

Photochemical & Photobiological Sciences

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Tuning the Concentration of Dye Loaded Polymer Films for Maximum Photosensitization Efficiency: Phloxine B in Poly(2-Hydroxyethyl Methacrylate)

Yair Litman,^a Hernán B. Rodríguez,^{*a,b} and Enrique San Román^{*a}

^a *INQUIMAE (UBA-CONICET) / DQIAyQF, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, Buenos Aires, Argentina*

^b *INIFTA (UNLP-CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Diag. 113 y Calle 64, La Plata, Argentina*

Corresponding Authors

* Enrique San Román, E-mail: esr@qi.fcen.uba.ar, Tel. +5411-4576-3378 Ext. 118, Fax +5411-4576-3341. Hernán Bernardo Rodríguez, E-mail: hernanrodriguez@inifta.unlp.edu.ar, Tel. +54221-425-7430 Ext. 130, Fax +54221-425-4642.

Abstract

Fluorescence and singlet molecular oxygen ($^1\text{O}_2$) quantum yields for Phloxine B loaded poly(2-hydroxyethyl methacrylate) thin films are determined at dye concentrations from 0.01 to 22 wt %. Fluorescence self-quenching and the fall off of the $^1\text{O}_2$ quantum yield observed above 0.1 wt % are attributed to very weakly interacting close-lying dye molecules acting as energy traps arising from molecular confinement. The maximum singlet oxygen generation efficiency (quantum yield \times absorption factor) lies at concentrations around 2 wt %, where fluorescence self quenching amounts to more than 80 %. Data are fitted quantitatively by a quenching radius model involving energy migration and trapping with $r_Q = 1.2$ nm. The present results constitute a proof of concept for the rational design of heterogeneous photosensitizers in general and, particularly, for applications in which the antimicrobial activity of singlet oxygen is central.

Introduction

Research on dye loaded polymer films covers different fields of practical interest as optical chemical sensing,¹ development of laser media,² high density optical data storage,³ security authentication,⁴ light trapping for water splitting devices,⁵ and singlet molecular oxygen ($^1\text{O}_2$) photosensitization,⁶ among others. For certain applications such as optical storage and photosensitization, small dye-to-dye distances or large absorbances, attainable at high concentrations, are required. However, interactions among dye molecules play a negative role in this case because chromophores lose their individuality and new channels for radiationless deactivation become operative. Eventually, organic dyes aggregate with formation of photochemically inactive dimers and oligomers. Interactions with the polymer backbone weaken ground state dye-to-dye interactions⁷ but they are generally ineffective in avoiding the coupling of excited state chromophores and ground state molecules. As a consequence, excitation energy trapping is produced also in cases where no dye aggregation is spectroscopically evidenced.⁸ As energy trapping increases at high loadings faster than the absorption factor,^{*} there is a practical dye concentration which maximizes energy exploitation. In spite of this, very few quantitative studies have been performed in polymers at different dye loadings in order to understand, and consequently to manage dye aggregation and energy wasting. Mirenda *et al.* studied Rose Bengal (RB) aggregation in polyelectrolyte aqueous alkaline solutions and layer-by-layer self-assembled thin films of positively charged poly[diallyldimethylammonium] chloride and negatively charged RB.⁹ At dye concentrations in the order of 1 M, though aggregation and energy trapping are unavoidable, measurable quantum yields of fluorescence, Φ_F , and singlet oxygen production, Φ_Δ , have been observed. A concentration dependence study was not possible in that case because self-assembly is ineffective at lower dye

* The absorption factor, also called absorptance, is the fraction of radiation absorbed by the film.

concentrations. Priimagi *et al.* investigated different polymers at high dye loadings and measured absorption spectral changes on increasing the dye concentration in order to evaluate dye aggregation.⁷ However, their results do not allow the quantification of energy wasting by dark excimer formation and other ways of energy trapping.

