



Novel quenchometric oxygen sensing material based on diiodine-substituted boron dipyrromethene dye



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ARTICLE INFO

Article history:

Received 29 November 2013

Received in revised form 13 February 2014

Accepted 22 February 2014

Available online 6 March 2014

Keywords:

Boron dipyrromethene

BODIPY

Iodine

Phosphorescence

Quenching

Oxygen sensor

ABSTRACT

Emission spectra of diiodine-substituted boron dipyrromethene (I_2 BODIPY) dye in ethanol solutions and in methylcellulose matrix were studied. The solid patterns were photoexcited at 520 nm and display room temperature phosphorescence with a maximum at 790 nm that is quenched by molecular oxygen at room temperature. Novel sensing material for oxygen concentration detection from 0% to 100% has been developed on the basis of I_2 BODIPY with 17-fold sensitivity (I_{Ar}/I_{O_2}), reverse, fast response (1 s) and linear calibration. The sensitivity dependence on the active substance concentration in matrix was shown.

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1. Introduction

Creation and development of oxygen sensors have attracted much attention of chemists worldwide because of their broad application in biology, food industry, aircrafting, ecology and life science [1,2]. Optical detecting method based on luminescence quenching of organic dye has some advantages over analogs; optical oxygen sensors are inexpensive, easily miniaturized and simple to use, and have extraordinary sensitivity and reversibility [3,4]. Probes available as oxygen sensors are organic dyes and metal-complexes of organic dyes, including the transition metals complexes with organic compounds and metalloporphyrins, which have intensive phosphorescence. Sensitivity of sensors based on transition metal complexes is relatively low ($I_0/I < 15$) [4]. Oxygen sensors based on metal-porphyrin complexes, especially Pt and Pd porphyrin complexes, have a great potential due to the high extinction coefficients, quantum yields, long lifetime and excellent photostability [5]. They possess extraordinary sensitivity at low oxygen concentrations, but are characterized by high cost. Among organic luminescent

probes, pyrene and its derivatives have been selected as luminescent probes for oxygen sensors due to their relatively long excited triplet state life-time and efficient quenching by oxygen (Table 1) [6]. Also, erythrosin B [7] and some other organic dyes have been applied as luminescent probes for oxygen detection [3,4,8]. The disadvantages of optical oxygen sensors based on organic dyes are low photostability, small Stokes shift, short-wave excitation (300–400 nm) and poor sensitivity [4].

Among other classes of organic dyes, borondifluorodipyrromethene (BODIPY) derivatives (Fig. 1) stand out as stable molecules with appropriate luminescent characteristics. BODIPY was first prepared in 1968 by Triebs and Kreuzer [9] and has been developed as a laser dye. For the last decade, fundamental properties of BODIPY dyes and their numerous applications are the point of interest for many scientific groups all over the world [10–12].

The synthesis of BODIPY dyes can be carried out from available pyrrole-based reagents and often in high yield. Substitution changes the photophysical properties of these dyes dramatically, depending on structure of a substitute, substitution pattern and type of group in meso-position. Some works illustrate it clearly [13–15]. Furthermore, self-aggregation of BODIPY dyes is insignificant compared with rhodamine-6G, for example, which is another advantage.

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Table 1
Comparison between previous dye-based materials and the current I₂BODIPY-based materials.

Substance	Matrix	Phosphorescence quantum yield, %	λ_{exc} , nm	I_0/I	Stern–Volmer plot	Response time to O ₂ , s	Ref.
Erythrosin B	Sol–gel silica	2	532	100	Nonlinear	1	[6]
1-decyl-4-(1-pyrenyl)butanoate	Silicon coating	–	300–380	–	–	10	[25]
1-pyrenedecanoic acid	Anodic oxidized aluminium plate	–	340	20.2	Nonlinear	8.5	[26]
Perfluorodecanoic acid		–		18.6		3.0	
LuTPP	Methylcellulose	40	420	40.0	Nonlinear	1.0	[19]
I ₂ BODIPY	Methylcellulose	60	500–520	17.2	Linear	1.0	This work
PtOEP	ethylcellulose	–	green LED	40	Linear	300	[27]
PTFPP	n-propyl-TriMOS/TFP-TriMOS film	8.8	–	68.7	Linear	3.7	[4]
[Ru(dpp)3] ³⁺	Ormosil	30	467	15	–	30	[4]

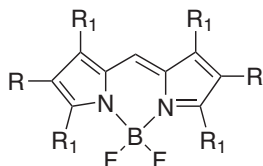


Fig. 1. Structure of BODIPY dye: R = R₁ = H–BODIPY; R = I, R₁ = CH₃–I₂BODIPY.

