

Energy transfer and photodegradation of Perylene Orange:LDS821 system in poly(methyl methacrylate)

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Abstract

The photodegradation and energy transfer of poly methyl methacrylate (PMMA) films containing Perylene Orange and LDS821 was investigated by luminescence detection following 532 nm excitation. Irradiation of Perylene Orange/LDS821/PMMA films resulted in (1) a maximum in the fluorescence vs. laser pulses photodegradation profile and (2) 400% fluorescence enhancement of the LDS821 fluorescence relative to LDS821/PMMA films. These observations are consistent with Perylene Orange to LDS821 Förster energy transfer with an energy transfer rate constant of $7.89 \pm 2.02 (2\sigma) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and a Förster critical radius of 48.3 Å. Half-quenching measurements confirmed Perylene Orange fluorescence quenching as Förster energy transfer.

1. Introduction

Infrared emitting laser dyes have been utilized in photonic devices for telecommunications due to their emission in the first transmission window of optical communications, 820 – 850 nm, where the absorption losses of telecommunication fibers due to iron and water impurities are minimal.¹

Recently an infrared emitting plastic waveguide was realized for the ionic infrared laser dye, 2-[[3-[2-[4-(dimethylamino)phenyl]ethenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene]methyl]-3-methylbenzothiazolium perchlorate (LDS821) by Kobayashi and coworkers.² When irradiated with 532 nm laser light ($165 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$, 10 Hz) an emission centered at 820 nm resulted in operational lifetimes of several thousand pulses and significant optical gain for planar waveguides composed of LDS821 dispersed in poly(1-vinyl-2-pyrrolidone). The infrared emission intensity decreased over time due to LDS821 photodegradation.

Organic light emitting diodes (OLEDs) consisting of LDS821 dispersed in poly(N-vinylcarbazole) exhibited an increase in electroluminescence with operation time under a constant bias.^{3,4} This was attributed to enhanced electron and hole injection caused by the alignment of the doped ionic dye molecules along the bias field. This was confirmed by noting a reduction of electroluminescence with time when a reverse bias was applied. This temporal decrease of electroluminescence may partially be attributed to LDS821 photodegradation.

The photosensitized LDS821 infrared emission has been accomplished by cascade energy transfer from other organic dyes.⁵ In this system 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) absorbs a 337 nm photon and nonradiatively transfers energy to Coumarin 490 (C490) and DCMII laser dyes, which subsequently transfers energy to LDS821. The resulting LDS821 infrared emission is much greater than LDS821/PBD films devoid of C490 and DCMII, since superior overlap is noted for the photoluminescence profiles of these dyes and LDS821 relative to PBD. This system effectively enhances LDS821 emission.

(Fig. 1)

In this report the photodegradation and Perylene Orange energy transfer is investigated for LDS821 dispersed in poly(methyl methacrylate) (PMMA). Both dyes absorb visible light consistent with their conjugated structure shown in Fig. 1. Relative to other laser

dyes including DCM dyes previously used in the energy transfer cascade, Perylene Orange has superior photostability.⁶ This LDS821/Perylene Orange/PMMA film serves as a NIR emitting waveguide utilizing 532 nm irradiation. This energy transfer photosensitization strategy for fabricating NIR emitting polymer/dye blends has been previously employed for organolanthanide emitters dispersed in polymers for 1.55 μm emission.⁷ Figure 2 shows significant overlap between the emission spectrum of Perylene Orange in PMMA and the absorption spectrum of LDS821 in PMMA, a necessary requirement for Förster energy transfer.

(Fig. 2).

2. Experimental

Laser dyes LDS821 and Perylene Orange were obtained from Exciton Inc. and used without further purification. Poly(methyl methacrylate) (PMMA, average molar mass \sim 120,000) was obtained from Aldrich Chemical Company. Thin film samples were fabricated by spin casting (3000 rpm, 30 seconds) dye/PMMA/chloroform solutions onto glass microscope slides. These films were heated to 60 $^{\circ}\text{C}$ for 20 hours under vacuum resulting in a thickness of 2.3 μm .

