VERSITA

Cent. Eur. J. Chem. • 11(7) • 2013 • 1132-1136
DOI: 10.2478/s11532-013-0238-z

Central European Journal of **Chemistry**

Oxygen sensing materials based on clay/metalloporphyrin hybrid systems

Research Article

Alexander Čeklovský*, Shinsuke Takagi

[1]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, 845 36 Bratislava, Slovakia*

[2]*Department of Applied Chemistry, Graduate Course of Urban Environmental Sciences, Tokyo Metropolitan University, Hachiohji, Tokyo 192-0397, Japan*

[3]*PRESTO (Precursory Research for Embryonic Science and Technology), Japan Science and Technology Agency, Saitama 351-0198, Japan*

Received 5 December 2012; Accepted 25 February 2013

Abstract: This study was focused on the investigation of novel hybrid organo/inorganic systems for oxygen sensing applications. As a host material, a synthetic clay mineral Sumecton SA was chosen, while, as guest materials, metalloporphyrins containing Pt(II) and Pd(II) were chosen. These are known to be very efficient agents for sensing applications because of a "heavy atom effect". This effect promotes a spin-orbit coupling, resulting in the fact that almost all of the radiation from a singlet excited state undergoes intersystem crossing, followed by a de-excitation *via* a triplet state. The combination of metalloporphyrin and layered materials enables unique oxygen sensing properties due to the steric effects of layered materials. The result is that the emission from the membrane was sensitive at the range around aerobic conditions. The spectroscopic analysis of hybrid systems – clay/porphyrin membranes (CPMs) showed that these materials can serve as prospective candidates for the construction of effective, reliable and economical oxygen sensors.

Keywords: *Porphyrin • Clay • Oxygen sensor • Visible spectroscopy • Phosphorescence*

1. Introduction

One of the most important groups of materials in present material chemistry is represented by clay minerals. These perspective and widely used materials have been the subject of investigation in various fields for their unique properties including swelling, ability to form stable colloidal suspensions, a large surface area and especially their capacity to incorporate both organic and inorganic compounds [1-3]. Due to their versatility, they provide a tremendous potential for a development of novel functional organic/inorganic hybrid materials with clay minerals in a role of an inorganic carrier component [4-6]. The formation of the hybrid materials composed of clay minerals and organic compounds can be easily controlled *via* ion-exchange reaction, intercalation or adsorption. Hence, the interaction between various layered inorganic materials and organic chromophores has been the subject of numerous studies [7-14].

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.* [15-17].

Recently, a new class of oxygen sensors based on luminescence quenching has been reported and has attracted a considerable amount of 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,

* *E-mail: alexander.ceklovsky@savba.sk*

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 [18]. 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 [19].

From this point of view, the most promising luminescent probes are the stable platinum metal porphyrin dyes, that have the lowest triplet excited state population probability close to unity due to the heavy atom effect [20]. For instance, platinum and palladium octaethylporphyrins embedded in a different polymer matrix are commonly used [21]. However, the challenge is to find and utilize a suitable luminescent indicator in which a phosphorescence is effectively quenched by a molecular oxygen, as well as a suitable material permeable to oxygen in which a luminophore molecules can be easily incorporated. Both the components should show a photostability to continuous light irradiation, used for the excitation of luminophore. Moreover, complexes of cationic water-soluble porphyrins with platinum metals (Fig. 1) are known to have a relatively long phosphorescence lifetime at room temperature [22]. Furthermore, their phosphorescence emission can be very effectively quenched by a molecular oxygen in aqueous solutions [23].

Finally, in order to form highly efficient, stable and reliable oxygen sensing hybrid systems, the choice of a suitable supporting material is of crucial importance. Clay minerals have been proven to be very promising candidates while the adsorption of sensing porphyrins is an easily achievable and controlled process, eliminating non-desirable processes such as dye molecular aggregation [24].

2. Experimental procedure

2.1. Materials

Synthetic clay mineral Sumecton SA (Kunimine Industries Co., Ltd.) was used as the inorganic carrier for the preparation of clay/porphyrin membranes (CPMs). Cationic metalloporphyrins, Pt(II) meso-tetrakis(*N*-methyl-4-pyridyl)porphine tetrachloride (Pt(II)TMPyP)