In this work, Phloxine B (PhB) was loaded into poly(2-hydroxyethyl methacrylate) (pHEMA), a bio-compatible polymer that forms hydrogels in water and, conveniently cross-linked, builds up hardly hydrolysable materials, which are mainly used in the production of contact lenses.^{10,11} PhB is a hydrophilic dye with low toxicity, used as a color additive in foods, drugs and cosmetic formulations, with $\Phi_{\Delta} = 0.65$ in water¹² and a low tendency to aggregation when included into microcrystalline cellulose particles.¹³ The dye is phototoxic for gram-positive and gram-negative bacteria,^{14,15} insects¹⁶ and individual cells of higher organisms.^{17,18} It is potentially useful for the prevention of endophthalmitis after cataract surgery through bonding to the surface of intraocular lenses, in analogy to the case of tetrakis(4-N-methylpyridyl)porphyrin, which was electrostatically bound to surface methacrylate groups of pHEMA-co-(methacrylic acid).¹⁹ Other possible application fields are the development of photoactive wound dressings for medicine and cosmetic applications and coatings for disposable materials, hospital doors and medical equipment, where the antimicrobial activity of singlet oxygen at the material surface is central.

Photophysical properties of PhB loaded pHEMA films, *i.e.* Φ_F and Φ_{Δ} , are determined as a function of dye concentration in order to obtain a practical concentration which maximizes the production of $^1\text{O}_2$. Results are interpreted in the context of a quenching radius model (QRM) and calculation of energy migration and trapping rates based on Loring, Andersen and Fayer (LAF) theory.^{20,21}

Experimental Section

Chemicals and preparation of films

Phloxine B disodium salt (PhB), certified dye purity 89 %, and poly(2-hydroxyethyl methacrylate) (pHEMA), 20000 KDa, density 1.15 g mL^{-1} at $25 \text{ }^\circ\text{C}$, were obtained from Sigma-Aldrich and used as received. Analytical grade ethanol and acetone from Biopack were used without further purification. Microscope slides were cleaned by ultrasonication in acetone, ethanol and water, 30 min in each solvent. Thin films were prepared by spin coating at increasing acceleration reaching an angular speed of 2500 rpm in 30 s, from 20 mg/mL or 30 mg/mL ethanolic solutions of pHEMA with different PhB concentrations, using a spin coater WS-400B-GNPP/Lite (Laurell Technologies). Reproducible thicknesses either of (150 ± 15) or (245 ± 15) nm were determined by stylus profilometry using a Dektak 150 Profilometer (Veeco). Thin films with PhB concentrations spanning more than three orders of magnitude, from 0.015 to 22 wt %, were prepared. Dye molar concentrations, needed for the calculation of absorption coefficients and application of the QRM, were calculated as $[\text{PhB}] = n\rho/m$, where n/m is the ratio between the number of moles of PhB and the mass of the film and ρ is its density. As a working approximation, valid at $n/m \rightarrow 0$, the mass and the density (1.15 g cm^{-3}) of the pure solid polymer were used. Within this approximation level,

$$[\text{PhB}] = (\rho \text{ wt \%} / M) / (100 - \text{wt \%}) \quad (1)$$

where M is the molar mass of PhB ($829.63 \text{ g mol}^{-1}$), leading to the concentration range 0.0002 to *ca.* 0.4 M. Thick films were prepared from the same solutions, depositing sequentially three layers over

microscope slides and evaporating the solvent at room temperature. Thicknesses of $16 \pm 3 \mu\text{m}$ were estimated assuming that the absorption coefficient is the same as in thin films. In all cases optically clear films were obtained.

Photophysical characterization

Absorption spectra were measured in a Shimadzu UV-3600 spectrophotometer. Measurements were performed by placing the film into a home-made holder which allows horizontal and vertical displacements in order to evaluate the absorption at different positions. Steady-state emission spectra were recorded on a PTI model QM-4 spectrofluorometer. Films were measured in back face with normal illumination ($\lambda_{\text{exc.}} = 505 \text{ nm}$) and a right-angle triangular prism (PS911 Thorlabs N-BK7) was used to drive emitted light into the detection channel. A suitable optical filter (Schott, OG515, 0.2 cm thickness) was positioned in front of the detector to block excitation stray light, which was further reduced changing the position of the emission lens. Spectra were corrected according to the dependence of the detection responsivity on wavelength obtained from the manufacturer and checked in our laboratory. Thin film Φ_{F} values were determined in reference to 0.5 – 1 μM PhB in ethanol in a 1 mm pathlength quartz cuvette, whereas the reference Φ_{F} values were determined against Rhodamine 101 in the same solvent. This setup was selected to avoid irreproducibility issues inherent to measurements in front face or back face when films are positioned angularly with respect to the normal to the excitation beam, which cause erratic quantum yield results. The difference in sample and reference geometries causes a negligible uncertainty in the measurement. Considering that pHEMA and glass have similar refractive indexes and according to Fresnel law for normal incidence, reflections at the two extra quartz-ethanol interfaces in the reference lead to an overestimation of Φ_{F} for the films in the order of only 0.5 %.

