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Hybrid Clay / Porphyrin Nanomaterials for Oxygen Sensing

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The presented research is focused on the investigation of hybrid systems of hosting clay minerals with incorporated metallated porphyrin molecules. These systems are used with intention to develop materials suitable for the construction of perspectively efficient oxygen sensors, as well as for the singlet oxygen production. As a guest materials, metalloporphyrins containing a heavy metals such as platinum and palladium are usually utilized. These are known to be very efficient for the oxygen sensing applications due to a “heavy atom effect”. This effect promotes a spin-orbit coupling, resulting in the fact that almost all of the radiation from singlet excited state undergoes the intersystem crossing, followed by a de-excitation via a triplet state. As a result, a phosphorescence from these systems can be observed in a presence of an inert gas, e.g. nitrogen. However, in a presence of a reactive oxygen the collisional quenching takes place, resulting in a diminish of phosphorescence. By changing the nitrogen-to-oxygen atmosphere and vice versa, one can study the behaviour of an “on-off” type sensing. It was found out that the clay/metalloporphyrin nanomaterials are perspective candidates for optical oxygen sensing applications.

Keywords: Hybrid systems, Spin-orbit coupling, Metalloporphyrin nanomaterials.

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1. INTRODUCTION

Clay minerals represent a numerous and one of the most important group of materials in a present material chemistry. These have attracted a serious attention for their special and interesting properties such as swelling, formation of stable colloids, large surface area and especially their capacity to adsorb both the organic and inorganic compounds [1-3]. Due to their versatility, they represent a unique base for the development of novel functional organic/inorganic hybrid materials with clay mineral in a role of an inorganic component [4-6].

The quantitative determination of oxygen in a gas or liquid phase is of high importance in several fields, e.g. environmental monitoring, chemical and food industry, medical and biological applications, analytical chemistry, etc. [7-9]. Recently, a new class of oxygen sensors based on luminescence quenching has been reported and has attracted a considerable attention. Optical oxygen sensors (OOSs) are a group of materials that are expected to fulfill several conditions, i.e. to be economically affordable, miniaturized, easy to use, with high sensitivity and reversibility, as well as not suffering from factors such as electrical interference or oxygen consumption. The utilization of OOSs depends on a three main parameters: optical sensing probes, supporting materials and determination methods [10]. In case of OOSs, the main mechanism is based on a luminescence quenching of the luminophore in a presence of oxygen, while the oxygen is a highly efficient quencher of the electronically excited states of dye molecules. The excited-state lifetime or the emission intensity of the luminophore alters with changes in oxygen concentration. Luminescent probes utilized as oxygen sensors are generally classified as oxygen-quenchable luminescent complexes and luminescent nanomaterials [11].

2. DISCUSSION

At a first stage, visible and phosphorescence spectra of clay-immobilized metal complexes of porphyrins were studied. As expected, porphyrins showed characteristic absorption, as well as a room temperature phosphorescence characteristics (Fig. 1). The adsorption of porphyrins leads to a bathochromic shift of clay/porphyrin hybrid complex (~50 nm) if compared to a pure Pd-porphyrin (PdTMPyP) solution. In case of clay minerals, the flattened or a slightly tilted orientation of adsorbed porphyrins takes place, while their photophysical and spectral characteristics are preserved. Due to these facts, one can judge the clay minerals as the exceptionally suitable and economically affordable carrier substances, suitable for an utilization in efficient optical oxygen sensors.

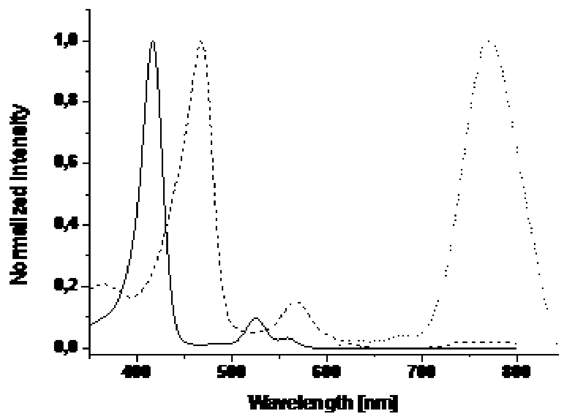

Fig. 1 – Absorption spectra of PdTMPyP solution (solid line), clay/porphyrin membrane (dashed line) and phosphorescence spectra of clay/porphyrin membrane upon excitation at 466 nm (dotted line)

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The important parameters employed in a characterization of OOSs are represented by a response time and recovery time.

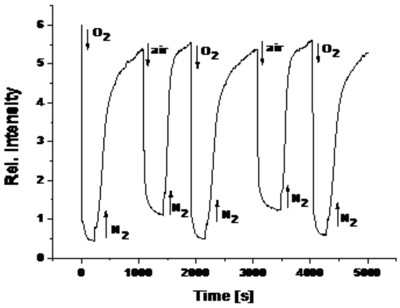

Fig. 2 – Gas dependent phosphorescence of the clay/porphyrin hybrid system.

The response time is a time when the phosphorescence intensity decreases by 95% by introducing the oxygen (t_{95} ($N_2 \rightarrow O_2$)). Analogically, the recovery time is the time needed to reach the original phosphorescence intensity by introducing the nitrogen, i.e. (t_{95} ($O_2 \rightarrow N_2$)).

Fig. 2 depicts a gas dependent phosphorescence of a clay/porphyrin system over time ("on-off" sensing). In the case of present system, the interlayer distance determined by XRD was estimated to be c.a. 0.5 nm. This narrow space would limit the diffusion of gas. It is known that the interlayer space of clay can be controlled by the change of the atmosphere or by the use of a pillar. This indicates the possibility to control the sensitivity against oxygen concentration as desired by changing the interlayer distance.

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