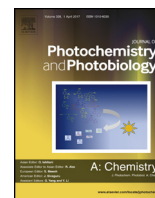




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

Invited paper

## Spectral-kinetic properties and efficiency of singlet oxygen generation by some dipyrromethenes



Iuliia V. Aksenova<sup>a,\*</sup>, Rimma T. Kuznetsova<sup>a</sup>, Ivan P. Pozdnyakov<sup>b</sup>, Victor F. Plyusnin<sup>b</sup>, Mikhail B. Berezin<sup>c</sup>, Natalia A. Bumagina<sup>c</sup>, Ekaterina S. Jarnikova<sup>d</sup>, Marina V. Parkhats<sup>d</sup>, Boris M. Dzhangarov<sup>d</sup>

<sup>a</sup> Tomsk State University, 36 Lenin Ave, Tomsk 634050, Russia<sup>b</sup> Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 3 Institutskaya Str., Novosibirsk 630090, Russia<sup>c</sup> Institute of Solution Chemistry RAS, 1 Akademicheskaya Str., Ivanovo 153045, Russia<sup>d</sup> Stepanov Institute of Physics National Academy of Sciences of Belarus, 68 Nezavisimosti Ave., Minsk 220072, Belarus

## ARTICLE INFO

## Article history:

Received 7 April 2017

Received in revised form 16 May 2017

Accepted 16 May 2017

Available online 17 May 2017

## Keywords:

Dipyrromethenes complexes

BODIPY

Laser flash photolysis

Triplet state

Singlet oxygen generation

## ABSTRACT

A comparative study of spectral-kinetic characteristics of excited states of new synthesized compounds – derivatives of dipyrromethene B(III) and Zn(II) complexes – and their dependence on the compound structure is carried out. Incorporation of halogen atoms into the dipyrromethene core leads to an increase in the quantum yield of triplet states due to the *heavy atom* effect. For aza-dipyrromethenes the decrease of the fluorescence lifetime and quantum yield due to a higher probability of non-radiative intersystem crossing processes are observed. The substitution of the central B(III) atom by Zn(II) causes not only a decrease in the flatness of the complexes, but also an increase in the contribution of non-radiative processes of excitation energy deactivation and hence, a decrease in the fluorescence quantum yield. For some complexes, the quantum yield of singlet oxygen (<sup>1</sup>O<sub>2</sub>) generation is determined. The maximum value is obtained for Br<sub>2</sub>-aza-dipyrromethene (0.62 in acetonitrile). The results obtained provide the basis for further investigation of the luminescence parameters of these complexes to search for compounds intended for the design of optical devices and application for photodynamic therapy of cancer.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

Dipyrromethenes (dipyrins) – the simplest representatives of chromophores with an open-chain oligopyrrole structure – were first synthesized by Triebs and Kreuzer in 1968 [1]. They can form stable covalent complexes with cations of *p*-, *d*-, and *f*-elements. The most promising representatives of this family are boron fluoride complexes of dipyrromethenes (BODIPY). They are well known as fluorescent dyes and their fluorescence properties have been widely studied by scientists all over the world over the last 50 years [2–4]. The BODIPY dyes have characteristics of ideal photosensitizer: high molar absorption coefficients, resistance to photobleaching, and light-dark toxicity ratios higher than other agents for photodynamic therapy (PDT). Given that reports on the application of the BODIPY derivatives for PDT [5,6] and oxygen sensing [7,8] appear in the last few years, the scientific community

has not lost interest in the study of the triplet states of BODIPY dyes [9]. To realize huge potential of the BODIPY triplet states for medicine and industry, comprehensive investigations of their photophysical properties are required.

Although BODIPY dyes are well known for their intense fluorescence, substitution by heavy atoms [10] or phenyl rings [11] significantly changes photophysics of the molecule. The substitution of the methine meso-spacer by the nitrogen atom in the dipyrromethene ligand also affects their properties [12]. Halogenated aza-dipyrromethene complexes are useful building blocks for extending conjugation and can be used as probes for the PDT and noninvasive methodology of tumor treatment [13,14].

In comparison with BODIPYs, their metal complexes with *d*-elements have advantages of easy self-assembly under mild conditions and of high sensitivity of their spectral and luminescent characteristics to a solvent [15–17]. Similarly types of metal complexes are used in medicine for imaging cells *in vivo*, catalysis technology, creation of metal–organic frameworks for optical data storage, electrochromic devices, and so on [18,19]. To successfully

\* Corresponding author.

E-mail address: [aksenova.iuliia@gmail.com](mailto:aksenova.iuliia@gmail.com) (I.V. Aksenova).

apply the dipyrromethene complexes, a systematic study of their photochemical and photophysical properties is required together with establishment of their dependence on the structure of the examined fluorophores. An analysis of the literature data on dipyrromethene chemistry demonstrated that the main attention has been paid to the synthesis of new systems, whereas much less attention has been paid to a study of the relationship between the dipyrromethene structures and properties. Therefore, investigation of the photophysical and photochemical properties of these compounds is of great importance.

In this paper we present information on the quantum fluorescence yield, energy, lifetime, and triplet state quantum yield as well as on the efficiency of  $^1\text{O}_2$  generation by several dyes based on a number of non-researched earlier dipyrromethenes obtained by the methods of optical spectroscopy, time resolved luminescence and nanosecond laser flash photolysis.