Photodegradation experiments were carried out by irradiating thin film samples with a Nd:YAG 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 with an $f/1$ lens. This fluorescence was imaged onto a monochromator equipped with either a photomultiplier tube or germanium photodiode for fluorescence less than or greater than 800 nm respectively. The detector output was integrated and averaged via a digital oscilloscope or a boxcar integrator. For samples under vacuum or in an O_2 atmosphere, a special o-ring joint cell was utilized as described in a previous report.⁸

The energy transfer information was obtained from fluorescence spectra of LDS821/Perylene Orange/PMMA thin films obtained by a Jobin Yvon Spex Fluorolog-3 spectrofluorimeter. Two types of samples were utilized: (1) fixed LDS821 with varying Perylene Orange to determine the enhancement of LDS821 fluorescence via Perylene Orange addition and (2) fixed Perylene Orange and varying LDS821 to determine the

quenching of Perylene Orange fluorescence by LDS821. Figure 2 below shows that the emission spectrum of LDS821 occurs from 600 to 850 nm, whereas Perylene Orange fluorescence occurs in the 500 – 650 nm range. For LDS821 fluorescence enhancement studies the dispersed emission spectrum was recorded utilizing 532 nm excitation for PMMA films containing 4.75×10^{-3} M LDS821 with varying amounts of Perylene Orange. A 560 nm cutoff filter utilized to minimize strong Perylene Orange fluorescence, since the primary aim was to record the 600 – 850 nm fluorescence. For Perylene Orange quenching experiments energy transfer parameters were obtained from measuring Perylene Orange fluorescence as a function of LDS821 concentration utilizing PMMA films containing 2.38×10^{-3} M Perylene Orange. These dispersed emission spectra utilized an excitation wavelength of 526 nm and the 560 nm filter was removed to obtain an accurate Perylene Orange fluorescence profile.

3. Results and discussion

A. Photodegradation

The oxygen dependence of LDS821/PMMA photodegradation is illustrated in Figure 3. A four-fold increase in the photodegradation half-life is observed for LDS821/PMMA films under vacuum relative to those in a 245 Torr oxygen atmosphere. The small partial recovery of fluorescence for the vacuum samples subsequently exposed to atmosphere (“vented”) shows a small contribution of LDS821 reversible photoreduction to photodegradation similar to that previously observed for Perylene diimide dyes,⁷ although photooxidation seems to predominate.

(Fig. 3)

The photodegradation of mixed dye films was carried out by irradiating LDS821/Perylene Orange/PMMA films at 532 nm and monitoring the fluorescence at

580 and 750 nm. Fluorescence at 580 nm was solely attributed to Perylene Orange, whereas fluorescence at 750 nm was attributed to LDS821. Figure 4a shows the oxygen dependence of photodegradation of these films.

(Fig. 4)

Photooxidation predominates for the LDS821 component (■,□) as evidenced by a faster decay for the ambient samples, similar to LDS821/PMMA films discussed earlier. A recovery is observed upon venting the vacuum samples for both components, indicative of reversible photoreduction. Fluorescence of the Perylene Orange component (●,○) rises with irradiation time. Note this is fluorescence is normalized to the initial fluorescence. The faster rise of the ambient sample Perylene Orange fluorescence over the vacuum sample is consistent with the previously reported photoreduction mechanism of Perylene Orange photodegradation.⁸ What is the mechanism for the increase the fluorescence of the Perylene Orange component with irradiation time?