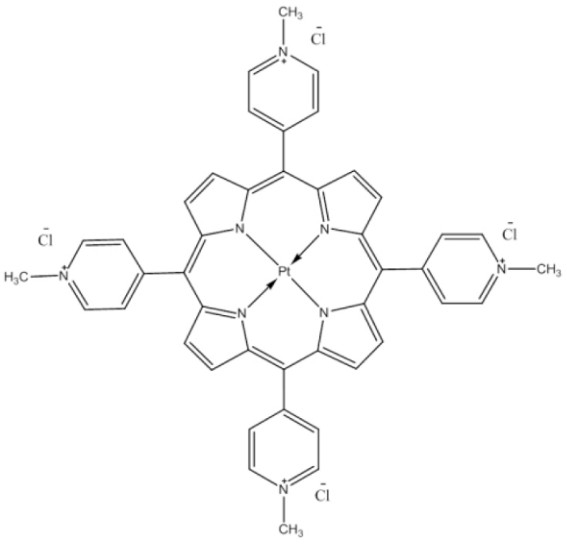

Figure 1. Pt(II) meso-tetrakis(N-methyl-4-Pyridyl)porphine tetrachloride.

and Pd(II) meso-tetrakis(*N*-methyl-4-pyridyl)porphine tetrachloride (Pd(II)TMPyP) were obtained from Frontier Scientific, Inc. and used as received. In a preparation of CPMs, Polytetrafluoroethylene (PTFE) membrane filters (Toyo Roshi Kaisha, Ltd., pore size - 0.1 μm, diameter - 25 mm) were employed. Quartz slides were obtained from SPI Supplies (USA). Needles used for the directing the gas flow into a cell were purchased from Terumo (Japan). Deionized water (Millipore Q-system) was used for all of the experiments.

2.2. Methods

The clay-porphyrin membrane was prepared as follows according to the literature [25]. Aqueous clay suspensions were prepared by adding the calculated amount of Sumecton SA into water and left under mild stirring until the suspension was transparent. The calculated volumes of Pt(II)TMPyP and Pd(II)TMPyP solutions were added into a clay suspension under stirring. Dye loading was set to a value of 5-15% *vs.* cation exchange capacity (CEC) in order to eliminate the possible negative effects of higher dye concentration. A small amount of dioxane was added into a suspension to accelerate clay stacking. The prepared clay/porphyrin suspension was then vacuum-filtrated through a PTFE membrane, followed by deposition of a filter cake to a quartz slide. The prepared clay/porphyrin membrane should be homogeneous, without obvious defects (*i.e.*, without regions not covered by a filter cake) and is ready to use for oxygen sensing experiments.

The absorption spectra of clay/porphyrin suspensions and CPMs were recorded using a Shimadzu UV-3600 UV–vis spectrophotometer. While

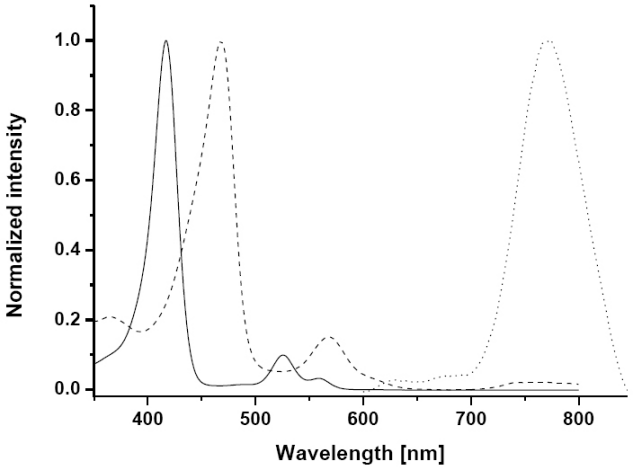

Figure 2. Absorption spectra of PdTMPyP solution (solid line), CPM/PdTMPyP (dashed line) and phosphorescence spectra of CPM/PdTMPyP upon excitation at 466 nm (dotted line).

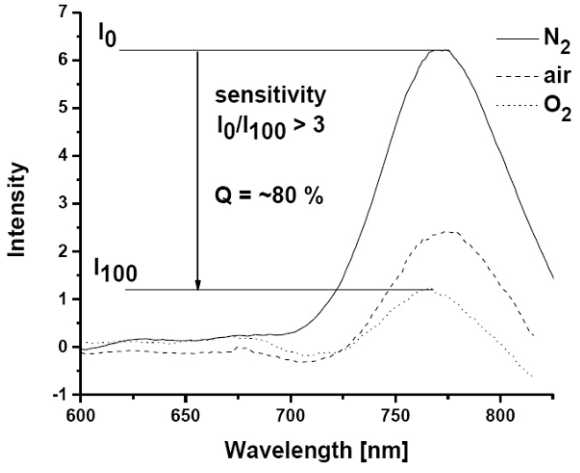

Figure 3. Phosphorescence spectra od PdTMPyP in the presence of molecular nitrogen, air and molecular oxygen.

the scattering effect of clay particles (due to a low concentration in a suspension) was very low, there was no need to perform the corrections for absorption measurements. Steady-state fluorescence spectra were recorded using a Jasco FP-6500 luminescence spectrophotometer upon excitation at 450 nm (λ_{max} absorption of PtTMPyP membrane) and 466 nm (λ_{max} absorption of PdTMPyP membrane).

