

Oxygen sensor based on hybrid material: Copper (I) complex incorporated in mesoporous silica matrix

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Abstract

We report the extinction of luminescence $\text{Cu}_4\text{I}_4\text{py}_4$ immobilized in mesoporous silica matrix in the presence of oxygen.

Introduction

Organometallic materials have been suggested for use in gas sensors when incorporated in substrates that provide a good interaction between the molecules of the complex and the gas to be detected. Their potential utility as sensors is due to the photoactive properties, chemical reactivity, redox activity, chirality and porosity¹. Furthermore, a porous matrix has a greater surface area which allows for greater interaction between the incorporated organometallic complex and the gaseous molecules of the gas to be detected. The copper (I) complex iodides, in particular $\text{Cu}_4\text{I}_4\text{py}_4$ offer advantages in relation to other complex, the ease of synthesis, relatively small and simple ligands with emission in the visible light region². The immobilization of these copper (I) complexes in the porous matrices has great potential for future applications in gas sensing devices, bio-imaging, bio-sensors, laser, and OLED. The copper (I) complexes were synthesized of according with the references⁸. The mesoporous silicate matrices were prepared by sol-gel method. For the incorporation of the copper (I) complex in the matrix, was added 300 mg of mesoporous silica in 10 ml of solution ($\text{Cu}_4\text{I}_4\text{py}_4$) in toluene at concentrations of 5.0 mM, 2.5 mM, 1.0 mM, 0.75 mM, 0.50 mM and 0.10 mM. The components (matrix + complex) remained under stirring of 80 Hz for a period of 48 hours. After this period, the sample was subjected to drying under nitrogen flow for 1 week. The optical absorption measurements in the UV/Vis region were realized in a spectrometer mark PerkinElmer Lambda model 25. The emission, excitation and lifetime measures were realized in a fluorometer brand Horiba Fluorolog model FL-1057.

Results and Discussion

The resulting composite materials present emission with intensity shifting from 580 to 720 nm as a function of concentration of the complex, very different from the complex in powder and solution forms. At room temperature, the emission designated as Low Energy (LE) is centered at 645 nm and at 77K it shifts to 620 nm. These results may

be due to a shortening of the Cu-N bond caused by the incorporation of the complex in the solid. The impregnated sample in inert N_2 atmosphere (298K) had a substantial increase in lifetime value for the LE emission in relation to the solution and powder ($\tau_{\text{impreg. (N}_2)} = 20 \mu\text{s}$, $\tau_{\text{powder}} = 10.6 \mu\text{s}$, $\tau_{\text{solution}} = 11.1 \mu\text{s}$). The luminescence quenching by oxygen at 645 nm indicates that some sites of porous silica containing guest molecules dispersed them enough so that the core of the cluster is able to interact reversibly with oxygen. This interaction causes the charge transfer from the excited state ${}^3\text{CC}$ for the oxygen molecule, decreasing the lifetime and the intensity of luminescence. The constant extinction estimated from the Stern-Volmer plot graph was $K_{\text{SV}} = 33.7$. This value is well above the value found for other copper (I) complexes of with larger and chemically distinct ligands to a value of $K_{\text{SV}} = 5.65^3$.

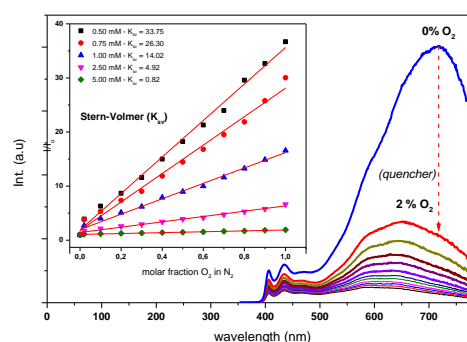


Figure 1. Quencher of luminescence ($\lambda_{\text{exc}} = 330 \text{ nm}$) to sample 0.75 mM in function of increase of oxygen concentration. Inset: Stern-Volmer plots.

Conclusions

The incorporation of the $\text{Cu}_4\text{I}_4\text{py}_4$ complex in mesoporous silicate matrices showed very promising as oxygen sensor, since in powder form, the complex showed no sensitivity to atmospheric oxygen.

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