform solution (prepared from various volume ratios of 2.00×10^{-3} M Perylene Red/$CHCl_3$ stock solution and 2.00×10^{-3} M acceptor dye/$CHCl_3$ stock solution) to 5 g of PMMA according to Table 1, where acceptor dye represents HITC or DTTC. Thin film samples were fabricated by spin casting (3000 rpm, 30 s) dye/PMMA/chloroform solutions onto glass 2.5 × 3.8 cm microscope slides. These films were dried in a vacuum oven for 20 h at 60 °C with an ultimate vacuum of 25 Torr resulting in films with an average thickness of approximately 6 μm. For each sample in Table 1 five films were fabricated. Reproducibility was determined by comparing film absorbance values of the five samples utilizing a PMMA film (sample no. 8) as the reference.

Mixed dye thin film samples suffered losses during fabrication as shown in Table 2. Acceptor dye concentrations for

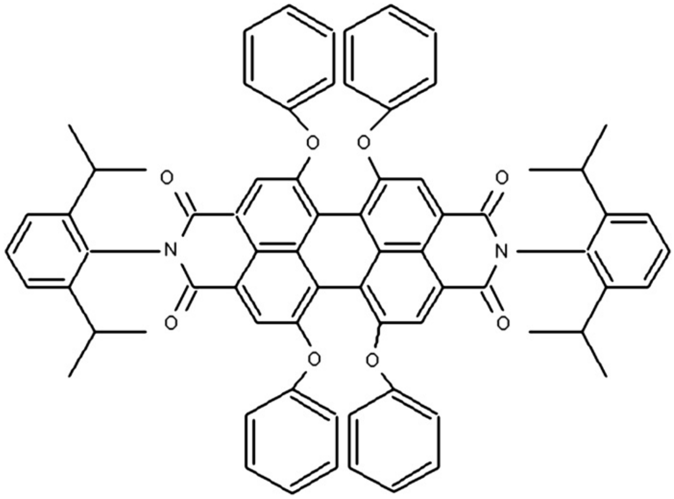

Fig. 2. Perylene Red.

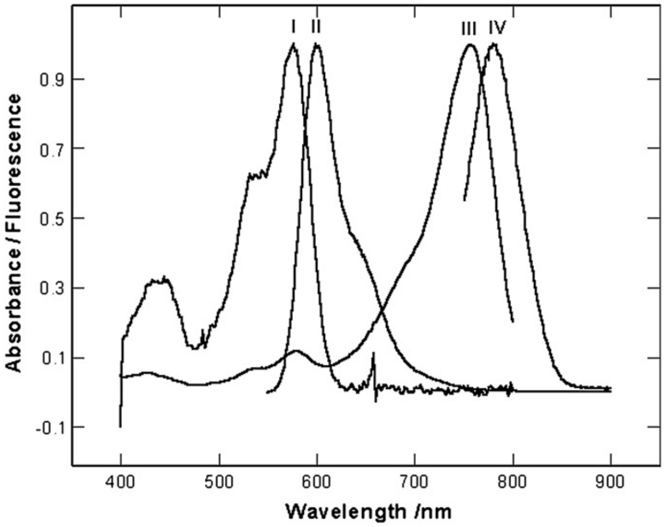

Fig. 4. I – Perylene Red absorbance; II – Perylene Red emission; III – HITC absorbance; IV – HITC emission (estimated from 7.14×10^{-3} M Perylene Red, 2.38×10^{-3} M HITC).

Table 1
Perylene Red/acceptor dye/PMMA thin films

Sample	Volume 2.00×10^{-3} acceptor/$CHCl_3$ (ml)	Volume 2.00×10^{-3} M Perylene Red (ml)	Volume $CHCl_3$ (ml)	Acceptor concentration in PMMA film (M)	Perylene Red concentration in PMMA (M)
1	5	0	15	2.38×10^{-3}	0
2	5	5	10	2.38×10^{-3}	2.38×10^{-3}
3	5	10	5	2.38×10^{-3}	4.75×10^{-3}
4	5	15	0	2.38×10^{-3}	7.14×10^{-3}
5	15	5	0	7.14×10^{-3}	2.38×10^{-3}
6	10	5	5	4.75×10^{-3}	2.38×10^{-3}
7	0	5	15	0	2.38×10^{-3}
8	0	0	20	–	–