To answer this question the normalized 580 nm fluorescence was recorded as a function of laser pulses for both LDS821/Perylene Orange/PMMA (○) and Perylene Orange/PMMA (□) films as shown in Figure 5. Fluorescence from Perylene Orange/PMMA decreases with time, attributed to the photodegradation of Perylene Orange. The upper curve shows a relative increase of Perylene Orange fluorescence with time, attributed to the photodegradation of LDS821, which serves a quencher of Perylene Orange fluorescence. Prior to normalization (initial intensity set equal to one), a stronger 580 nm fluorescence intensity was observed for the Perylene Orange/PMMA sample relative to that of mixed film sample, suggesting quenching of Perylene Orange fluorescence by LDS821. However, the sample positioning was such that the fluorescence intensities could not be quantitatively compared, hence the use of normalized initial intensities. However, the normalized Perylene Orange emission from Perylene Orange/LDS821/PMMA could be scaled for quenching by LDS821 based upon the quenching rate constant discussed later in this report. Essentially this involves multiplying the initial normalized intensity by $(1 + k_{ET}\tau_{OD}[A])^{-1}$, defined below, resulting in the lower curve in Fig. 5. Thus, the 580 nm Perylene Orange fluorescence is not

enhanced, but simply recovers from the initial quenched fluorescence with increasing laser pulses. The overlap of Perylene Orange fluorescence and LDS821 absorption shown in Fig. 2, provides the necessary condition for radiative and nonradiative energy transfer from Perylene Orange to LDS821.

(Fig. 5)

Perylene Orange fluorescence resulting from 532 nm irradiation of LDS821/Perylene Orange/PMMA was measured as a function of laser fluence. The results are illustrated in Figure 6.

(Fig. 6)

At low laser fluence, LDS821 is degraded with a slower degradation of Perylene Orange resulting in a slow rise and an even slower decay in the 580 nm fluorescence with irradiation time. With increased laser fluence, LDS821 undergoes rapid destruction while Perylene Orange undergoes a slower destruction, resulting in earlier attainment and lower intensity for the 580 nm fluorescence maximum. This is consistent with LDS821 quenching of Perylene Orange 580 nm fluorescence.

To determine the effect of Perylene Orange on LDS821 photodegradation, the photodegradation rates of LDS821/PMMA films with various amounts of Perylene Orange were compared in Figure 7. The photodegradation half-lives are 14400, 36480, and 30857 pulses for 4.75×10^{-3} M LDS821/PMMA samples with 0 M, 1.9×10^{-3} M, and 1.42×10^{-2} M Perylene Orange respectively. A similar acceptor half-life extension via donor addition was previously reported for Perylene Red upon addition of donors coumarin 440 and 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene difluoroborate complex (P567).⁹ The transmitted 532 nm laser light for samples containing 1.9×10^{-3} M and 1.42×10^{-2} M Perylene Orange are 87% and 63% respectively. Since both samples yield essentially the same half-life, the apparent LDS821 half-life extension upon Perylene Orange addition may not be adequately explained by the *filter effect*, i.e.

attenuation of laser light. The increased LDS821 photostability might be attributed to $^1\text{O}_2$ quenching and/or radical scavenging by Perylene Orange.

(Fig. 7)

B. Enhanced LDS821 Fluorescence

Dispersed emission spectra of LDS821/Perylene Orange/PMMA films as a function of Perylene Orange concentration are displayed in Figure 8. Unlike previous results of Su et al.⁹ who reported a maximum in the Perylene red acceptor fluorescence for a given concentration of P567 donor dye, the LDS821 fluorescence continually increases as a function of Perylene Orange donor in the concentrations up to 10^{-2} M. Furthermore, the spectrum does not exhibit a blue shift in the maximum as reported for other dye mixture systems.¹⁰ The Perylene Red maximum for P567 concentration was attributed to donor self-quenching, so this suggests Perylene Orange does not undergo self-quenching to the same extent as P567. At 3:1 Perylene-Orange:LDS821 the relative fluorescence enhancement is 460% and 430% for 729 nm and 816 nm respectively. At these wavelengths there is no interference from P-Orange fluorescence and minimal LDS821 absorbance. This fluorescence enhancement exceeds that of the previously reported 226% fluorescence enhancement of Rhodamine B acceptor and Rhodamine 6G donor in PMMA for a 5:1 donor:acceptor ratio.¹⁰

