



Action of a Fluorescent Chemosensor for Cu²⁺ Encapsulated in Silica Xerogel

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Abstract. The fluorescent chemosensor of the type Ant-NH-O-O-NH-Ant for Cu²⁺ ions has been designed by means of a supramolecular approach, as follows: two anthracene (Ant) fragments as fluorophore subunits have been linked by a noncyclic NH-O-O-NH quadridentate ligand as a receptor. The interaction of Cu²⁺ – receptor is signalled through the enhancement of the anthracene fluorescence when the receptor, i.e., the dioxodiamine chain subunit of the sensor is able to stop a photoinduced electron-transfer mechanism. The experiments with the chemosensor encapsulated in silica xerogel by the sol-gel processing are described.

Key words: fluorescent chemosensor, silica xerogel, Cu²⁺ ions, fluorescence enhancement.

1. Introduction

Fluorescent materials are now used for a wide variety of sensing applications [1] and there is considerable current interest in the development of sensors for metal ions. Fluorescence quenching and enhancement can be used effectively for the identification of metal ions in solution. In developing such systems, one seeks both specificity and sensitivity toward the ion of interest [2]. Bissel *et al.* [3] have synthesised a number of novel fluorescent probes and sensors involving photoinduced electron transfer (PET). There are also many reports of systems which are both specific and sensitive to particular metal ions (e.g., Kłonkowski *et al.* [4], Fabrizzi and Poggi [5] and Fabrizzi *et al.* [6] for Cu²⁺) but where the sensing action involves fluorescence quenching. Our opinion is that although such systems can be of interest in a sensor design, the ubiquitous nature of fluorescence quenching reduces their practical utility.

A fluorescent ion signalling system should include a fluorophore and an ion receptor as critical components. In the present design, these are distinct modules separated by an all- σ -bonded spacer, i.e., the only communication between the optical and ligating modules is *via* relatively long-range forces. Compounds of this type are called fluorescent chemosensors [1]. One of the signalling possibilities arises from the fact that the ‘fluor-spacer-receptor’ system in the cation free

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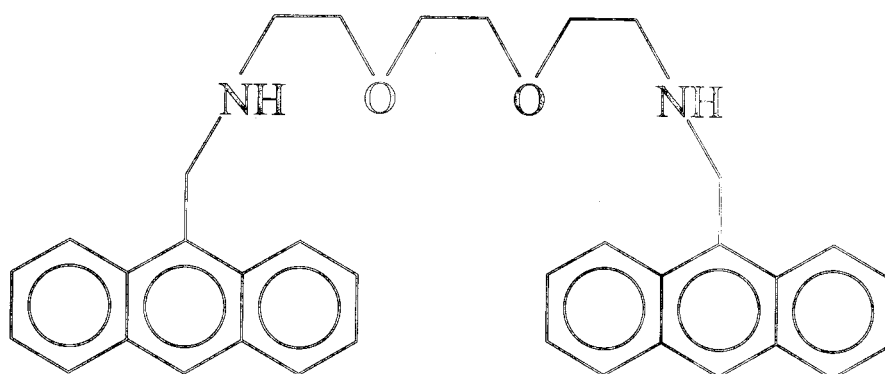


Figure 1. Dianthraceno-derivative, abbreviated as Ant-NH-O-O-NH-Ant.

situation has been chosen such that its fluorescence is 'switched-off' by the PET process. Thus, the PET process can be suppressed by the entry of a cation into the receptor by the cation-induced increase of the ionisation/oxidation potential of the receptor. Such a suppression of the PET process means that fluorescence becomes the dominant decay channel of the excited fluorophore [3]. This sensing strategy has been exploited by the present work. The Ant-NH-O-O-NH-Ant system, where Ant = anthracene ring, has been design to combine the photophysical properties of the anthracene chromophore and the complexing ability of the chain with donating N and O atoms. In our study the fluorescent ion signalling molecules have been entrapped in silica xerogel, a porous support, prepared by the sol-gel method. The leaching problems are practically avoided in our case because the sensing molecules are immobilised by hydrogen bonding. The goal of our work is to prepare and use a fluorescing transition metal ion system attached to a solid support.

2. Experimental

2.1. SYNTHESIS AND PREPARATION

The compound shown in Figure 1 was prepared according to a published procedure [7] which allows us to introduce a bridge with heteroatoms of the type N₂O₂ between two anthracene rings (Ant). The product was purified by recrystallisation and gave satisfactory NMR spectra and elemental analyses.

