Octahedral iron(II) phthalocyanine complexes: multinuclear NMR and relevance as NO_2 chemical sensors†

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Received 20th November 2009, Accepted 5th May 2010
First published as an Advance Article on the web 3rd June 2010
DOI: 10.1039/b924429h

The synthesis of new phthalocyanine iron(II) (FePc) based coordination complexes **2–7**, their structural characterization by multinuclear NMR (^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{57}Fe), and their use as improved sensitive and cheap optical NO_2 sensors is described. $\delta(^{15}N)$ and $\delta(^{57}Fe)$ values obtained *via* HMQC NMR methods show an interesting trend, the larger the chemical shift value the more the selectivity towards NO_2. Among all the sensing films prepared, the novel mixed ligand phosphite-amine [FePc(benzylamine)($P(OEt)_3$)] (**7**) immobilized into AP200/19 showed the best sensitivity, reversibility (LOD and LOQ of 1.2 ppb and 4.0 ppb, respectively), and thermostability in the range of 4 to 25 °C.

Introduction

Chemical sensors are devices that transform chemical information into an analytically useful signal. This information may originate from a chemical reaction or from a physical property of the system. The development of instrumentation, microelectronics and computers makes possible the design of sensors using most of the known chemical and/or physical principles. Nitrogen dioxide (NO_2) is an extremely toxic gas generated primarily from the liberation of nitrogen contained in fuel as a byproduct of combustion processes.[1] NO_2 is also a source of acid rain, damaging buildings and polluting water sources.[2] Thus, monitoring NO_2 plays an important role making the environment safer and cleaner. The implementation of optical sensors has received growing interest since they offer potential advantages over other analytical methods,[3] *i.e.* sensors are easily miniaturized, they can be prepared as disposable low-cost sensors and, when coupled to optical fibers, pose potential non-invasive monitoring capabilities which are less sensitive to electromagnetic interference.[4]

Phthalocyanines (Pc's) and their analogues have been investigated for many years, especially with regard to their properties as dyestuffs, paints and colors.[5] Together with porphyrins, both represent a large family of functional molecular materials with high chemical and thermal stability. The Pc molecule has a two dimensional π-electron conjugated system (18 electrons) that can incorporate about 70 different metals.[6] Metallo-phthalocyanines and metallo-porphyrins are attractive systems for the optical detection of volatiles because of their open coordination sites for axial ligation[5b] and intense coloration. Organic thin films based on metals different than iron have been developed and described as optical chemically interacting materials for the detection of a variety of molecules.[7] The use of iron as a low cost and reduced environmental impact transition metal makes exploring their use in sensing layers a worthwhile pursuit.

Representative varieties of optical devices and sensors have been developed to date, *i.e.* azo compounds immobilized at the nanopores of a sol–gel structure,[8] porous glass doped with sulfanilamides and naphthylamines,[9] blue-green sol–gel acid–base indicators embedded in a hydro-gel matrix,[10] poly(3-octylthiophene-2,5-diyl) systems,[11] ZnO nanowires,[12] or phenylenediamines immobilized in polydimethylsiloxanepolycarbonate block copolymers.[13] Some of us have already reported AlOOH nanostructured films doped with phthalocyaninato-iron(II) complexes, and tested their sensor abilities against CO and NO_x.[14]

In this paper we present the synthesis of some new iron(II) Pc-based coordination complexes, their structural characterization by multinuclear NMR (^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{57}Fe), and their use as reactive, sensitive and cheap optical sensors for NO_2 determinations.

Results and discussion

Synthesis of FePc complexes

Inspired by the work of Watkins and Balch in the 70's,[15] where a number of bis adducts and mixed-ligand ferrous phthalocyanine were isolated, we decided to extend the variety of these two families of compounds and apply their attractive coordination properties of the iron metal on the field of sensors. As shown in Scheme 1, reaction of two equivalents of amine (decylamine, bencylamine, *para*-methoxybencylamine, or trimethylsilylmethylenamine) with FePc (**1**), in THF solution, affords complete conversion to the bis-amine iron complexes, **2–5**, respectively. Complexes **2** and **3** had been previously characterized by us[14] and they will be considered as model compounds.

The NMR spectra of compounds **2–5** indicate that they are all diamagnetic. Supporting the proposed composition is the elemental analysis of freshly prepared samples, which were thoroughly consistent for all of them. These iron complexes investigated may be ascribed into derivatives of six-coordinate bis-amine

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† Electronic supplementary information (ESI) available: 1D and 2D NMR spectra, absorption spectra, spectrophotometry calibration curve, and stability graphs as a function of time and temperature. See DOI: 10.1039/b924429h