3. Results and discussion

At the first stage, visible and phosphorescence spectra of clay-immobilized metal complexes of porphyrins were studied. As expected, porphyrins showed characteristic absorption, as well as room temperature phosphorescence characteristics (Fig. 2). It was found that the adsorption of porphyrins leads to a spectral band shift of pure PdTMPyP solution of ~50 nm when compared to CPM complex (Fig. 2). This is a rather common phenomenon, related to stabilization of dye molecules upon adsorption on a clay mineral's surface, as described elsewhere [5,8, and references therein]. In the case of clay minerals, the flattened or slightly tilted orientation of adsorbed porphyrins takes place [5,9] while their photophysical and spectral characteristics are preserved. Owing to these facts, one can judge clay minerals as exceptionally suitable and economically affordable carrier substances, suitable for utilization in efficient optical oxygen sensors.

The phosphorescence of porphyrins was effectively quenched by molecular oxygen (Fig. 3).

Room temperature phosphorescence, as well as a photostability over time, are important characteristics of OOSs. However, there are other requirements for the OOSs to be fulfilled, *i.e.*, sensitivity of quenching membrane, expressed as a ratio I_0/I_{100}, where I_0 and I_{100} represent the phosphorescence intensities in

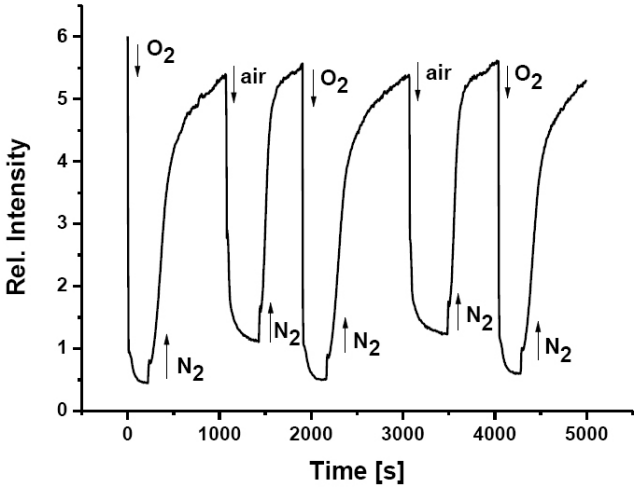

Figure 4. Gas dependent phosphorescence of CPM/PdTMPyP system.

the presence of 100% nitrogen and 100% oxygen, respectively. A material suitable for optical oxygen sensing should have the ratio $I_0/I_{100} > 3$ [23], which is fulfilled in a demonstrated case of CPM with PdTMPyP (Fig. 3). Key requirements include quenching response, response time and recovery time. Quenching response (*Q*) is defined as a ratio $Q = (I_{N2} - I_{O2}) / I_{N2}$ and was determined to be approximately 80% for the system containing PdTMPyP (see Fig. 3). It should be noted that the emission from CPM is sensitive at normal aerobic conditions.

Another important parameter employed in the characterization of OOSs includes response time and recovery time. The response time is described as a time when the phosphorescence intensity decreases by 95% by introducing oxygen (t_{95} ($N_2 \rightarrow O_2$)). Analogically, recovery time is the time needed for CPM to reach the original phosphorescence intensity by introducing the nitrogen, i.e. (t_{95} ($O_2 \rightarrow N_2$)). Fig. 4 depicts a gas dependent phosphorescence of CPM/PdTMPyP over time ("on-off" sensing). From the data, response and recovery time for this system were found to be around 10 and 800 seconds, respectively. It can be seen that oxygen permeation is different (faster) when entering the membrane than the rate of intensity increase of oxygen diffusion outward the CPM. This observation is in accordance with previous theoretical studies [26] and may be related to the homogeneity of the clay mineral surface available for a porphyrin adsorption. In the case of present CPM, 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 a change of atmosphere or by the use of a pillar. This indicates that it is possible to control the sensitivity against oxygen concentration as needed by changing the interlayer distance.

In the case of the CPM/PtTMPyP system (not shown), the above mentioned characteristics and requirements for OOS were determined to be similar, although the CPM/PdTMPyP system was proven to be a more prospective candidate for OOSs because of higher sensitivity, photostability and better overall spectral properties.

