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Photophysics and oxygen sensing properties of tetraphenylporphyrin lanthanide complexes

Elena G. Ermolina [a,*], Rimma T. Kuznetsova [a], Tat'yana A. Solodova [a], Evgenii N. Tel'minov [a], Tat'yana N. Kopylova [a], Georgii V. Mayer [a], Nikolai N. Semenishyn [b], Natal'ya V. Rusakova [b], Yurii V. Korovin [b]

[a] Tomsk State University, Laboratory of Laser Physics, Novosobornaya Sq. 1, 634050 Tomsk, Russia
[b] A.V. Bogatskii Physical-Chemical Institute of the National Academy of Sciences of Ukraine, 65080 Odessa, Ukraine

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ABSTRACT

Absorption and phosphorescence emission spectra of complexes of lutetium(III) and gadolinium(III) with tetraphenylporphyrin in ethanol solutions and in thin films of polytretbutylmethacrylate, polystyrene and methylcellulose are studied. The complexes were photoexcited at 420 nm and display room temperature phosphorescene with a maxima at 780 nm that is quenched by molecular oxygen at room temperature. This quenching effect was exploited to optically sense oxygen. The response time is 1.0–1.2 s, and the detection limit is 0.05% of oxygen.

1. Introduction

Methods of determining oxygen in gas mixtures are widely used in chemistry, oceanography, meteorology, biology, clinical analysis, and environmental monitoring. Among them the ammeter method based on the application of an oxygen electrode in which the rate of oxygen diffusion to the cathode is measured is most popular [1,2]. However, a serious disadvantage of this method is the electrode surface instability. In the last few years, the optical direction of oxygen sensing, based on quenching of organic dye luminescence by O_2 molecules, has actively been developed [3,4].

Metalloporphyrins possess enormous potential for optical sensing due to their large molar extinction coefficients, long radiation lifetime, high phosphorescence intensity, and good photostability. Platinum and palladium porphyrins possess intense phosphorescence at room temperature ($\varphi_{ph} = 0.45$ for PtOEP in a liquid solution [5]), which makes them promising for optical oxygen sensing [6–9]. The active search for compounds possessing high sensitivity to oxygen is directed toward related metalloporphyrins and other compounds including transition metal complexes [10,11] and polycyclic aromatic hydrocarbons [12,13].

In addition to the active sensor molecule, the matrix is of great importance for high material sensitivity to oxygen [3,14]. It must be highly porous and transparent in a wide spectral range and must not provoke photochemical degradation of the dye molecule. The most important practical results have been obtained with a dye incorporated in porous organically modified sol–gel films [7,9].

The sensor ability of lanthanide complexes with tetraphenylporphyrin incorporated in different polymeric films is investigated in the present work. These complexes are used for the first time as agents for optical oxygen sensing.

2. Experimental

2.1. Substances and material preparation

We investigated the tetraphenylporphyrin complexes with lanthanide ions Lu(III) and Gd(III) and Cl^- anion as the axial ligand synthesized by the method described in [15]. The indicated complexes were investigated in ethanol solutions, polymeric films of different compositions, and films based on methylcellulose. The structures of the compounds and polymers are shown in Fig. 1.

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[*] Corresponding author. Tel.: +7 3822 533426; fax: +7 3822 533034.
E-mail addresses: yaskolka@inbox.ru, ermolina.phch@gmail.com (E.G. Ermolina).

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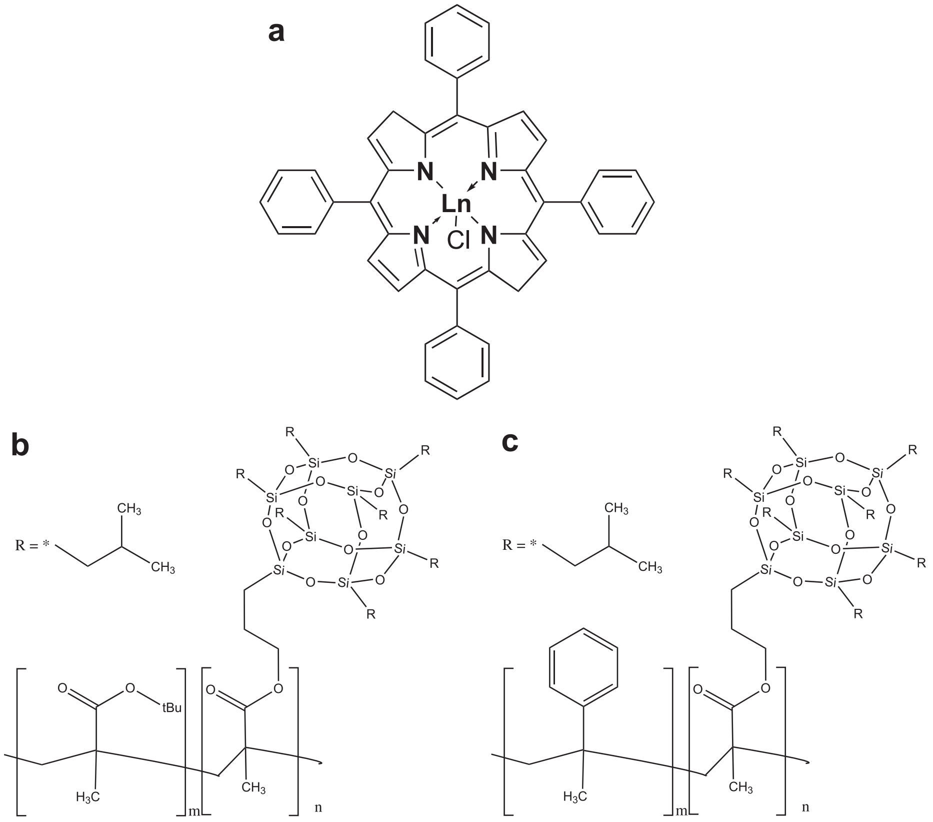

