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THE HEAVY-ATOM EFFECT ON SINGLET OXYGEN GENERATION IN THE PRESENCE OF PLASMONIC SILVER NANOPARTICLES

E.P. Menshova, N.Kh. Ibrayev
Institute of Molecular Nanophotonics, Buketov University, Karaganda, Kazakhstan
E-mail: menshovayevgeniya@gmail.com

The effect of heavy atoms on singlet oxygen generation in the plasmon field of silver nanoparticles was investigated. Rhodamine 123 and dibromo-rhodamine 123 dyes embedded in polyvinyl butyral films were selected as sensitizers. The dye films were deposited via spin coating onto silver island films synthesized on quartz substrates. The results indicate that the presence

of a heavy atom (bromine) in dye molecules enhances phosphorescence efficiency and singlet oxygen generation. The calculated Stern-Volmer constants demonstrate an increased rate of oxygen quenching of the dye triplet states in the presence of Ag nanoparticles.

Keywords: heavy-atom effect, intersystem crossing, singlet oxygen generation, silver island films, photosensitizer.

Introduction

Organic dyes, particularly rhodamines, which exhibit high fluorescence and efficient energy transfer to oxygen, are widely used to study singlet oxygen ($O_2(^1\Delta_g)$) generation. One of the key factors influencing $O_2(^1\Delta_g)$ yield is the incorporation of heavy atoms into dye molecules, which promotes intersystem crossing (ISC), thereby increasing the probability of molecules transitioning to the triplet state [1]. This strategy is extensively applied in the development of novel photosensitizers for photodynamic therapy and other applications requiring efficient reactive oxygen species generation [2].

Additionally, significant attention has been devoted to the interaction of organic photosensitizers with plasmonic nanoparticles, which can considerably enhance luminescence intensity and shorten its lifetime. The local electromagnetic field induced by silver or gold nanoparticles facilitates radiative transitions and accelerates the deactivation of excited sensitizer states [3]. Plasmonic effects can also enhance sensitizer sensitivity and selectivity towards oxygen by improving energy transfer efficiency from the triplet state of the sensitizer to oxygen molecules. Notably, silver island films (SIFs) can boost luminescence by generating localized surface plasmons and increasing overall signal intensity [4].

This study investigates the photophysical processes in systems with brominated rhodamine derivatives and silver plasmonic structures, aiming to enhance $O_2(^1\Delta_g)$ generation efficiency.

Efficient singlet oxygen generation is crucial for applications such as photodynamic therapy (PDT) in oncology and antimicrobial treatments. The combined use of heavy atoms and plasmonic nanoparticles presents promising opportunities for the development of highly effective and targeted photosensitizers. Future research will focus on optimizing nanomaterial-organic molecule combinations to improve the kinetics and selectivity of $O_2(^1\Delta_g)$ generation processes.

Experimental

To study the heavy-atom effect on $O_2(^1\Delta_g)$ generation, the following were chosen as photosensitizers (PSs): rhodamine 123 (Rh123) and dibrom-

rhodamine 123 (Rh 123-2Br). The molecular structure of the investigated dye molecules is given in Figure 1. The dye films in polyvinyl butyral (PVB) were deposited by spin-coating at 1500 rpm for 30sec. The concentration of dye in 7 wt% polymer was $5 \cdot 10^{-4}$ mol/L. Micro-weighing was used to control the thickness of the films deposited on different substrates. The mass of the dye films on the surface was almost the same.

From the normalized absorption and fluorescence spectra of Rh123 and Rh123-2Br in the polymer films, it can be seen that the spectra of Rh123-2Br are bathochromically shifted, due to the presence of two bromine atoms (Figure 2c). The maximum of the absorption spectrum (λ_{abs}^{max}) of Rh123 falls at 516 nm, Rh123-2Br at 520, and fluorescence (λ_{fl}^{max}) at 535 nm for Rh123 and at 540 nm for Rh123-2Br.