4. Conclusions and concluding remarks

In this present study, novel hybrid materials based on synthetic clay and platinum metal porphyrins for optical oxygen sensing are proposed. It was found that clay minerals are economically affordable substances that can serve as reliable inorganic carriers for immobilization of phosphorescently active porphyrin molecules, preserving their luminescence activity that is sufficient to reach oxygen sensing processes at aerobic conditions. The results indicate that the hybrid system containing PdTMPyP is a better candidate for OOSs applications than its platinum counterpart, although the latter is worth investigating in further studies. In these systems, the role and parameters (such as variable expandability) of clay mineral matrix is important while the layered structure can affect oxygen permeation, thus having an influence on response and recovery time parameters of the oxygen sensor. More detailed studies on such factors is in progress and will be published in the near future.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0291-11, grant agency VEGA (2/0089/09), grant agency VEGA (2/0107/13), Grant-in-Aid from Japan Society for the Promotion of Science (JSPS) postdoctoral fellowship for foreign researchers, and Precursory Research for Embryonic Science and Technology (PRESTO) from Japan Science and Technology Agency (JST) is also acknowledged. The authors would like to thank Dr. Dai Masui for valuable discussions during this work.

References

[1] A.C.D. Newman, Chemistry of clays and clay minerals, Monograph No. 6 (Mineralogical Society, New York, 1987)
[2] H. van Olphen, An Introduction to Clay Colloid Chemistry, 2nd edition (John Wiley and Sons, New York, 1977)
[3] R.E. Grim, Clay Mineralogy, International Series in Earth and Planetary Sciences, 2nd edition (Pergamon Press, New York, 1968)
[4] T. Shichi, K. Takagi, J. Photochem. Photobiol. C: Photochemistry Reviews 1, 113 (2000)
[5] S. Takagi, M. Eguchi, D.A. Tryk, H. Inoue, J. Photochem. Photobiol. C: Photochemistry Reviews 7, 104 (2006)
[6] M. Ogawa, K. Kuroda, Chem. Rev. 95, 399 (1995)
[7] P.M. Dias, D.L.A de Faria, V.R.L.Constantino, J. Inclusion Phenom. Macrocyclic Chem. 38, 251 (2000)
[8] S. Takagi, D.A. Tryk, H. Inoue, J. Phys. Chem. B 106, 5455 (2002)
[9] Z. Chernia, D. Gill, Langmuir 15, 1625 (1999)
[10] C. Sanchez, B. Lebeau, F. Chaput, J.-P. Boilot Adv. Mater. 15, 1969 (2003)
[11] J. Bujdák, N. Iyi, Y. Kaneko, R. Sasai, Clay Miner. 38, 561 (2003)
[12] Ch.A. Schalley, A. Lutzen, M. Albrecht, Chem. Eur. J. 10, 1072 (2004)
[13] M. Eguchi, S. Takagi, H. Tachibana, H. Inoue, J. Phys. Chem. Solids 65, 403 (2004)
[14] R. Sasai, N. Iyi, T. Fujita, F. López Arbeloa, V. Martínez Martínez, K. Takagi, H. Itoh, Langmuir 20, 4715 (2004)
[15] S. Lee, I. Okura, Analyst 122, 81 (1997)
[16] S. Lee, I. Okura, Anal. Chim. Acta 342, 181(1997)
[17] F. Tan, L. Chen, B. Yang, Y. Guan, J. Ma, Sens. Actuators, B 99, 272 (2002)
[18] A. Mills, Platinum Metals Rev. 41, 115 (1997)
[19] X. Wang, H. Chen, Y. Zhao, X. Chen, X. Wang, Trends Anal. Chem. 29, 319 (2010)
[20] V.V. Vasilev, I.A. Blinova, I.V. Golovina, S.M. Borisov, J. Appl. Spectrosc. 66, 583 (1999)
[21] Y. Amao, Microchim. Acta 143, 1 (2003)
[22] S.M. Borisov, V.V. Vasilev, J. Anal. Chem. 59, 176 (2004)
[23] V.V. Vasilev, S.M. Borisov, Sens. Actuators, B 82, 272 (2002)
[24] Y. Ishida, D. Masui, H. Tachibana, H. Inoue, T. Shimada, S. Takagi, Appl. Mater. Interf. 2, 811 (2012)
[25] S. Takagi, T. Shimada, D. Masui, H. Tachibana, Y. Ishida, D. A. Tryk, H. Inoue, Langmuir 26, 4639 (2010)
[26] A. Yekta, Z. Masoumi, M. A. Winnik, Can. J. Chem 73, 2021 (1995)