Fig. 1. Structure of the (Cl)MTPP complexes with M = Lu(III) or Gd(III) – a, poly[(propylmethacryl-hepta-iso-butyl-POSS)-co-(tert-butylmethacrylate)] (t-Bu POSS) – b and poly [(propylmethacryl-hepta-iso-butyl-POSS)-co-styrene] (St POSS) – c copolymers.

To prepare the polymeric films, the polymer (0.1 g) was added to tetrahydrofuran (THF) (1.0 mL) of the dye solution (10^{-3} mol/l). Then the films were put on a glass plate by the centrifuging method (spin-coating) and dried in vacuum at 60 °C. Copolymers of tert-butylmethacrylate or styrene with propylmethacrylate, comprising 15 or 25% of octa(propylmethacrylate) polyhedral oligomerous silsesquioxane (POSS) as a lateral substituent: poly[(propylmethacryl-hepta-iso-butyl-POSS)-co-(tret-butylmethacrylate)] (t-Bu POSS-15) and poly[(propylmethacryl-hepta-iso-butyl-POSS)-co-styrene] (St POSS-15 and St POSS-25) were used (Fig. 1). POSS was added to increase the permeability of polymer for oxygen molecules [16,17]. Since positive results on incorporation of sensor compounds based on porphyrins into methylcellulose were reported in the literature [18], we prepared such samples. To prepare a film based on methylcellulose, the suspension prepared by methylcellulose swelling in dimethylsulfoxide (DMSO) solution (10^{-3} mol/l) for a week and subsequent treatment in an ultrasonic bath was put on a glass plate by either a pouring or spin-coating method and dried in vacuum.

2.2. *Methods*

2.2.1. *Luminescent measurements*

The luminescence spectra of solutions were registered at 298 and 77 K using a Cary Eclipse (Varian) spectrometer equipped with an Optistat DN cryostat (Oxford Instruments) which allowed degassing of the frozen solutions to be performed by the method of cyclic unfreezing-freezing with pumping down to 10^{-3} atm. The quantum radiation yield was determined by the standard method with an error of 10% using the ZnTPP standard [19]. The phosphorescence lifetime was estimated from the exponential I_0/I dependences on time t with variable radiation delay time [18].

2.2.2. *Sensor properties*

The sensor properties of polymeric films with incorporated complexes were investigated on the setup built around an SM2203 spectrofluorimeter consisted of a UFPGS-4 device intended for generating gas mixture flow, a gas cell with the examined sample put in the cell block of the spectrofluorimeter, and a personal computer. A UFPGS-4 device generated initial gas flow with a preset volume discharge and provided its mixing to prepare a uniform gas mixture.

Gas flow control devices with large dynamic range of flow regulation and small time of establishing a preset flow rate were used in the setup. The setup was equipped with an USB interface and was computer-controlled. Gas mixtures of up to 4 components with preset concentrations could be prepared using the UFPGS-4 device. The UFPGS-4 specifications are presented below.

• Input initial gas pressure	0.5–0.6 MPa (5–6 atm)
• Output pressure of the gas mixture	0–0.3 MPa (0–3 atm)
• Number of initial gases	4
• Range of gas flow rates	0.1–1300 cm^3/min
• Range of concentrations of gas mixture components	From 10 ppm to 10% (with preliminary diluted mixtures) and from 100 ppm to 100% with pure gases
• Error in setting and adjusting the composition and flow rate of the gas mixture	≤2%.

Pure oxygen was used as a gas-analyte, and argon was used as a gas-diluent.