Determinations of singlet oxygen quantum yields were performed using 1,3-diphenylisobenzofuran (DPBF, Aldrich) in dichloromethane (DCM, Cicarelli, analytical grade) as a chemical monitor.^{22,23} The absorbance of DPBF was monitored at 415 nm. A 0.1 μ M Methylene Blue (Química Bonaerense, analytical grade) solution in DCM was used as reference ($\Phi_{\Delta} = 0.57$). A halogen lamp (OSRAM HLX 64657, 250 W, 24V) was used for illumination. A water filter and two glass filters (Schott, KG5, 0.2 cm thickness) were interposed between the lamp and the film in order to block the IR component of the light source. A second pair of filters (Schott, OG495 and OG515, 0.2 cm thickness) were used to avoid direct excitation of the monitor. The emission spectrum of the lamp and filter transmittance were taken into account in order to calculate the fraction of absorbed light. Experiments were carried out on dry and humidified films, the latter pretreated with a flow of water saturated oxygen.

Laser flash photolysis (LFP) measurements were performed on thick films. A Nd-YAG laser (Spectron, 8 ns @ 532 nm) and a horizontally driven Xe lamp (OSRAM XBO 150 W/1 OFR) were used for excitation and analysis, respectively. The film was placed inside a quartz cuvette in a LP920 laser flash photolysis compartment (Edinburgh Instruments) at an angle of 45° with respect to both light sources. Correct overlapping of both beams on the film surface was ensured. Two filters (Schott, GG475, 0.2 and 0.3 cm thickness) were placed in front of the film to block unwanted analysis light below 450 nm to avoid dye bleaching. Laser-induced luminescence (LIL) experiments were carried out with the same setup blocking analysis light. The analysis light in LFP and emitted light in LIL experiments were detected using a photomultiplier tube (PMT Hamamatsu R929), after passing through appropriate filters (Schott, OG580, 0.2 cm thickness and Schott, OG590, 0.3 cm thickness) and a computer controlled high throughput 1/4 m f/2.5 monochromator (Sciencetech 9055F). To increase signal-to-noise ratio, currently 64 traces were averaged. Analysis wavelengths were 610 nm for LFP

and 695 nm for LIL. They were selected as a compromise between signal-to-noise ratio, interference of the laser beam, interference of phosphorescence in LFP and dye photobleaching. The system was purged either with dry or water saturated oxygen or water saturated argon.

Quenching radius model

The quenching radius model used to fit Φ_F against dye concentration was similar to that applied elsewhere⁸ to evaluate the self-quenching of Rhodamine 6G adsorbed on microcrystalline cellulose. In the present case a 3D random distribution of dye molecules was assumed. Traps were identified as pairs of molecules within a distance $\leq r_Q$, the quenching radius, and Poisson statistics was used to estimate monomer and trap concentrations. Energy migration and trapping rates were calculated using Loring, Andersen and Fayer (LAF) theory under the assumption of non-fluorescing, perfect traps.^{20,21} Förster radii were calculated as $R_{0,M-M} = 52.3 \text{ \AA}$ and $R_{0,M-T} = 58.7 \text{ \AA}$ for monomer-monomer and monomer-trap energy transfer, respectively. An orientational parameter $\kappa^2 = 0.476$ (randomly distributed orientations fixed in time) and a refraction index $n = 1.51$ for pHEMA²⁴ were considered. $R_{0,M-T}$ was calculated considering that the absorption coefficient of traps is twice the absorption coefficient of the monomeric dye, consistent with traps arising from weakly interacting ground state dye molecules.