samples 1–4 decreased 31–63% following vacuum oven drying as determined for absorbance measurements, at 774–800 nm for DTTC and at 758–800 nm for HITC. Higher Perylene Red concentrations resulted in a retardation of the photodegradation of DTTC and HITC. As illustrated in Figs. 2 and 3, as the absorbance spectrum of Perylene Red overlaps with HITC and DTTC, it was difficult to determine the extent of degradation of Perylene Red as a function of HITC and DTTC concentration in samples 5–8. Initial dye mole ratios prior to thermal degradation are cited in the results.

Energy transfer information was obtained from the fluorescence spectra of dye/PMMA thin films recorded using a Jobin Yvon Spex Fluorolog-3 spectrofluorimeter. Two types of samples were utilized namely an acceptor dye:

- using varying Perylene Red concentrations to determine the Perylene Red concentration-dependence of HITC (DTTC) fluorescence enhancement;
- a fixed Perylene Red employing varying acceptor dye concentrations to determine the quenching of Perylene Red fluorescence by the acceptor dye.

Photodegradation experiments were carried out by irradiating thin film samples with a Nd:YAG laser second harmonic (532 nm, 2–20 Hz, 8–50 mJ cm^{-2} $pulse^{-1}$) and collecting the waveguided fluorescence orthogonal to the laser propagation axis using an *f*/1 lens. This fluorescence was imaged onto a monochromator equipped with a germanium photodiode ($\lambda_{emission} > 800$ nm). The detector output was integrated and averaged via a digital oscilloscope or a boxcar integrator. For samples under vacuum a special o-ring joint cell was utilized, as described previously [3].

3. Results and discussion

DTTC and HITC fluoresce in the near-IR (750–850 nm). The absorbance values of DTTC and HITC at 532 nm were minimal compared to that of Perylene Red. It is proposed that Perylene Red absorbs a 532 nm photon and transfers energy to HITC (DTTC) leading to an enhancement in near-IR fluorescence compared to HITC (DTTC) devoid of Perylene Red. The maximum of the near-IR fluorescence occurred around 790 nm for DTTC and near 780 nm for HITC. The enhancement of the fluorescence of DTTC and HITC are shown in Figs. 5 and 6. A quantitative analysis of fluorescence enhancement for DTTC and HITC for increasing Perylene Red concentration is shown in Table 3. The addition of Perylene Red to HITC/DTTC in PMMA resulted in a 100-fold enhancement in near-IR fluorescence. A comparable system of UV/visible to IR energy transfer consisting of coumarin-2 donor and a perylene dendrimer acceptor demonstrated a 6.2-fold increase in near-IR fluorescence (700–850 nm) [5].

Figs. 7 and 8 show the quenching of Perylene Red fluorescence upon the addition of DTTC and HITC. The Perylene Red fluorescence maximum occurred at about 600 nm.

The transfer efficiency (η) at 600 nm is tabulated for increasing DTTC and HITC concentrations in Table 4. These are calculated according to Eq. (1) where I_D is the fluorescence intensity of the donor (Perylene Red) for dye/PMMA films and I_{OD} is the fluorescence intensity of the donor for PMMA films containing only the donor [1,2].

$$\eta = 1 - \frac{I_D}{I_{OD}} \tag{1}$$

Table 2
Thermal degradation of HITC and DTTC

Sample	Perylene Red concentration (M)	Initial HITC/DTTC concentration (M)	HITC concentration after vacuum oven drying (M)	DTTC concentration after vacuum oven drying (M)
1	0	2.38×10^{-3}	1.10×10^{-3}	8.79×10^{-4}
2	2.38×10^{-3}	2.38×10^{-3}	1.43×10^{-3}	1.05×10^{-3}
3	4.75×10^{-3}	2.38×10^{-3}	1.54×10^{-3}	1.16×10^{-3}
4	7.14×10^{-3}	2.38×10^{-3}	1.65×10^{-3}	1.32×10^{-3}