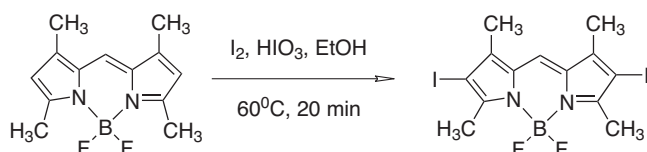
Emission from BODIPY dyes is quite intense; fluorescence quantum yield reaches 99% [16]. The energy of triplet stay is low (12800 cm⁻¹), and in fact phosphorescence is rarely seen. Intersystem crossing can be enhanced via the heavy atom effect [17]. Nevertheless, there are no papers about optical oxygen sensing properties of iodine-substituted BODIPY.

Based on this background, in this work we report a photo-physical study of diiodinated BODIPY dye in ethanol solution and analytical properties of diiodinated BODIPY dye incorporated in methylcellulose matrix, Stern–Volmer quenching constants (K_{SV}) and bimolecular quenching constant (k_q) that describes the interaction between the quencher molecules (O₂) and luminophor molecule in matrix.

2. Experimental details

2.1. Chemicals and reagents

4,4-difluoro-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (I₂BODIPY) was synthesized according to the approach published in [18] under some modification (Scheme 1). 0.188 g (0.74 mmole) of iodine and 0.065 g (0.37 mmole) of HIO₃ were added to 0.23 g (0.927 mmole) 3,3',5,5'-tetramethyl-2,2'-dipyrrromethene difluoroborate solution in 20 ml of methanol. The solution was boiled for 20 min before the iodine color disappears. The solution was cooled down, the precipitate was filtered, washed with methanol and air dried. The resulting mixture of difluoroborates of mono- and diiodine-3,3',5,5'-tetramethyl-2,2'-dipyrrromethene was separated by multiple recrystallization from methylene chloride. The yield was 47% (0.22 g, 0.44 mmole). The structure of product was confirmed by spectrophotometry and ¹H NMR (CDCl₃) (in. st. TMS) δ , ppm: 7.13 s (2H, ms-H); 2.61 s, 2.25 s (2 × 6H, CH₃). Ethanol (HPLC grade) was used as a solvent.



Scheme 1. The synthesis of 4,4-difluoro-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (I₂BODIPY).

2.2. Sample preparation

For sample preparation, the fibers of methylcellulose (MC-100, ReaChem) were pressed in tablets with thickness of about 1 mm and diameter of about 7 mm, which were impregnated by dye solution in ethanol with concentration of 10⁻⁵, 10⁻⁴ and 10⁻³ M (5 tablets for each concentration) and dried under standard conditions. Polymer swelling in ethanol was not observed because of small quantities of solvent: volume of impregnating solution was 0.15 ml. After impregnating the volume of tablet increased by 20%.

2.3. Instrumentation

The instrumentation has been described in details in [19]. The UFGS-4 device with PC-control was used to introduce mixtures of Ar and O₂ over the matrix surface within a flow cell. The O₂ concentrations were set accurate to $\pm 0.05\%$. The dye-impregnated matrix was excited by LED (λ_{ex} = 500–520 nm), the emission was registered at 790 nm. The AvaSpec-2048-2 spectrometer (Avantes BV) was used for luminescence registration.

The phosphorescence intensity, quantum yields and life time were registered at 77 K in ethanol with spectrofluorimeter Cary Eclipse (Varian) and Cryostat DN (Oxford Instruments).

3. Results and discussion

3.1. Properties in solution

BODIPY dyes are highly coloured and display narrow absorption band with high extinction coefficient in the visible range. The absorption spectra of BODIPY dyes are only slightly affected by a solvent. Although BODIPY dyes are well-known for their intense fluorescence, substitution by heavy atoms changes the photophysics of the molecule to a great extent. Halogenated BODIPY dyes are the most useful building blocks for conjugation extending procedures and can find application as probes for photodynamic therapy (PDT), noninvasive methodology for tumour treatment. Recently, it has been shown that iodine or bromine incorporation into the BODIPY core enhances intersystem crossing, and a few promising sensitizers for use in PDT have been reported as an alternative to the porphyrin-based photosensitizers [20,21]. Different ways to achieve halogenated BODIPY dyes were proposed: halogenation of the pyrrole ring, halogenation of the dipyrromethene precursors or electrophilic substitution reactions on the previously synthesized BODIPY dye. BODIPY dyes halogenated at different positions were synthesized and studied [22].

Absorption spectrum of I₂BODIPY in ethanol (Fig. 2a) is presented by narrow bands at 534 nm. Fluorescence (Fig. 2a) maximizes at 553 nm and is characterized by quantum yield 0.04 at room temperature. Phosphorescence at 77 K (Fig. 2a) is presented

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