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PHOTONICS OF BENZ [C, D] INDOLE-BASED POLYMETHINE DYES MOLECULES AND SINGLET OXYGEN SENSITIZATION

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Abstract. This study presents a comparative study of the photophysical properties of the basic polymethine dye bcd based on benz[c,d]indole and its modified derivative 2848SL. Replacing the phenyl groups (Ph) at the nitrogen atoms with butyl radicals (Bu), as well as introducing phenylmercapto groups (-SPh) into the 2848SL molecule, improves electron conjugation, resulting in a bathochromic shift of the absorption and fluorescence maxima to the near-IR region. This modification was found to increase the lifetime of the triplet state from 21.1 to 33.2 μ s and leads to an increase of the quantum yield of singlet oxygen generation $O_2(^1\Delta_g)$ to 0.10. The obtained results confirm the effectiveness of triplet-triplet energy transfer, making the 2848SL derivative a promising agent for photodynamic therapy.

Keywords: benz[c,d]indole, polymethine dyes, intersystem crossing, triplet state, singlet oxygen, photodynamic therapy.

1. Introduction

The development of organic photosensitizers in the near-infrared (IR) range is a key challenge in modern biophotonics and photodynamic therapy (PDT) for cancer [1-3]. The key requirement for such molecules is the ability to effectively absorb light within the «therapeutic transparency window of biological tissues» (700–1100 nm) and possess a high quantum yield of singlet oxygen generation ($O_2(^1\Delta_g)$) [1,4].

The main method for shifting the absorption bands of polymethine dyes (PD) to the long-wavelength region of the spectrum is the lengthening of the polymethine chain [5]. However, such an increase of chain length causes a violation of the uniformity of the charge distribution in the dye chromophore. That leads to strong nucleophilic solvation in liquid and polymeric media. Such solvation causes a decrease in the absorption intensity in the near-IR range of the spectrum [6]. In addition, the lengthening of the polymethine chain leads to a decrease of the photostability and thermal stability of the dyes [5]. A real breakthrough in this area is the use of the heterocyclic ring of benz[c,d]indole. Due to the rigid, developed aromatic π -system, it provides a bathochromic shift of up to 800–1000 nm with a minimal chain length, while maintaining high extinction and stability of the molecule [1].

A fundamental spectral feature of all benz[c,d]indole derivatives is their extremely low fluorescence quantum yields (ϕ), which do not exceed a few percent [7]. Until recently, it was believed that the benz[c,d]indole residue merely enhances bond order heterogeneity and vibronic interactions, converting all excitation energy into heat. This undoubtedly opens up possibilities for photothermal therapy.

By analogy with classical heterocyclic systems, the rigid π -system of the benz[c,d]indole nucleus forms a spatially closed electron circuit – a conditional «loop». According to modern quantum chemical concepts [8], the peculiarities of π -electron delocalization in such a circuit during the optical transition determine the specific overlap of the wave functions of the singlet and triplet states. The resulting effective configurational perturbations dramatically enhance the spin-orbit interaction in the molecule. This weakens the quantum-mechanical prohibition on changes in multiplicity and sharply increases the rate constant of intersystem crossing (k_{ISC}) between the singlet (S_1) and triplet (T_1) levels [9-13].

Thus, the energy of the absorbed quantum of light is not simply wasted on heating the medium, but is effectively accumulated in the long-lived triplet level (T_1) of the dye. Since the triplet state of the dye molecule is capable of interacting energetically and according to the laws of spin conservation with the ground triplet state of molecular oxygen ($O_2(^3\Sigma_g^-)$), efficient energy transfer occurs. The result of this process is the sensitization of $O_2(^1\Delta_g)$.

This paper presents the spectral and luminescence characteristics of benz[c,d]indole-based PDs and evaluates their potential as agents for generating $O_2(^1\Delta_g)$.

2. Materials and methods

To establish the «structure – property» relationship, a comparative analysis of two systems was carried out: the basic symmetric dye bcd and the modified derivative 2848SL, which were synthesized at the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine (Kyiv). The chemical structures of the benz[c,d]indole polymethine dyes studied in the work are shown in Fig. 1.