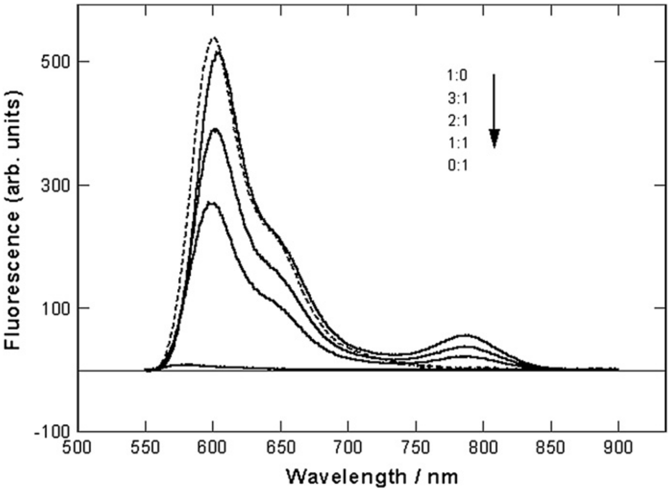

Fig. 5. DTTC fluorescence as a function of Perylene Red/DTTC mole ratio dispersed in PMMA. The DTTC concentration is 2.38×10^{-3} M.

As expected the transfer efficiency increased with increasing acceptor dye concentration.

From Tables 3 and 4, DTTC displayed more effective fluorescence enhancement with increasing concentration, whereas HITC demonstrates a more effective transfer efficiency.

The photodegradation of DTTC/Perylene Red/PMMA and HITC/Perylene Red/PMMA under ambient conditions are shown in Figs. 9 and 10, respectively. The 620 nm fluorescence increases with laser pulses, in contrast to the slight decrease of 800 nm fluorescence with cumulative laser pulses. This disparity of fluorescence time behavior may be understood by determining the relative contributions of Perylene Red and HITC (DTTC) at each wavelength. The contrast of the fluorescence spectra of acceptor dye/PMMA and Perylene Red/PMMA films of Figs. 5 and 7 suggests that the fluorescence at 620 and 800 nm of Figs. 9 and 10 can be attributed to Perylene Red and acceptor dyes, respectively.

Table 3
Fluorescence enhancement

Perylene Red/acceptor dye initial mole ratio[a]	DTTC relative fluorescence at 790 nm	HITC relative fluorescence at 780 nm
0:1	1	1
1:1	52	45
2:1	88	68
3:1	130	100

[a] Acceptor dye 2.38×10^{-3} M.

The increase in the 620 nm fluorescence with cumulative laser pulses is consistent with the fast photodegradation of the acceptor dyes, quenchers of Perylene Red fluorescence, relative to Perylene Red. As the HITC and DTTC concentration decrease with increasing laser pulses, these are not available to quench the fluorescence of Perylene Red, thus leading to an initial rise in Perylene Red fluorescence. Previously a similar increase in Perylene Orange fluorescence with cumulative laser pulses was observed for PMMA films containing Perylene Orange donor and LDS821 acceptor dyes [3]. With continued laser irradiation, the rise in Perylene Red fluorescence was followed by a decrease due to Perylene Red photodegradation. The near-IR emission (800 and 820 nm) shown in Figs. 9 and 10 do not reveal a dramatic decrease in contrast to the dramatic fluorescence of the acceptor dye fluorescence recorded in a previous study of the Perylene Orange/LDS821 system [3]. The reason for this difference is not well understood; retardation of the decrease in IR fluorescence may possibly be attributable to IR fluorescence of photoproducts. Carboxylic bisimides are a common contaminant of the Perylene Red synthesis [6,7]. The peculiar photochemical behavior manifested in the IR region may be partially attributed to the photoproducts of these contaminants. Photodegradation thus far, has been described solely in terms of the dyes; however, dye induced PMMA photodegradation leading to fluorescence quenching products may also contribute to the observed photodegradation.