Tetramethoxysilane, methanol and Cu(ClO₄)₂·5H₂O, from Aldrich Chemical Co., were used without further purification. The sols were prepared by a typical sol-gel procedure [7] from a starting mixture of tetramethoxysilane (TMOS), methyl alcohol as diluent, distilled water (TMOS:H₂O = 1:4), NH₃(aq) catalyst and the Ant-N₂O₂-Ant dopant. The mixture was vigorously mixed at room temperature. The sol was allowed to gel for 3 days and then dried. The xerogel obtained was heated for 3h at 120 °C to remove ammonia and methanol as well as some of the water from pores. The concentration of the supramolecular device

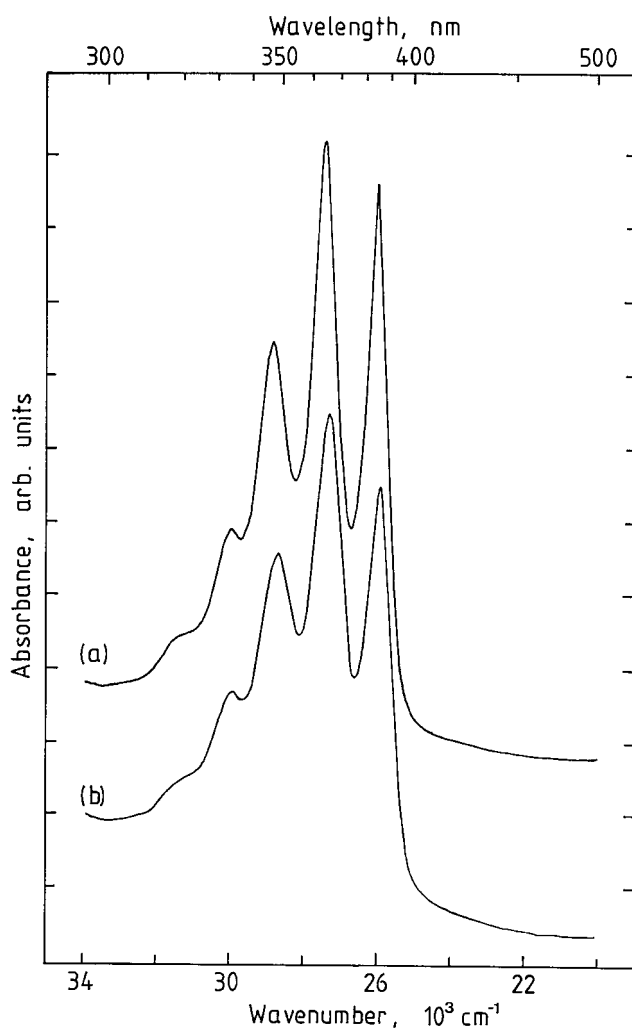


Figure 2. Optical absorption spectra of Ant-NH-O-O-NH-Ant (a) and the complex with Cu^{2+} (b) in methanol solution.

in the xerogel was 2.5×10^{-5} mole g^{-1} SiO_2 . Particles of the doped silica were immersed in aqueous solution containing Cu^{2+} ions, maintaining the molar ratio [metal ion]:[supramolecule] = 10:1. The immersed xerogel was filtered off after 24 h, rinsed with distilled water and then dried. By this chemisorption method complexes of the receptor part with the metal ions were formed.