(Fig. 8)

C. Fluorescence Quenching of Perylene Orange

To quantitatively characterize the energy transfer, dispersed emission spectra were recorded for LDS821/Perylene Orange/PMMA films consisting of 2.38×10^{-3} M Perylene Orange with varying LDS821 concentration. No change in the shape of the Perylene Orange absorption or fluorescence spectrum was observed upon addition of LDS821, which suggests no complex formation between LDS821 and Perylene Orange. From

these spectra the transfer efficiency (η) and transfer probability (P_{DA}) are tabulated in Table 1. These are calculated according to the formulae below where I_D is the fluorescence intensity of the donor (Perylene Orange) for donor-acceptor PMMA films; I_{OD} is the fluorescence intensity of the donor for PMMA films containing only the donor; τ_{OD} is the fluorescence lifetime of the donor; and [A] is the concentration of the acceptor (LDS821).^{9,10} As expected the transfer efficiency and transfer probability increase with increasing LDS821 concentration.

$$\eta = 1 - \frac{I_D}{I_{OD}} \quad (1)$$

$$P_{DA} = \frac{1}{\tau_{OD}} \left(\frac{I_{OD}}{I_D} - 1 \right) \quad (2)$$

Table 1. Energy transfer parameters for $\lambda_{\text{observation}} = 550 \text{ nm}$

LDS821:Perylene Orange	Transfer efficiency $\eta(\%)$	Transfer probability $P_{DA}(10^{-8} \text{ s}^{-1})$
6	83.3	13.9
4	75.5	8.56
2	69.3	6.27
0.8	54.5	3.33

The entries in Table 1 are average values obtained from the fluorescence spectra of four samples recorded for each LDS821:Perylene Orange composition.

The decrease of time-resolved Perylene Orange fluorescence with increasing LDS821 concentration in PMMA for 514 nm excitation resulted in an energy transfer rate constant of $5.19 \pm 0.75 (2\sigma) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, and a lifetime (τ_{OD}) of 1.378 ns as shown in Fig. 9. These values are comparable to the energy transfer of rate constant of $5.0 \pm 0.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ for the quenching of Perylene Orange by Perylene Red¹¹ but the lifetimes

are lower than the lifetime of Perylene Orange in PMMA of 3.6 ± 0.5 ns reported by Sharma.¹²

$$\frac{\tau_{OD}}{\tau_0} = 1 + k_{ET}\tau_{OD}[LDS821] \quad (3)$$

(Fig. 9)

Utilizing the energy transfer rate constants in Eq. (3) leads to half-quenching concentrations, $[A]_{1/2}$ of 1.40×10^{-3} M for the Perylene Orange fluorescence intensities. The Förster critical radius is the donor-acceptor distance at which donor decay and energy transfer occur at equal rates. This may be determined from the half-quenching concentration by¹³:

$$R_0 = \frac{7.35}{[A]_{1/2}^{1/3}} \quad (4)$$

This leads to R_0 values of 65.7 Å for the Perylene Orange-LDS821 energy transfer. To determine whether these values reflect the true Förster energy transfer process, R_0 was calculated from the spectral overlap of Perylene Orange fluorescence and LDS821 absorption. This calculation utilized the Perylene Orange fluorescence corrected for system response in PMMA, report by Sheridan *et al.*¹¹ a value of 1.490 for PMMA index of refraction, a value of 0.476 for the orientation factor,¹⁴ a value of 1.378 ns for the Perylene Orange fluorescence, a value of 0.85 for the Perylene Orange fluorescence quantum yield,¹¹ and a molar extinction coefficient of $2.97 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (determined at 582 nm in this laboratory for Perylene Orange PMMA films). These values served as the input for the *PhotochemCad* program¹⁵ to yield a calculated R_0 of 52.6 Å. Radiative energy transfer alone cannot account for the observed decrease in the Perylene Orange fluorescence lifetime with increased LDS821 concentration, since radiative energy transfer would affect only the donor fluorescence amplitude and not the decay lifetime.