Results and discussion

Absorption and emission spectra at different dye concentrations are shown in Figure 1. Both spectra show constant shapes for films containing up to 10 wt % PhB. For more concentrated films, minimal changes are observed on increasing the dye concentration, namely a small increase of the absorption

shoulder relative to the main band and small red shifts in the main band and some distortions in the long wavelength band of fluorescence spectra. Changes in fluorescence spectra at the highest concentrations can be partly attributed to small reabsorption effects. In the figure inset a linear relationship between A_{\max} / d and concentration, where A_{\max} is the absorbance at maximum, (552 ± 1) nm, and d the film thickness, is observed above 1 wt % (slope 1 in the log-log plot). From these results, the PhB absorption coefficient in the films and the absorbance of very dilute films, which could not be experimentally determined, were calculated. The absorption coefficient, $(9.9 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 552 nm, is similar to the value measured in ethanol solution, $9.87 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at the same wavelength. Absorption spectra were measured against a film devoid of dye. Films were masked to a small area and spectra were determined at different positions for the same film. No significant differences were observed. Fluorescence spectra ($\lambda_{\text{exc}} = 505 \text{ nm}$) were measured in back face and quantum yields were calculated against PhB ethanolic solutions in a 1 mm pathlength regular absorption cell (see Experimental Section).

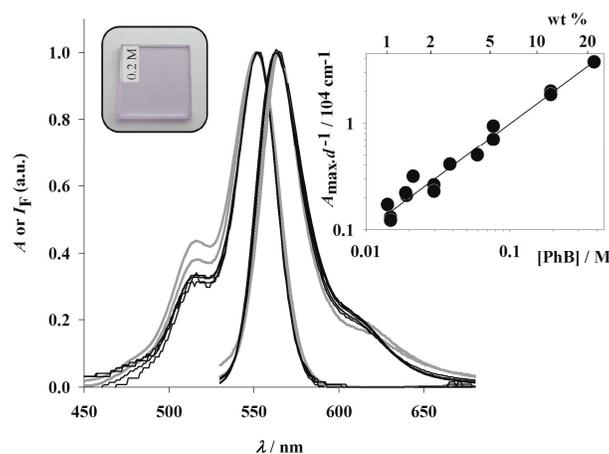


Figure 1. PhB-pHEMA films absorption and emission ($\lambda_{\text{exc}} = 505 \text{ nm}$) spectra at PhB concentrations 21.7; 12.2; 5.2; 4.1; 2.7; and 2.1 wt %. Gray lines correspond to the two most concentrated films. Inset:

Absorbance at maximum, (552 ± 1) nm, per unit pathlength as a function of concentration for 150 and 245 nm thick films.

Fluorescence quantum yields are shown as a function of dye concentration in Figure 2. Up to PhB *ca.* 0.3 wt %, the values are similar, within experimental uncertainty, to that obtained in ethanol solution ($\Phi_F = 0.76 \pm 0.02$). For more concentrated films a dramatic decrease is observed until undetectable values are observed above PhB *ca.* 7 wt %.

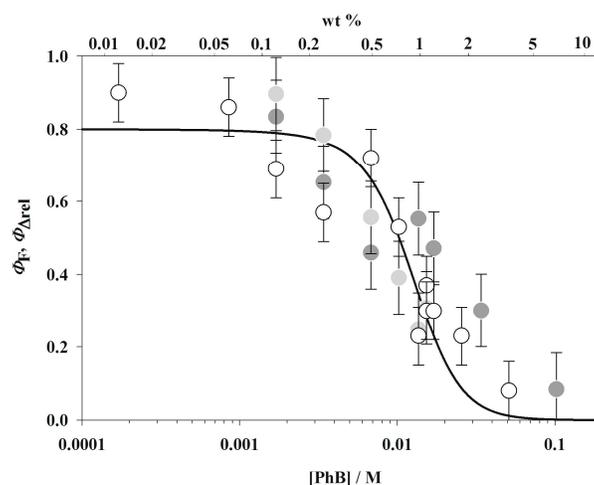


Figure 2. Fluorescence (hollow circles) and scaled singlet oxygen quantum yields in dry (dark gray circles) and humidified (light gray circles) 245 nm thick films as a function of PhB concentration. The solid line is a fit according to a quenching radius model and LAF theory calculations (see text).