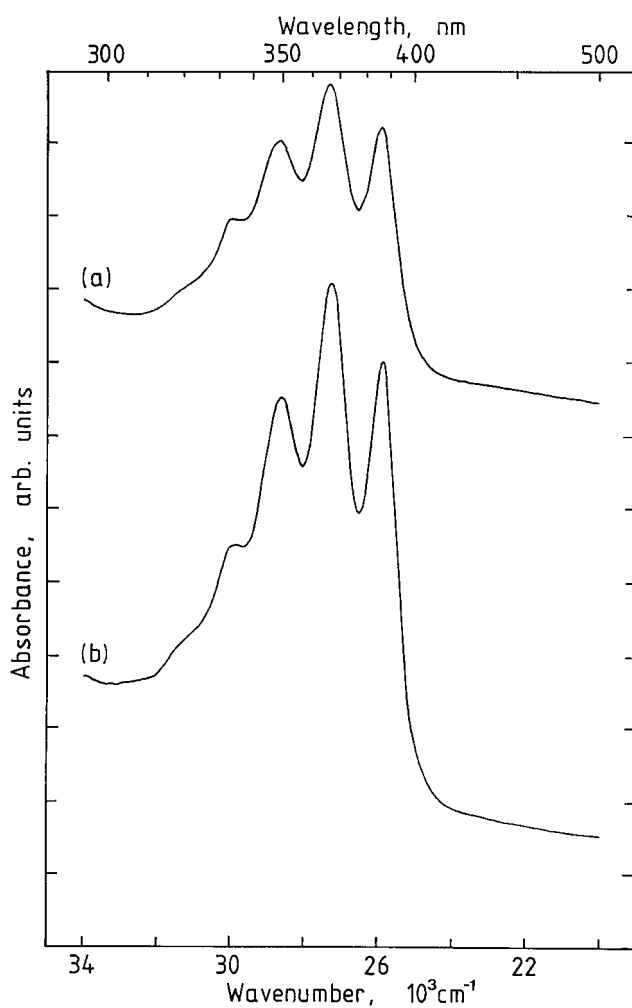


Figure 3. Diffuse reflectance spectra of Ant-NH-O-O-NH-Ant (a) and the complex with Cu^{2+} (b) encapsulated in silica xerogel.

2.2. INSTRUMENTATION

Optical absorption measurements in the UV-visible region were recorded on a C. Zeiss (Jena) 650 spectrophotometer. Spectra of the crushed xerogel samples were obtained in a silicon oil mull and were collected between 250 and 600 nm. Fluorescence emission ($\lambda_{\text{exc}} = 315$ nm) and excitation spectra ($\lambda_{\text{em}} = 360$ nm) were measured with a Perkin-Elmer LS 50B spectrofluorometer with a reflection spectra attachment. None of the excitation spectra were corrected for the lamp and photomultiplier response. Fluorescence decays were measured using an Edinburgh Analytical Instruments CD 900 fluorometer.

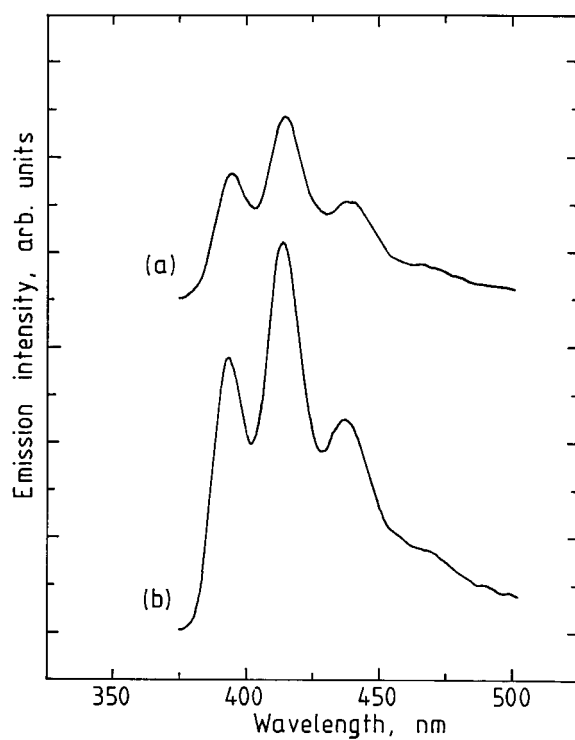


Figure 4. Fluorescence emission spectra of Ant-NH-O-O-NH-Ant (a) and the complex with Cu^{2+} (b) in methanol solution. The excitation wavelength $\lambda_{exc} = 368$ nm.