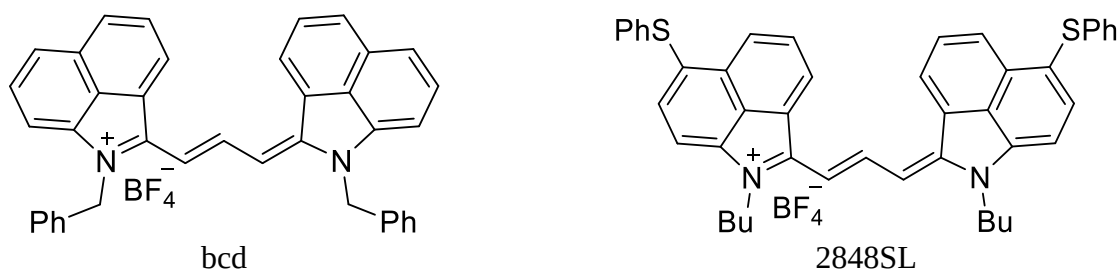


Fig.1. Structural formulas of the studied benz[c,d]indole PDs

The structural differences between the base dye bcd and the derivative 2848SL include the substitution of phenyl groups (Ph) at the nitrogen atoms of the indole cores with butyl radicals (Bu) and the introduction of electron-donating phenylmercapto groups (-SPh) into the heterocyclic core structure. These changes of the chemical structure provide more efficient conjugation of the π -system in the 2848SL molecule. That explains the observed bathochromic shift of the absorption and fluorescence maxima to the near-IR region compared to the base compound bcd.

Ethanol was used as the liquid medium. The dye concentration in the ethanol solutions was 10^{-5} mol/L. Measurements were performed in quartz cuvettes with a 10 mm optical path length. Electronic absorption spectra of the solutions and films were recorded in the spectral range of 200–1100 nm on a Cary 300 automated dual-beam spectrophotometer (Agilent). Fluorescence spectra were measured on a CaryEclipse spectrofluorimeter (Agilent). The kinetics of triplet state deactivation and singlet oxygen phosphorescence were studied on an FLS 1000 stationary spectrometer (Edinburgh Instr.). A tunable laser system (SolarLS) was used as a source of pulsed photoexcitation. It consisted of a solid-state Nd:YAG laser LQ529 and a parametric light generator OPO LP604 with the following output radiation parameters: pulse energy up to 47 mJ and a repetition rate of 10 Hz. The formation of $O_2(^1\Delta_g)$ was confirmed by direct recording of its emission at 1270 nm. Mathematical analysis, deconvolution, and approximation of the experimental decay curves with multiexponential functions were performed using the Fluoracle software package (Edinburgh Instr.).

The quantum yield (Φ_Δ) of $O_2(^1\Delta_g)$ generation was determined using the relative method [14] according to the formula:

$$\Phi_\Delta(x) = \Phi_\Delta^{st} \cdot \left(\frac{S_x}{S_{st}}\right) \cdot \left(\frac{f_{st}}{f_x}\right) \cdot \left(\frac{P_{st}}{P_x}\right) \quad (1)$$

where S_x and S_{st} – integrated phosphorescence intensities of $O_2(^1\Delta_g)$ at a wavelength of 1270 nm for the sample under study and the standard, respectively; f_x and f_{st} – fractions of light absorbed by the sample and the standard at the excitation wavelength ($f=1-10^{-D}$, where D is the optical density); P_x and P_{st} – excitation laser power during measurements of the sample and the standard; Φ_{Δ}^{st} – $O_2(^1\Delta_g)$ quantum yield for the standard compound. Rose Bengal (RB) was used as the standard [15,16]. Measurements of $O_2(^1\Delta_g)$ phosphorescence decay kinetics were performed at room temperature in an open cuvette (1 cm) to allow free access of oxygen. The integrated intensity was calculated by numerically integrating the experimental decay curves using the trapezoidal rule in OriginPro 8.0 software [17].