As chemical monitor, 1,3-diphenylisobenzofuran (DPBF) in dichloromethane (DCM) solution was used to estimate singlet molecular oxygen quantum yields. Its absorbance at $\lambda = 415$ nm decreases

when the film is immersed in the solution and irradiated at wavelengths within the absorption range of PhB. No change was observed in the dark and a negligible decrease was detected under illumination in the absence of film. No desorption of PhB was observed in all cases. The oxygen diffusion coefficient in hydrated (35 vol %) pHEMA crosslinked with tetraethylene glycol dimethacrylate²⁵ is $D = 1.36 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and the $^1\text{O}_2$ lifetime in the polymer can be estimated as $\tau \approx 20 \text{ } \mu\text{s}$.²⁶ Assuming these values apply to the system under study and according to the Brownian motion equation in one-dimension, $\langle x^2 \rangle = 2D\tau$, the average distance traveled by a $^1\text{O}_2$ molecule during time τ is around 23 nm. This value implies that only a fraction of the total singlet oxygen formed, roughly 10 % for 245 nm thick films, is able to reach the film surface and react with the chemical monitor. Therefore, a strongly underestimated, effective value of Φ_{Δ} is obtained. Thinner films can, in principle, be considered but the uncertainty in absorbance determination would be too high. Nevertheless measured values are proportional to the actual quantum yields. Results show a marked decrease of Φ_{Δ} with PhB concentration and a large, nearly 10-fold increase when films are humidified with water saturated oxygen prior to immersion in DCM, approaching at low PhB concentration 0.01 for humidified films and 0.001 for dry films. Humidity induces swelling of the polymer matrix, increasing the O_2 diffusion coefficient and, consequently, increasing effective Φ_{Δ} values. Recall that actual Φ_{Δ} values cannot exceed $1 - \Phi_{\text{F}} \approx 0.20$, much lower than in water (see above). This is in accordance with the general behavior of xanthene dyes, which strongly increase their Φ_{F} and accordingly reduce Φ_{T} values when passing from water to environments with less proton donating capacity.²⁷ In Figure 2, Φ_{Δ} values scaled to match absolute Φ_{F} values at low concentrations are displayed. It may be seen that both quantum yields follow similar trends with concentration.

The formation of the PhB triplet state was evidenced by laser flash photolysis and time resolved phosphorescence. As a consequence of the small absorption of thin films, thick films ($\sim 16 \mu\text{m}$) were used in these experiments (see Experimental section). Transient decays are shown in Figure 3. After purging the film with humidified argon, similar triplet absorption and phosphorescence signals are obtained, which can be fitted by a biexponential function with decay times of 1.6 ($\sim 50\%$) and 3.1 ($\sim 50\%$) ms. After purging with humidified oxygen the amplitude of both signals decreases up to a negligible value (triplet signal reported in the figure). This behavior is consistent with triplet detection in the absence of oxygen and quantitative triplet quenching in its presence. Saturation with water is needed in order to swell the film and activate transport of the purging gas.²⁸ Purging a previously oxygenated film with dry oxygen has the consequence of partially recovering the triplet and phosphorescence signals, showing that drying leads to an important deoxygenation of the film even in the presence of gaseous oxygen.

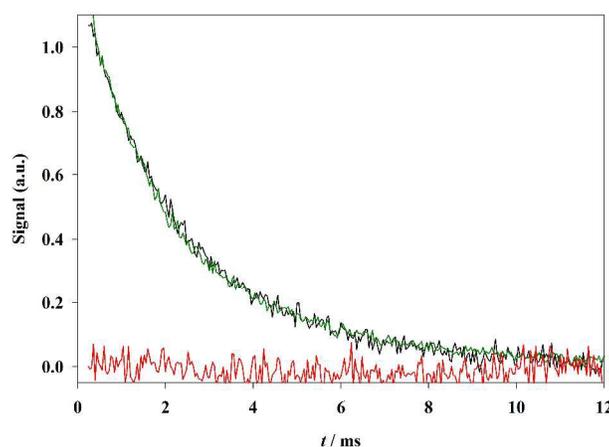


Figure 3. Phosphorescence intensity measured at 695 nm (black) and triplet-triplet absorption measured at 610 nm (green) after purging with humidified argon and triplet signal (red) after purging with humidified oxygen obtained from a thick film containing 0.7 wt % in PhB (see text).