Thus the energy transfer must be primarily attributed to a Dexter and/or Förster energy transfer. A Dexter energy transfer utilizes electron cloud overlap and thus is associated with R_0 values smaller than those of the Förster mechanism. The larger observed (half-quenching) value of R_0 relative to R_0 determined from the spectral overlap method suggests the contribution of Förster energy transfer rather than the Dexter transfer. Furthermore, the observed R_0 of 65.7 is consistent with a Förster energy transfer of 30-80 Å.

4. Conclusion

An enhancement of the fluorescence and photostability of LDS821 upon Perylene Orange addition demonstrates the feasibility of solid-state dye lasers and planar waveguide amplifiers active in the near infrared region fabricated from a polymer-dispersed mixture of these dyes. The enhancement of LDS821 fluorescence and the peculiar Perylene Orange emission versus the laser pulses “photodegradation” profiles are partially attributed to the energy transfer from excited Perylene Orange to LDS821. The LDS821 dependent modulation of Perylene Orange temporal fluorescence decay profiles and the half-quenching R_0 value suggest the Förster energy transfer as a major component of the Perylene Orange-LDS821 energy transfer. The Dexter energy transfer is deemed not to be a significant contributor to energy transfer, although radiative energy transfer may contribute.

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References

1. M. Ghioni, F. Zappa, V. P. Kesan, V. P., and J. Warnock, "A VSLI-compatible high-speed silicon photodetector for optical data link applications," *IEEE Trans. Electron Devices* **43**, 1054-1060 (1996).
2. T. Kobayashi, J. Savatier, G. Jordan, W. J. Blau, Y. Suzuki, and T. Kaino, "Near-infrared laser emission from luminescent plastic waveguides," *Appl. Phys. Lett.* **85**, 185-187 (2004).
3. H. Suzuki, "Self-enhancement in the electroluminescence of a near-infrared ionic dye," *Appl. Phys. Lett.* **76**, 1543-1545 (2000).
4. H. Suzuki, "Organic light-emitting materials and devices for optical communication technology," *J. Photochem. Photobiol. A: Chem.* **166**, 155-161 (2004).
5. M. Berggren, A. Dodabalapur, R. E. Slusher, and Z. Bao, "Light amplification in organic thin films using cascade energy transfer," *Nature* **389**, 466-469 (1997).
6. A. Dubois, M. Canva, A. Brun, F. Chaput, and J. Boilot, "Enhanced photostability of dye molecules trapped in solid xerogel matrixes," *Synthetic Metals* **81**, 305-308 (1996).
7. R. Pizzoferrato, L. Lagonigroa, T. Zillerb, A. Di Carlo, R. Paolesse, F. Mandoj, A. Ricci, and C. Lo Sterzo, "Forster energy transfer from poly(arylene-ethynylene)s to an erbium-porphyrin complex," *Chem. Phys.* **300**, 217-225 (2004).
8. N. Tanaka, N. Barashkov, J. Heath, and W. N. Sisk, "Photodegradation of Polymer-dispersed perylene diimide dyes" *Appl. Opt.* *to be published*.
9. D. Su, Y. Yang, G. Qian, Z. Wang, and M. Wang, "Influence of energy transfer on fluorescence and lasing properties of various laser dyes co-doped in ORMOSILs," *Chem. Phys. Lett.* **397**, 397-401 (2004).
10. G. A. Kumar, V. Thomas, G. Jose, N. V. Unnikrishnan, and V. P. N. Nampoori, "Energy transfer in Rh 6G:Rh B system in PMMA matrix under cw laser excitation," *J. Photochem. Photobiol. A: Chem.* **153**, 145-151 (2002).
11. A. K. Sheridan, A. R. Buckley, A. M. Fox, A. Bacher, A., D. D. C. Bradley, and I. D. W. Samuel, "Efficient energy transfer in organic thin films—implications for organic lasers," *J. Appl. Phys.* **92**, 6367-6371 (1992).