3. Results and discussion

A preliminary analysis of the electronic absorption and fluorescence spectra of compound bcd confirmed that the incorporation of the rigid benz[c,d]indole heterocyclic core, possessing the developed aromatic π -system, provides substantial shifts of the electronic transitions into the near-IR region without the need to lengthen the polymethine chain [1,18]. That is consistent with the well-known ability of a number of heterocyclic terminal groups (4-pyrylium, 4-thiopyrylium, and benz[c,d]indole) to shift the absorption and emission bands of cyanine dyes deep into the near-IR region owing to the nature of the terminal fragment [19]. Measurements showed that the main absorption band of the dye lies in the 600-800 nm region and has an asymmetric shape, characteristic of polymethine dyes, with a gentle rise and a vibrational maximum at the short-wavelength edge. In the UV region of the spectrum, a declining absorption curve was recorded in the 250-500 nm region (Fig. 2).

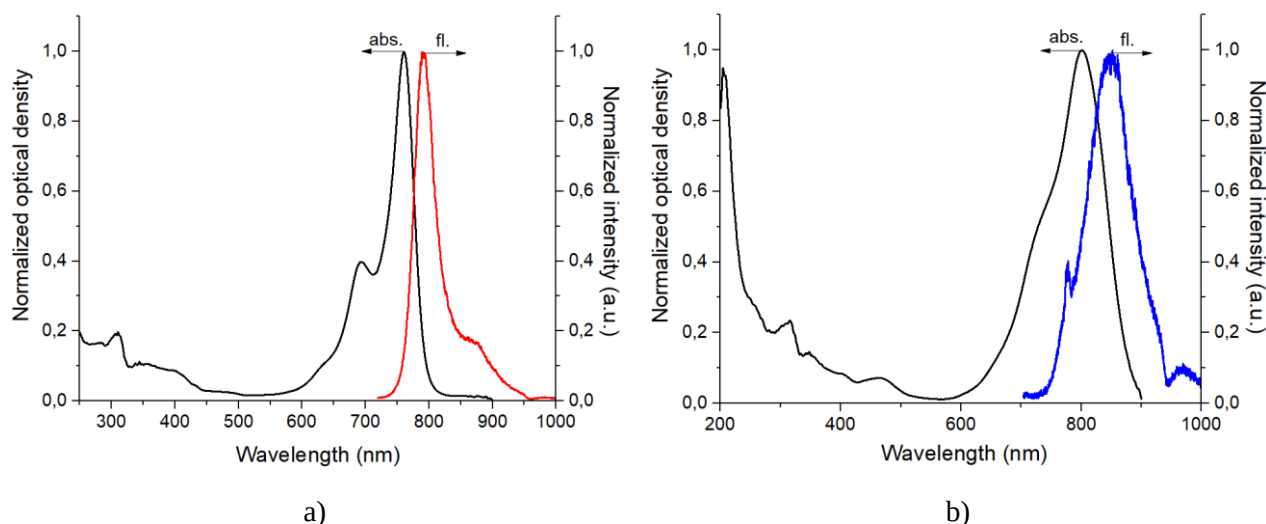


Fig.2. Absorption and fluorescence spectra of PD bcd (a) and 2848SL (b) in solution (ethanol, 10^{-5} mol/L)

The fluorescence spectra of PD bcd are almost mirror-symmetrical to their absorption spectra. In solution, the absorption band maximum of PD bcd is at 760 nm with a shoulder at approximately 690 nm. The fluorescence band maximum is at 790 nm.

The incorporation of a phenylmercapto group (-SPh) into the benz[c,d]indole core shifts the absorption and fluorescence bands of PD into the near-IR region [18]. Replacing the phenyl groups on the nitrogen atoms with butyl groups alleviates steric hindrance. In the case of bcd, phenyl groups disrupt the planarity of the chromophore and partially interrupt conjugation along the chain; in contrast, the butyl groups in 2848SL do not interfere in this way, resulting in a more planar molecule and more effective conjugation, which further enhances the bathochromic shift. Thus, the shift in the absorption maximum from 760 to 800 nm and the fluorescence maximum from 790 to 830 nm results from the combined effect of the electronic influence of the -SPh group and improved molecular conjugation achieved by replacing Ph with Bu.