The tendency of xanthene dyes to aggregate increases with the number and polarizability of halogen atoms.²⁹ PhB, together with Eosin Y, Erythrosin B and RB, belong to the xanthenes containing heavy halogens and, therefore, they aggregate strongly in water and ethanol solutions, with important changes in the absorption spectrum even at concentrations below 10^{-4} M. Our results show that deviations of the absorption spectrum do not take place in pHEMA even at three orders of magnitude larger concentrations. A similar tendency has been observed for xanthene dyes adsorbed on cellulose.³⁰ However, the lack of spectroscopically detectable aggregates does not guarantee the absence of concentration quenching. López *et al.* applied a QRM in their study on the dependence of Φ_F on dye loading for Rhodamine 6G adsorbed on cellulose microparticles.⁸ Dye molecules are distributed randomly in space and, below a critical radius, $r_Q \approx 1.2 - 1.5$ nm, dye pairs act as non-fluorescing energy traps. Interaction between dye molecules in traps is too weak to cause detectable spectroscopic changes. In this work, the model applied to the system PhB-pHEMA (see Experimental section) yields a similar value, $r_Q = 1.2$ nm. The agreement between Φ_F values calculated by the QRM and the experimentally determined Φ_F and scaled Φ_Δ values against PhB concentration (Figure 2) show that energy traps quench the excited singlet state, blocking simultaneously triplet state formation. The quenching is of both static (light absorption by traps) and dynamic (energy transfer from excited nearly isolated dye molecules to traps) nature.

In reference (7) Priimagi *et al.* claim that interaction between dye molecules and the polymer chain inhibits the dye aggregation tendency and allows high loadings to be used, enhancing the performance of the film. However, as we demonstrate in this work, the lack of spectroscopic evidence of aggregation does not imply the absence of energy wasting processes because statistical traps cannot be avoided for random dye distributions. It is clear from our results that working at unnecessarily high dye

concentrations has detrimental effects. The singlet oxygen generation efficiency can be calculated as the product between Φ_{Δ} and the absorption factor. However, considering that scaled Φ_{Δ} values follow the same trend than Φ_F and the latter quantum yields are obtained with higher accuracy, results on Φ_F were used to estimate the maximum efficiency. As shown in Figure 4, it lies at dye concentrations in the order of 2 wt %, where fluorescence self quenching amounts to more than 80 % (see Figure 2). It is also evident that, if the objective is the production of singlet molecular oxygen as a reactant for targets in solution, film thicknesses in excess of a few tens of nm are not necessary.

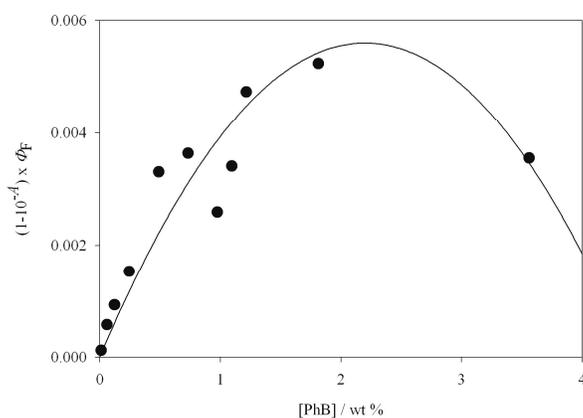


Figure 4. Excited state generation efficiency, calculated as the product between absorption factor and fluorescence quantum yield, as a function of PhB concentration for 245 nm thin films. The line is a quadratic function without physical meaning.

Conclusions

Interactions leading to energy trapping are common in arrays of dye molecules at high concentrations and constitute one of the main factors in lowering the efficiency of heterogeneous photosensitizers. Our

results show that the product between absorption factor and fluorescence quantum yield grows up to a certain dye concentration and begins to decrease thereafter. For random arrays, the concentration which maximizes the product is the optimum value. This concentration is in turn determined by the quenching radius, r_Q , whose knowledge helps the rational design through the application of suitable models. In an ordered sequence of dye molecules, the quenching radius represents the minimum distance at which dye molecules may be located. Film thickness is also relevant when the action of the photosensitizer is restricted to its surface. If the objective is to generate singlet molecular oxygen, its diffusion length determines the maximum film thickness, which must be considered to avoid unnecessary reactive species to be produced in the bulk. The present results can be regarded as a proof of concept for the development of heterogeneous photosensitizers in general, and particularly for photoactive coatings with antimicrobial activity.