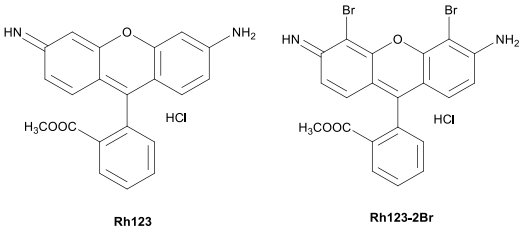
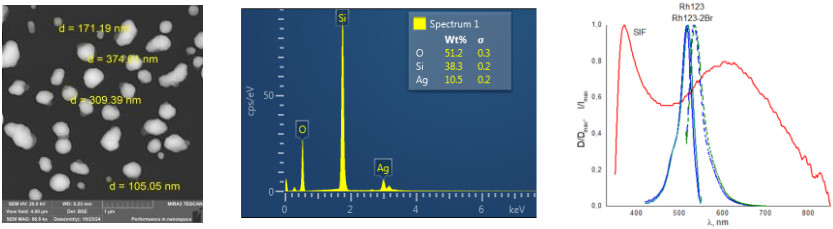


Figure 1. Molecular structure of the investigated molecules

To study the effect of plasmonic nanoparticles on the generation of $O_2(^1\Delta_g)$ in the presence of heavy atom, substrates of silver island films (SIFs) were prepared by chemical deposition. According to scanning electron microscope (Mira 3LMU, Tescan) data, spherical islands of size 105-375 nm were uniformly distributed on the surface of the films (Figure 2a). Energy dispersive X-ray spectroscopy analysis of the SIF surface showed the presence of silver, silicon and oxygen, where silicon and oxygen are related to the composition of silica glass (Figure 2b). The absorption spectra of the SIFs is broadened and has two peaks at 365nm and 605nm (Figure 2c). The broadening is due to the large variation in the size of the islets. The peak at 365nm is related to the excitation of electrons from the filled zone to the conduction zone and is due to transitions between electronic zones, while the peak at 605nm arises due to electron oscillations on the surface of silver nanoparticles under the action of the electromagnetic field of incident light. It depends on the shape, size and distance between nanoparticles, as well as on the dielectric properties of the environment.



a b c

Figure 2. (a) SEM image of SIFs obtained by chemical deposition on quartz glass, (b) EDS spectrum of SIFs and (c) Absorption spectra of SIFs (red line), Rh123 (blue solid line), Rh123-2Br (green solid line) and fluorescence spectra of Rh123 (blue dashed line), Rh123-2Br (green dashed line) in PVB film on quartz glass (λ_{exc} = 510 nm, λ_{reg} = 540 nm)

Results and Discussion

Under photoexcitation, phosphorescence of singlet oxygen was observed in the absorption band of Rh123-2Br, while Rh123 does not contribute to its formation. Under the influence of plasmon field the generation of singlet oxygen sensitized by Rh123-2Br increases by 2.49 times (Fig.3).

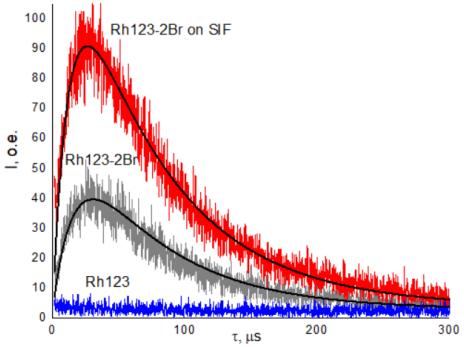


Figure 3: Phosphorescence attenuation kinetics of singlet oxygen (λ_{reg} = 1270nm) sensitized by Rh123 and Rh123-2Br dyes on quartz glass and SIFs at atmospheric pressure (λ_{exc} = 510nm)

The attenuation kinetics of singlet oxygen phosphorescence is represented by two phases - rise and decay (Figure 3) and can be approximated according to the two-exponential equation:

$$I(t) = I_0\left[\exp\left(-\frac{t}{\tau_{decay}}\right) - \exp\left(-\frac{t}{\tau_{rise}}\right)\right] \quad (1)$$

where $I(t)$ is the phosphorescence intensity $O_2(^1\Delta_g)$ per second, I_0 is the pre-exponential multiplier, and τ_{decay} and τ_{rise} are the time constants of the decay and rise phases.

The rising phase is determined by the rate of singlet oxygen formation as a result of energy transfer from Rh123-2Br triplets to $O_2(^3\Sigma_g^-)$, the decay phase by the process of singlet oxygen deactivation.