The photodegradation of Perylene Red/HITC mixed dye/PMMA films was further investigated under both vacuum

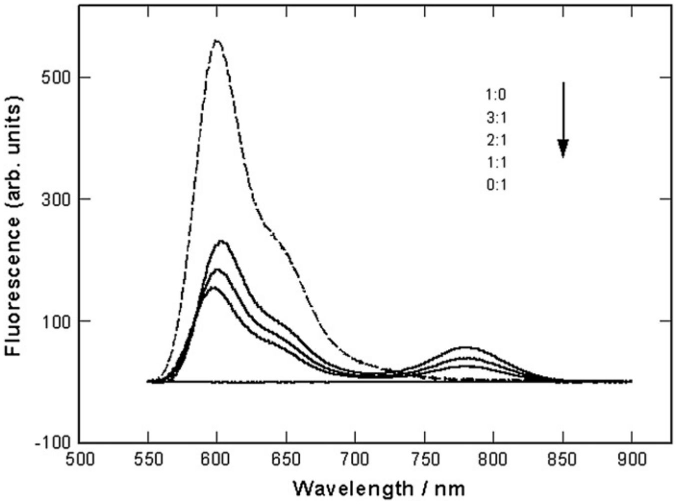

Fig. 6. HITC fluorescence as a function of Perylene Red/HITC mole ratio dispersed in PMMA. The HITC concentration is 2.38×10^{-3} M.

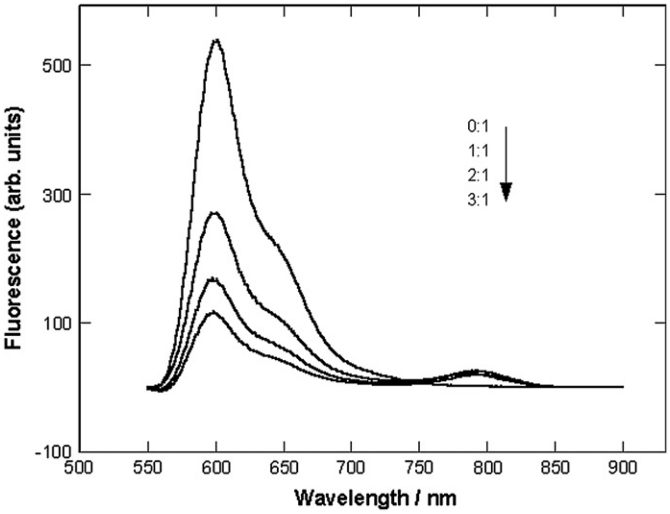

Fig. 7. Perylene Red fluorescence as a function of DTTC/Perylene Red mole ratio dispersed in PMMA. The Perylene Red concentration is 2.38×10^{-3} M.

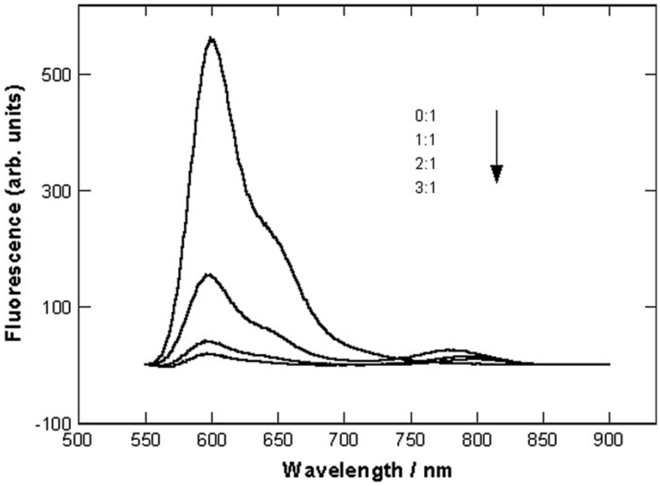

Fig. 8. Perylene Red fluorescence as a function of HITC/Perylene Red mole ratio dispersed in PMMA. The Perylene Red concentration is 2.38×10^{-3} M.