Acknowledgements

This work has been supported by the University of Buenos Aires, the National Research Council of Argentina (CONICET) and the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT). H. B. R. and E. S. R. are staff members of CONICET. Y. L. acknowledges a fellowship from the Consejo Interuniversitario Nacional (CIN).

References

1. F. Baldini, A. N. Chester, J. Homola and S. Martellucci, *Optical Chemical Sensors*, Springer: Dordrecht, 2006.

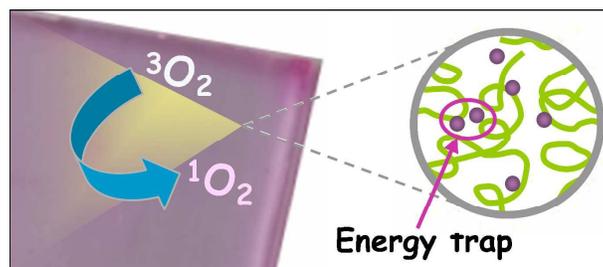
2. Y. Huang and S.-T. Wu, Multi-Wavelength Laser from Dye-Doped Cholesteric Polymer Films, *Opt. Express*, 2010, **18**, 27697-27702.
3. S. Kawata and Y. Kawata, Three-Dimensional Optical Data Storage Using Photochromic Materials, *Chem. Rev.*, 2000, **100**, 1777-1788.
4. R. Waning and S. Muke, Authentication Means. PCT Int. Patent WO 2004087430, 2004.
5. H. Dotan, O. Kfir, E. Sharlin, O. Blank, M. Gross, I. Dumchin, G. Ankonina and A. Rothschild, Resonant Light Trapping in Ultrathin Films for Water Splitting, *Nature Mater.*, 2013, **12**, 158-164.
6. M. Nowakowska, M. Kepczynski and K. Szczubialka, New Polymeric Photosensitizers, *Pure Appl. Chem.*, 2001, **73**, 491-495.
7. A. Priimagi, S. Cattaneo, R. H. A. Ras, S. Valkama, O. Ikkala and M. Kauranen, Polymer-Dye Complexes: A Facile Method for High Doping Level and Aggregation Control of Dye Molecules, *Chem. Mater.*, 2005, **17**, 5798-5802.
8. S. G. López, G. Worringer, H. B. Rodríguez and E. San Román, Trapping of Rhodamine 6G Excitation Energy on Cellulose Microparticles, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2246-2253.
9. M. Miranda, C. A. Strassert, L. E. Dicalio and E. San Román, Dye-Polyelectrolyte Layer-by-Layer Self-Assembled Materials: Molecular Aggregation, Structural Stability, and Singlet Oxygen Photogeneration, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1556-1560.

10. A. Opdahl, S. H. Kim, T. S. Koffas, C. Marmo and G. A. Somorjai, Surface Mechanical Properties of pHEMA Contact Lenses: Viscoelastic and Adhesive Property Changes on Exposure to Controlled Humidity, *J. Biomed. Mater. Res. A*, 2003, **67A**, 350-356.
11. C. Maldonado-Codina and N. Efron, Dynamic Wettability of pHEMA-Based Hydrogel Contact Lenses, *Ophthalm. Physiol. Opt.*, 2006, **26**, 408-418.
12. E. Gandin, Y. Lion and A. Van de Vorst, Quantum Yield of Singlet Oxygen Production by Xanthene Derivatives, *Photochem. Photobiol.*, 1983, **37**, 271-278.
13. P. Duarte, D. P. Ferreira, I. Ferreira Machado, L. F. Vieira Ferreira, H. B. Rodríguez and E. San Román, Phloxine B as a Probe for Entrapment in Microcrystalline Cellulose, *Molecules*, 2012, **17**, 1602-1616.
14. A. Rasooly and A. Weisz, In Vitro Antibacterial Activities of Phloxine B and Other Halogenated Fluoresceins Against Methicillin-Resistant *Staphylococcus aureus*, *Antimicrob. Agents Chemother.*, 2002, **46**, 3650-3653.
15. R. Rasooly, Expanding the Bactericidal Action of the Food Color Additive Phloxine B to Gram-Negative Bacteria, *FEMS Immunol. Med. Microbiol.*, 2005, **45**, 239-244.
16. D. S. Moreno, H. Celedonio, R. L. Mangan, J. L. Zavala and P. Montoya, Field Evaluation of a Phototoxic Dye, Phloxine B, Against Three Species of Fruit Flies (Diptera: Tephritidae), *J. Econ. Entomol.*, 2001, **94**, 1419-1427.