12. P. Sharma, "Polymeric thin films for integrated optics," Ph.D. dissertation (University of Durham, 1992).
13. N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, 1991.
14. R. S. Roller and M. A. Winnik, "The Determination of the Foerster Distance (R₀) for Phenanthrene and Anthracene Derivatives in Poly(methyl methacrylate) Films," *J. Phys. Chem. B* **109**, 12261-12269 (2005).
15. H. Du, R.-C. A. Fuh, J. Li, J., L. A. Corkan, and J. S. Lindsey, "PhotochemCAD: A computer-aided design and research tool in photochemistry," *Photochem. Photobiol.* **68**, 141-142 (1998).

Figure Captions

Fig. 1. (a) LDS821 (b) Perylene Orange.

Fig. 2. (i) Perylene Orange absorbance, (ii) Perylene Orange emission, (iii) LDS821 absorbance, and (iv) LDS821 emission.

Fig. 3. Normalized LDS821 fluorescence following 532 nm irradiation ($37 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 2 Hz, $\lambda_{\text{obs}} = 816 \text{ nm}$) for $4.75 \times 10^{-3} \text{ M}$ LDS821/PMMA samples in an oxygen environment (245 Torr) \circ and under vacuum \bullet . \blacksquare designates the normalized fluorescence for vacuum samples exposed to ambient atmosphere for 2 and 4 minutes following irradiation under vacuum. ----- designates 50% fluorescence decrease.

Fig. 4. Normalized fluorescence following 532 nm irradiation ($17 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 20 Hz) for $4.75 \times 10^{-3} \text{ M}$ LDS821/ $1.9 \times 10^{-3} \text{ M}$ Perylene Orange/PMMA samples under ambient conditions \bullet , \blacksquare and under vacuum \circ , \square . The circles and squares denote fluorescence observed at 580 and 750 nm respectively. The “exposed” points designate fluorescence collected for vacuum samples exposed to the atmosphere for 5 and 10 minutes.

Fig. 5. Normalized Perylene Orange fluorescence following 532 nm irradiation ($9 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 10 Hz, $\lambda_{\text{obs}} = 580 \text{ nm}$) for $4.75 \times 10^{-3} \text{ M}$ LDS821/ $2.38 \times 10^{-3} \text{ M}$ Perylene Orange/PMMA, \circ , and $2.38 \times 10^{-3} \text{ M}$ Perylene Orange/PMMA, \square . \bullet designates Perylene Orange fluorescence from $4.75 \times 10^{-3} \text{ M}$ LDS821/ $2.38 \times 10^{-3} \text{ M}$ Perylene Orange/PMMA in which the initial normalized intensity has been scaled to correct for $4.75 \times 10^{-3} \text{ M}$ LDS821 quenching.

Fig. 6. Normalized Perylene Orange fluorescence observed at 580 nm following 532 nm irradiation for $4.75 \times 10^{-3} \text{ M}$ LDS821/ $1.9 \times 10^{-3} \text{ M}$ Perylene Orange/PMMA, at 15 \bullet , 48 \square , and 95 \circ $\text{mJ cm}^{-2} \text{ pulse}^{-1}$ laser fluence.

Fig. 7. Normalized LDS821 fluorescence observed at 750 nm following 532 nm irradiation ($40 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$, 20 Hz) for $4.75 \times 10^{-3} \text{ M}$ LDS821/PMMA with 0 M (\blacktriangledown), $1.9 \times 10^{-3} \text{ M}$ (\circ) and $1.42 \times 10^{-2} \text{ M}$ (\diamond) Perylene Orange.