To study the dynamics of triplet states and singlet-triplet annihilation processes, the dyes were embedded in a solid polyvinyl butyral (PVB, 7.5%) matrix. The delayed fluorescence (DF) kinetic curves of the studied compounds are shown in the Fig. 3. As can be seen from the graphs, a characteristic increase of luminescence intensity is observed for both compounds, followed by monoexponential decay. Calculation of the triplet state

lifetimes revealed significant differences between the samples. The triplet state lifetime for the base bcd dye is $21.1 \pm 0.7 \mu\text{s}$, while for the modified 2848SL compound, it increases to $33.2 \pm 0.8 \mu\text{s}$. The increased triplet lifetime in the 2848SL derivative indicates more effective protection of the triplet level from nonradiative deactivation, which is ensured by a change in the molecular structure. The observed DF indicates the presence of long-lived triplet states of the dye.

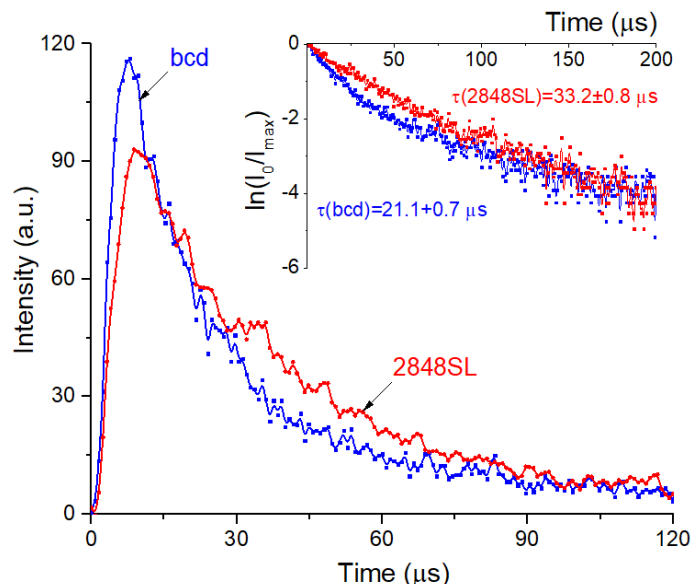


Fig.3. Kinetics of the DF of bcd and 2848SL dyes in PVB films (7.5%) at atmospheric pressure

To quantitatively assess the photosensitizing capacity, the $\text{O}_2(^1\Delta_g)$ phosphorescence decay kinetics was recorded at a wavelength of 1270 nm under pulsed laser excitation (Fig. 4). Comparative analysis showed that the photosensitizing activity of the dye 2848SL significantly exceeds that of the base compound bcd.

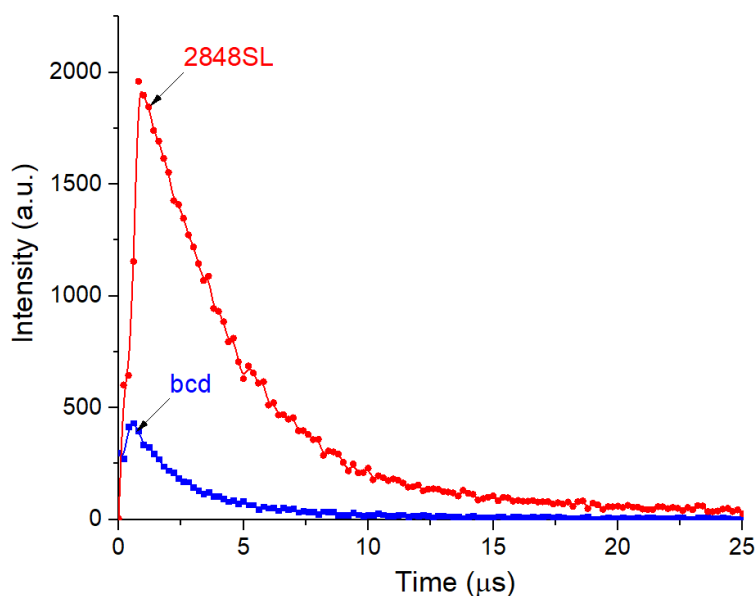
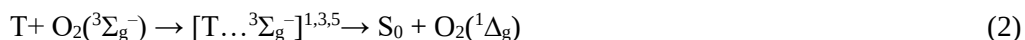


Fig.4. Decay kinetics of $\text{O}_2(^1\Delta_g)$ sensitized by dyes bcd and 2848SL in ethanol, $C=10^{-5} \text{ mol/L}$

Kinetic analysis allowed us to determine the lifetime τ and quantum yields Φ_Δ of $\text{O}_2(^1\Delta_g)$ for both systems. When excited at 760 nm, the bcd dye demonstrated a lifetime of $4.22 \pm 0.57 \mu\text{s}$ and $\Phi_\Delta=0.02$. In turn, for the 2848SL dye, when excited at 800 nm, the lifetime was $7.08 \pm 0.9 \mu\text{s}$ and $\Phi_\Delta=0.10$. The higher signal intensity and increased values of these parameters in the presence of 2848SL indicate the efficiency of photoinduced energy transfer processes in this system [20].