Table 4
Fluorescence quenching

Acceptor dye/Perylene Red mole ratio	DTTC transfer efficiency η (%)	HITC transfer efficiency η (%)
0:1	0	0
1:1	50	73
2:1	69	93
3:1	79	97

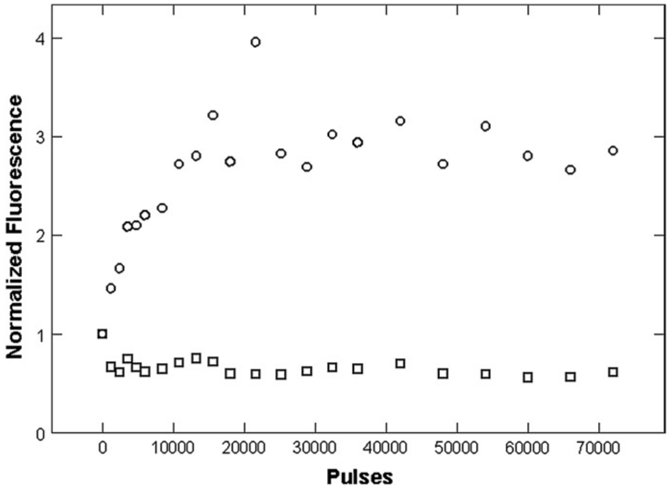

Fig. 9. Normalized fluorescence following a 532 nm irradiation (16 mJ cm^{-2} pulse^{-1} at 20 Hz) for 7.14×10^{-3} M DTTC/2.38×10^{-3} M Perylene Red/PMMA samples under ambient conditions. The circles and squares denote fluorescence observed at 620 and 800 nm, respectively.

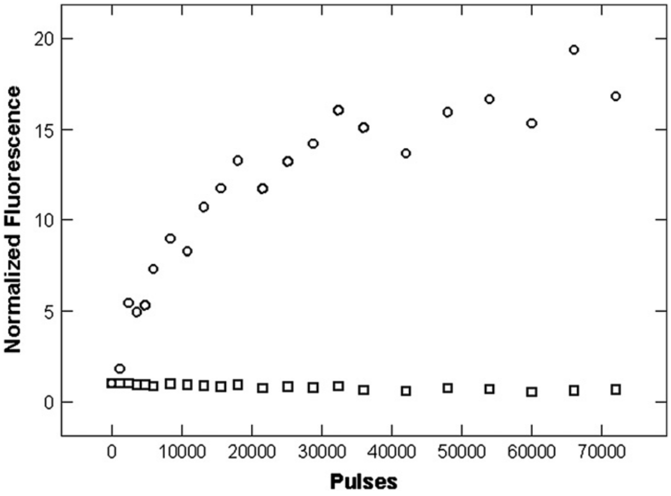

Fig. 10. Normalized fluorescence following a 532 nm irradiation (16 mJ cm^{-2} pulse^{-1} at 20 Hz) for 7.14×10^{-3} M HITC/2.38×10^{-3} M Perylene Red/PMMA samples under ambient conditions. The circles and squares denote fluorescence observed at 620 and 800 nm, respectively.

and ambient conditions. Fig. 11 shows Perylene Red fluorescence and HITC fluorescence as a function of 532 nm laser pulses for Perylene Red/HITC/PMMA films under vacuum and ambient conditions. The larger initial increase in Perylene Red fluorescence (640 nm) under ambient conditions relative to that under vacuum conditions can be ascribed to the photoreduction mechanism of Perylene Red photodegradation [8]. This is supported by the dramatic increase in Perylene Red fluorescence for Perylene Red/HITC/PMMA films subjected to 38,000 laser pulses under vacuum and subsequently exposed to the atmosphere. Very little difference was observed for HITC fluorescence in the cases of mixed films under vacuum and atmospheric conditions. Fig. 12 shows a slightly faster decrease in the 860 nm fluorescence of HITC/PMMA films under vacuum relative to ambient conditions as a function of 532 nm laser pulses. This monotonic decrease in IR fluorescence with cumulative laser pulses for HITC/PMMA films contrasts with the seemingly constant IR fluorescence intensity of HITC/Perylene Red/PMMA films, consistent with the IR