Fig. 8. LDS821 fluorescence as a function of Perylene Orange/LDS821 ratio dispersed in PMMA. The LDS821 concentration is $4.75 \times 10^{-3} \text{ M}$.

Fig. 9. Stern-Volmer plot of Perylene Orange fluorescence observed at 550 nm following 526 nm excitation for uncorrected (\circ) and corrected (\square) Perylene Orange fluorescence. Lines represent linear regression fits.

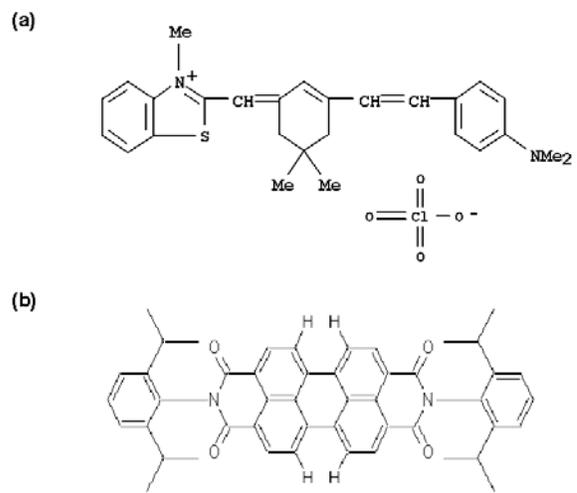