## 2. Experimental

We investigated a series of new derivatives of boron fluoride complexes of dipyrromethenes and aza-dipyrromethenes synthesized at the Institute of Solution Chemistry RAS by the method described in [20–23]. The purity of the obtained compounds was confirmed by the methods of thin layer chromatography, NMR, and infrared spectroscopy. The synthesis of the corresponding zinc complexes was described in [17]. Fig. 1 shows the structures and designations of the examined compounds. Ethanol, ethyl acetate, and acetonitrile (all HPLC grade) were used to prepare samples. The solubility of the compounds was reasonably good in these solvents, and no undesired effect of the solvent itself was observed for the employed excitation densities. The typical dye concentration was about  $10^{-5}$  M. The molar absorption coefficients of the

complexes were determined from three independent measurement runs with accuracy better than 10%. Unless otherwise specified, all described experiments were performed in a 1 cm quartz cell at a temperature of 298 K and atmospheric pressure. If necessary, oxygen-free samples were prepared by bubbling solutions with gaseous high-purity argon.

The stationary absorption spectra were recorded using Shimadzu UV 2501 PC and Agilent HP8453 spectrophotometers. The fluorescence spectra and kinetics were recorded with an FLS920 spectrofluorimeter (Edinburg Instruments). A Xe900 xenon lamp ( $\lambda_{\text{ex}}=520$  and 420 nm) was used as a steady-state excitation source. Fluorescence kinetic curves were obtained by the single photon counting technique using an EPLED-375 diode laser ( $\lambda_{\text{ex}}=375$  nm and pulse duration of 60 ps) and a LED-560 laser diode ( $\lambda_{\text{ex}}=560$  nm and pulse duration of 1.6 ns) as pulsed excitation sources.

The setup of laser flash photolysis was described in [24] and was based on an LS-2137U Nd:YAG laser (Lotis TII, Belarus) with excitation wavelength of 532 nm, pulse duration of 5–6 ns, illumination spot area of 0.03 cm<sup>2</sup>, and energy per pulse from 0.1 to 10 mJ. The temporal resolution of the setup was about 50 ns. The laser intensity was measured with a SOLO 2 laser power meter (Gentec EO).

Singlet oxygen luminescence was studied using a nanosecond laser NIR spectrometer developed at the Institute of Physics National Academy of Sciences of Belarus [25,26]. Samples were excited by pulses of a Nd:YAG laser (DTL-314QT, Laser-export Co. Ltd, Russia) (pulse duration of 10 ns, energy  $\leq 1$   $\mu\text{J}$ , and frequency of 2.5 kHz at  $\lambda=532$  nm). A bandpass interference filter (with maximum at 1272 nm and halfwidth of 34 nm) was used for spectral selection. The quantum yields of photosensitized singlet oxygen generation were determined by a relative method using

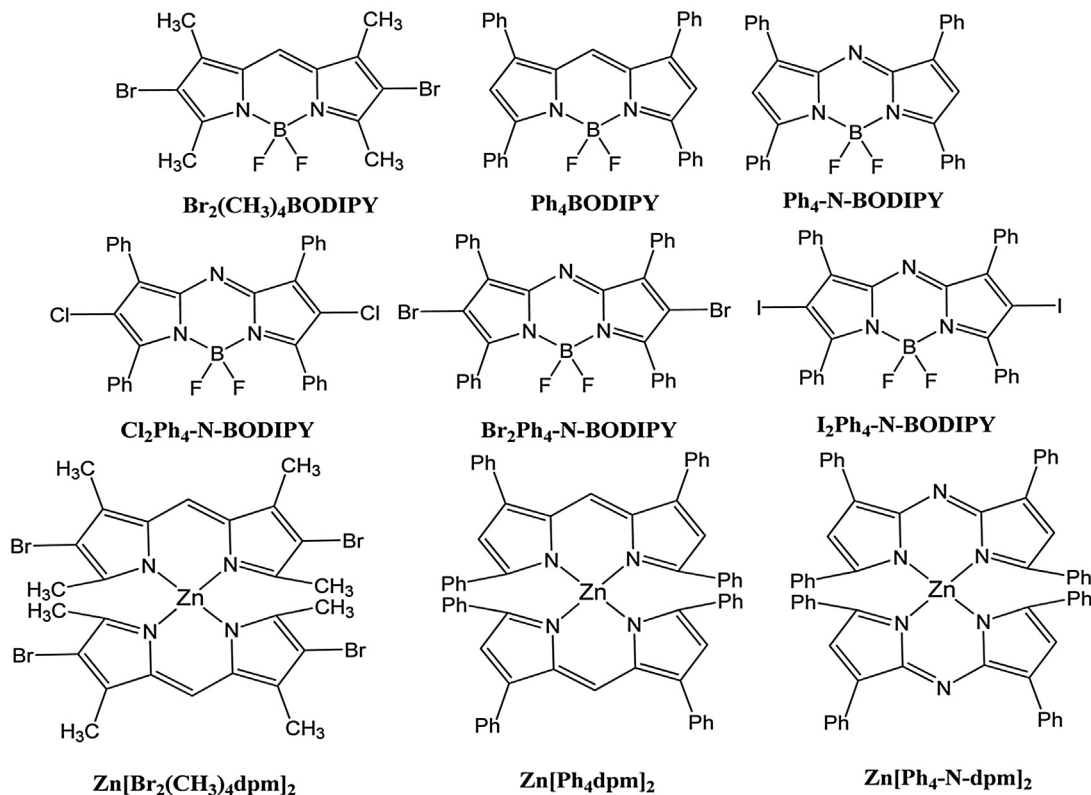


Fig. 1. Structures and designations of the investigated compounds.

Download English Version:

<https://daneshyari.com/en/article/4753931>

Download Persian Version:

<https://daneshyari.com/article/4753931>

[Daneshyari.com](https://daneshyari.com)