Table 1- Plasmon effects on the intensity and lifetime of singlet oxygen phosphorescence (λ_{reg} = 1270 nm at atmospheric pressure (λ_{exc} = 510nm))

	I, o.e.	τ_{rise}, μs	τ_{decay}, μs	I/I_0	$\tau_{rise}/\tau_{rise\,0}$	$\tau_{decay}/\tau_{decay\,0}$
$O_2(^1\Delta_g)$ on glass	60	16.13±0.77	75.60±0.91	-	-	-
$O_2(^1\Delta_g)$ on SIFs	112	12.25±1.61	71.89±0.61	2.49	0.76	0.95

According to the results of phitting, the duration of the rising phase was 16.13 μs and the duration of the quenching phase was 75.60 μs. Under the action of plasmon, the duration of these phases decreased by 14% and 3%, respectively (Table 1). The decrease in the phosphorescence lifetime $O_2(^1\Delta_g)$ is due to the enhancement of the radiative transition $^1\Delta_g \rightarrow {}^3\Sigma_g^-$.

The value of the quenching coefficient (k_q) from the Stern-Folmer equation can be used as an indicator of efficiency of singlet oxygen generation.

$$\frac{I_{ph}^0}{I_{ph}} = 1 + k_q\tau_0 \cdot [Q], \quad (2)$$

where I_{ph}^0 is the intensity of phosphorescence in the absence of O_2, I_{ph} is the intensity of phosphorescence in the presence of O_2, k_q is the quenching factor, τ_0 is the lifetime of phosphorescence in the absence of O_2, and $[Q]$ is the concentration of O_2.

Since k_q reflects how effectively oxygen quenches the triplet state of the dye-sensitizer, its value can be indirectly related to the yield $^1\Delta_g$.

On the dependence of the relative decrease of the dye phosphorescence intensity in the presence of plasmons and without them on the concentration of O_2 (Figure 4), the straight line, which represents the dependence with plasmons, has a steeper slope. This is due to the increased interaction between the fluorescent substance and plasmons, which leads to a larger quenching coefficient.

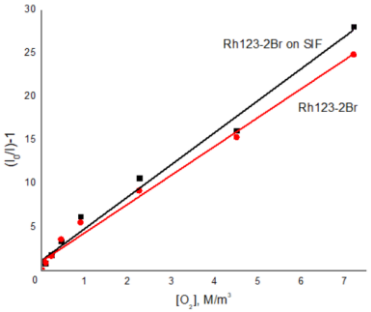


Figure 4: Stern-Follmer quenching constants of Rh123-2Br phosphorescence by O_2 molecules on glass (red line) and SIFs (black line)

For Rh123-2Br films:

On glass: k_q =6.2 ● 10^2 $M^{-1}s^{-1}$

On SIFs: k_q =9.1 ● 10^2 $M^{-1}s^{-1}$

A higher k_q indicates more efficient energy transfer from the sensitizer triplet state to oxygen molecules, enhancing $O_2(^1\Delta_g)$ yield.

Conclusions

In this study, a comparative analysis of the $O_2(^1\Delta_g)$ generation efficiency of the photosensitizers Rh123 and Rh123-2Br in polymer films in the presence of plasmonic silver nanoparticles is performed. The input of a heavy bromine atom into rhodamine 123 molecules leads to a significant increase in the probability of intersystem crossing and singlet oxygen generation, as evidenced by an increase in the intensity and decrease in the phosphorescence lifetime. The presence of silver plasmonic nanostructures further enhances the luminescence processes due to the Purcell effect, reducing the lifetime of excited states and increasing the luminescence intensity. The Stern-Volmer constants for Rh123-2Br on SIFs show a higher quenching coefficient, indicating an increase in the efficiency of energy transfer to the triplet oxygen state and singlet oxygen generation in the plasmon field.

Acknowledgements

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СУ ТОЛҚЫНЫНЫҢ ЭНЕРГИЯСЫН ТҮРЛЕНДІРУ ЖӘНЕ ОНЫҢ ТИІМДІЛІГІН АРТТЫРУ ӘДІСТЕРІ

Балтабай Дильназ Дәулетқызы, Өмірбек Ерасыл Ержанұлы
Ш.Уәлиханов атындағы Көкшетау университеті
«Математика, физика және информатика» кафедрасының 1-курс студенттері
Ғылыми жетекшісі: Шуюшбаева Нургуль Найзабековна
Математика, физика және информатика кафедрасының профессоры, PhD, Көкшетау қ., Қазақстан

Мақалада тұрақты энергия көздеріне жаһандық көшу контекстіндегі өте өзекті мәселелер және қазба отындарына тәуелділікті азайту қажеттілігі қарастырылған. Климаттың өсуі мен энергияға сұраныстың артуы аясында жаңартылатын ресурс ретінде толқындық энергия ерекше маңызға ие. Тақырыптың мазмұны