Fig. 1

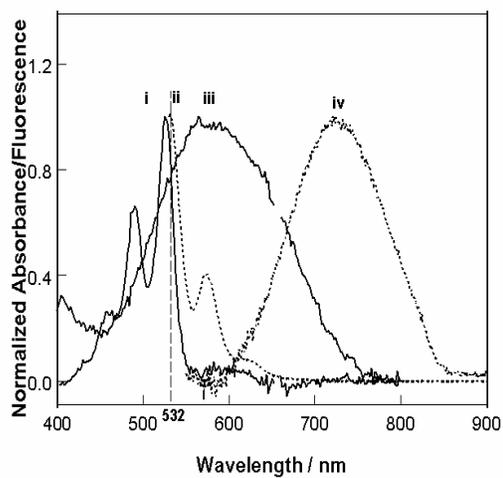


Fig. 2

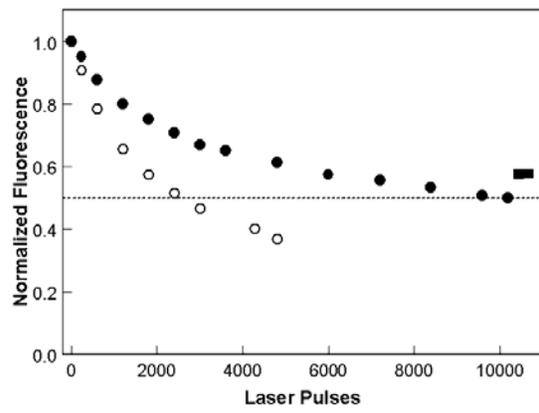


Fig. 3

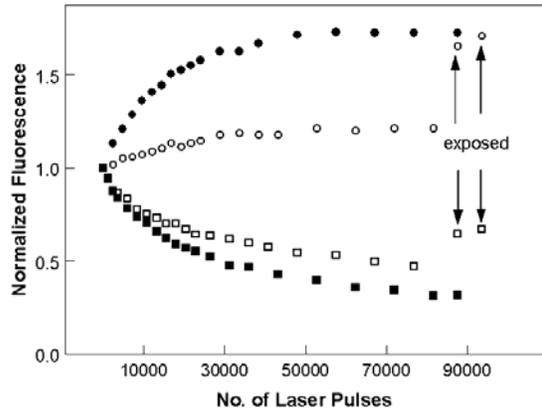


Fig. 4

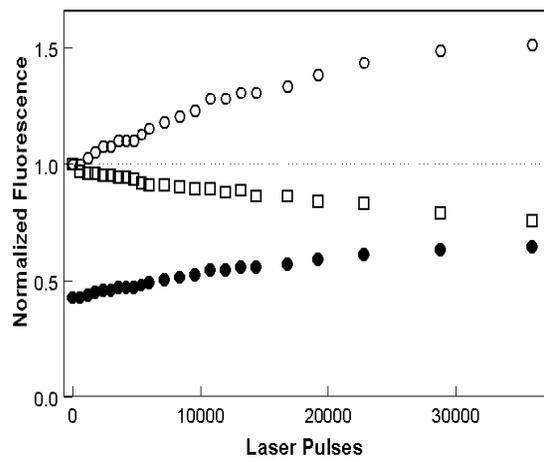


Fig. 5

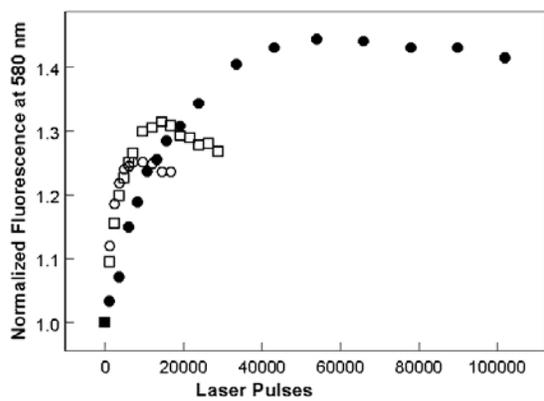


Fig. 6

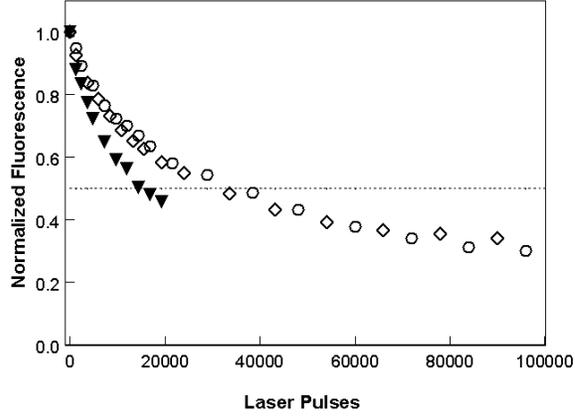


Fig. 7

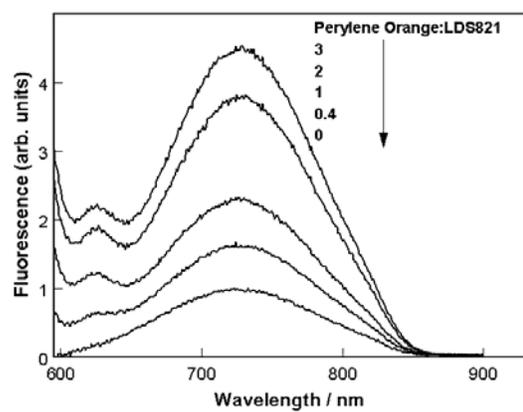


Fig. 8

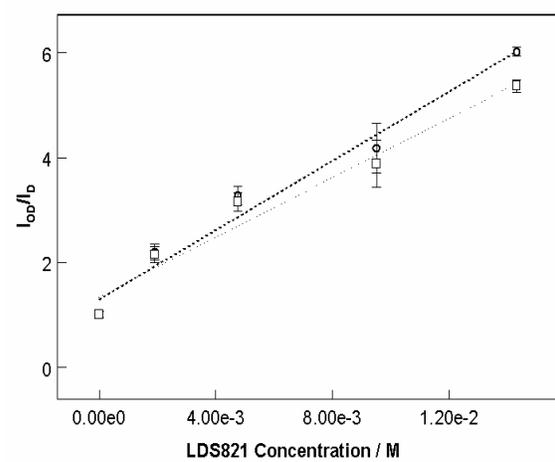


Fig. 9