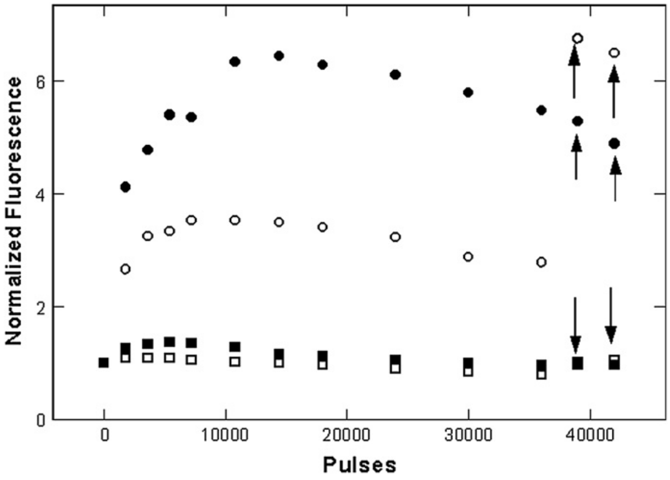

Fig. 11. Normalized fluorescence following a 532 nm irradiation (31 mJ cm^{-2} pulse^{-1} at 10 Hz) for 2.38×10^{-3} M HITC/2.38×10^{-3} M Perylene Red/PMMA samples under ambient (●, ■) and under vacuum (○, □) conditions. The circles and squares denote fluorescence observed at 640 and 820 nm, respectively. The last two points (↑) designate fluorescence collected for vacuum samples exposed to the atmosphere and optically blocked for 5 and 10 min for vacuum samples and ambient samples optically blocked for 5 and 10 min.

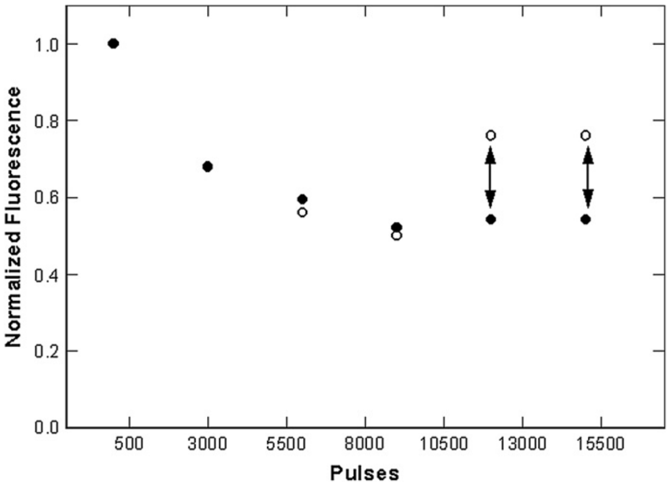

Fig. 12. Normalized 860 nm fluorescence following a 532 nm irradiation (142 mJ cm^{-2} pulse^{-1} at 2 Hz) for 4.75×10^{-3} M HITC/PMMA samples under ambient (●) and vacuum (○) conditions.

fluorescence of photoproducts and/or Perylene Red. Upon exposure to the ambient atmosphere, HITC/PMMA films irradiated under vacuum demonstrated a dramatic increase in 860 nm fluorescence relative to samples irradiated under ambient conditions. This observed increase upon air exposure can possibly be attributed to oxidation of the HITC anion to HITC. This shows that the photodegradation of HITC contains a component of reversible photoreduction.

4. Conclusions

A dramatic enhancement of near-IR fluorescence was observed upon the addition of Perylene Red to PMMA films containing HITC or DTTC following 532 nm irradiation. This enhancement of near-IR fluorescence and the accompanying decrease in Perylene Red fluorescence can be attributed to efficient energy transfer from Perylene Red to HITC (DTTC). A further manifestation of this energy transfer is the observation of an initial rise of Perylene Red emission with cumulative 532 nm laser pulses of the Perylene Red/PMMA films containing HITC (DTTC), due to the rapid photodegradation of HITC and DTTC, Perylene Red fluorescence quenchers. The similarity of the decrease in fluorescence with laser irradiation under both vacuum and ambient conditions and the large recovery of fluorescence intensity upon air exposure of evacuated irradiated HITC/PMMA films suggests that HITC photodegradation is partially attributed to reversible photoreduction. The slow decrease of HITC IR fluorescence bodes well for a future fabrication of an infrared emitting energy transfer dye laser based on HITC and Perylene Red.

Acknowledgments

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