The obtained experimental data indicate that $O_2(^1\Delta_g)$ is generated due to energy transfer from the dye to $O_2(^3\Sigma_g^-)$. When dye triplets collide with oxygen molecules, the quintet, triplet, and singlet states of the collision complex $[T \dots ^3\Sigma_g^-]^{1,3,5}$ are formed (reaction 2). For the singlet, the decay reaction with the formation of the S_0 state of the dyes and $O_2(^1\Delta_g)$ is spin-allowed.



This interaction facilitates overcoming the spin inhibition during the collision of a triplet-excited dye with an oxygen molecule in its ground triplet state. As a result, an efficient energy transfer occurs, accompanied by a change in the spin state of the oxygen molecule and the generation of its $O_2(^1\Delta_g)$.

$O_2(^1\Delta_g)$ molecules, emitting phosphorescence, deactivate into the ground state of $O_2(^3\Sigma_g^-)$:



Thus, the obtained results confirm that the studied benz[c,d]indole dyes effectively sensitize $O_2(^1\Delta_g)$ due to triplet-triplet energy transfer, that makes them promising agents for photodynamic therapy.

4. Conclusion

This study presents a comparative study of the photophysical properties of the benz[c,d]indole polymethine dyes bcd and 2848SL. It was experimentally demonstrated that the introduction of a phenylmercapto group (-SPh) and butyl substituents into the 2848SL structure leads to a bathochromic shift of the absorption and fluorescence bands to the near-IR region (absorption maximum at 800 nm, fluorescence maximum at 830 nm), that corresponds to the «therapeutic window» of biological tissues.

Measurements of the delayed fluorescence kinetics revealed an increase of the triplet state lifetime from $21.1 \pm 0.7 \mu\text{s}$ for bcd to $33.2 \pm 0.8 \mu\text{s}$ for 2848SL, indicating more effective protection of the triplet level from nonradiative deactivation.

Oxygen phosphorescence detection at 1270 nm confirmed $O_2(^1\Delta_g)$ generation. For the bcd dye, upon excitation at 760 nm, the $O_2(^1\Delta_g)$ lifetime was $4.22 \pm 0.57 \mu\text{s}$ with a quantum yield of $\Phi_\Delta = 0.02$, while for 2848SL, upon excitation at 800 nm, these parameters increased to $7.08 \pm 0.9 \mu\text{s}$ and $\Phi_\Delta = 0.10$.

Thus, structural modification of benz[c,d]indole dyes provides the targeted enhancement of the triplet channel and significantly increases the efficiency of $O_2(^1\Delta_g)$ sensitization. The 2848SL dye exhibits higher photosensitizing activity than the parent bcd, making it a promising agent for photodynamic therapy and photocatalysis.

The obtained results demonstrate the potential of benz[c,d]indole derivatives for combined photodynamic and photothermal therapy, owing to a combination of near-IR absorption, effective generation of $O_2(^1\Delta_g)$ and the predominance of thermal relaxation over fluorescence – features that enable a dual mechanism of action that is innovative for this class of compounds.

Conflict of interest statement

The authors declare that they have no known financial or personal conflicts of interest that could influence the results of the work presented in this article.

CRediT author statement

Ibrayev N.Kh.: Writing – review & editing, Resources, Project administration, Methodology, Conceptualization. **Amanzholova G.S.:** Writing – original draft, Visualization, Validation, Investigation, Data curation. **Aimagambetova A.A.:** Visualization, Validation, Investigation.

Statement on the use of Artificial Intelligence.

During the preparation of this manuscript, artificial intelligence tools were used solely for language editing and grammatical improvement. No AI tools were used to generate scientific content, analysis, results, or conclusions.

Data Availability Statement

The data are available upon reasonable request from the authors.

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