17. H. Qi, H. Takano, Y. Kato, Q. Wu, C. Ogata, B. Zhu, Y. Murata and Y. Nakamura, Hydrogen Peroxide-Dependent Photocytotoxicity by Phloxine B, a Xanthene-Type Food Colorant, *Biochim. Biophys. Acta*, 2011, **1810**, 704-712.
18. H. Qi, B. Zhu, N. Abe, Y. Shin, Y. Murata and Y. Nakamura, Involvement of Intracellular Oxidative Stress-Sensitive Pathway in Phloxine B-Induced Photocytotoxicity in Human T Lymphocytic Leukemia Cells, *Food Chem. Toxicol.*, 2012, **50**, 1841-1847.
19. C. P. McCoy, R. A. Craig, S. M. McGlinchey, L. Carson, D. S. Jones and S. P. Gorman, Surface Localisation of Photosensitisers on Intraocular Lens Biomaterials for Prevention of Infectious Endophthalmitis and Retinal Protection, *Biomater.*, 2012, **33**, 7952-7958.
20. R. F. Loring, H. C. Andersen and M. D. Fayer, Electronic Excited State Transport and Trapping in Solution, *J. Chem. Phys.*, 1982, **76**, 2015-2027.
21. L. Kulak and C. Bojarski, Forward and Reverse Electronic Energy Transport and Trapping in Solution. II. Numerical Results and Monte Carlo Simulations, *Chem. Phys.*, 1995, **191**, 67-86.
22. Y. Usui, Determination of Quantum Yield of Singlet Oxygen Formation by Photosensitization, *Chem. Lett.*, 1973, **2**, 743-744.
23. M. Nowakowska, Solvent Effect on the Quantum Yield of the Self-Sensitized Photoperoxidation of 1,3-Diphenylisobenzofuran, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2119-2126.
24. A. De Girolamo Del Mauro, A. I. Grimaldi, V. La Ferrara, E. Massera, M. L. Miglietta, T. Polichetti and G. Di Francia, A Simple Optical Model for the Swelling Evaluation in Polymer Nanocomposites, *J. Sensors*, 2009, Article ID 703206.

25. J. W. Parker and M. E. Cox, Mass Transfer of Oxygen in Poly(2-Hydroxyethyl Methacrylate), *J. Polym. Sci., Part A: Polym. Chem.*, 1988, **26**, 1179-1188.
26. J. F. Rabek, *Photodegradation of Polymers: Physical Characteristics and Applications*, Springer Verlag, Berlin, 2012, p. 87.
27. G. R. Fleming, A. W. E. Knight, J. M. Morris, R. J. S. Morrison and G. W. Robinson, Picosecond Fluorescence Studies of Xanthene Dyes, *J. Am. Chem. Soc.*, 1977, **99**, 4306-4311.
28. Y. Tian, B. R. Shumway, W. Gao, C. Youngbull, M. R. Holl, R. H. Johnson and D. R. Meldrum, Influence of Matrices on Oxygen Sensing of Three Sensing Films with Chemically Conjugated Platinum Porphyrin Probes and Preliminary Application for Monitoring of Oxygen Consumption of *Escherichia coli* (*E. coli*), *Sens. Actuators B Chem.*, 2010, **150**, 579-587.
29. O. Valdez-Aguilera and D. C. Neckers, Aggregation Phenomena in Xanthene Dyes, *Acc. Chem. Res.*, 1989, **22**, 171-177.
30. H. B. Rodríguez, E. San Román, P. Duarte, I. Ferreira Machado and L. F. Vieira Ferreira, Eosin Y Triplet State as a Probe of Spatial Heterogeneity in Microcrystalline Cellulose. *Photochem. Photobiol.*, 2012, **88**, 831-839.

Graphical Abstract



Excitation of a dye confined in a polymeric matrix leads to energy trapping at high concentrations.