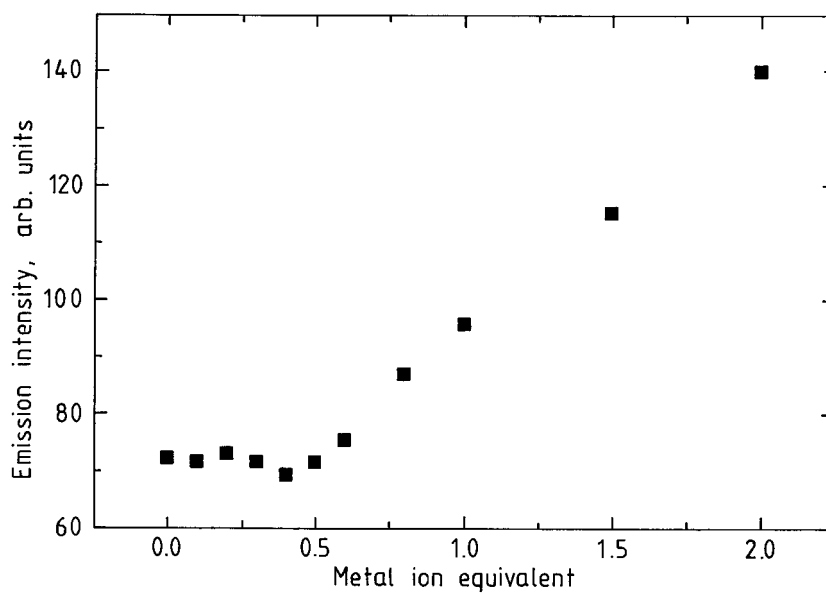


Figure 5. Variation of fluorescence intensity at 412 nm of Ant-NH-O-O-NH-Ant with the number of added Cu^{2+} equivalents.

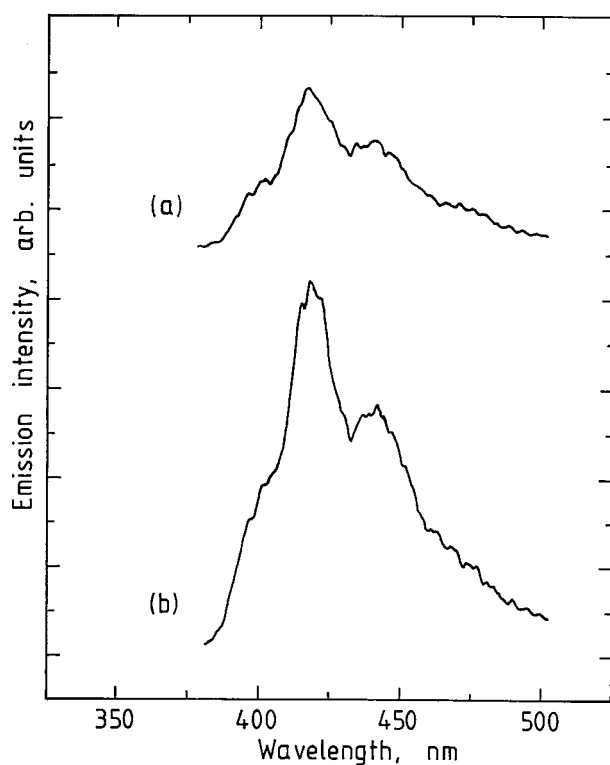


Figure 6. Fluorescence emission spectra of Ant-NH-O-O-NH-Ant (a) and the complex with Cu^{2+} (b) encapsulated in silica xerogel. The excitation wavelength $\lambda_{exc} = 368$ nm.

3. Results and Discussion

Silica gels prepared under basic conditions ($\text{pH} > 7$) and high water to silane ratios, produce highly branched clusters which behave as discrete species. Gelation occurs by linking clusters together [7]. This procedure makes the xerogels porous, these consequently being able to encapsulate and attach large supramolecular systems of the type shown in Figure 1. Probably owing to the hydrogen bond between the oxygen and/or nitrogen atoms in a molecule and the silanol group, the supramolecular devices are practically non-leachable in aqueous solution.

3.1. UV-VIS ABSORPTION SPECTRA

Absorption spectra of Ant-NH-O-O-NH-Ant and the Cu^{2+} complex with this chemosensor in a molar ratio 1 : 1 system in diluted methanol solution ($5,4 \times 10^{-5}$ M) are characteristic of 9-substituted alkylanthracenes [Figures 2(a) and (b)] and additionally have the same position. Spectra of the free chemosensor and its complex with Cu^{2+} encapsulated in silica xerogel are similar to those in the solution

[Figures 3(a) and (b)]. The encapsulated species present a slight but significant shift to red in comparison to the situation in methanol solution.

3.2. FLUORESCENCE EMISSION SPECTRA

A high emission intensity was observed from the chemosensor and the metal complex in methanol solution on excitation with light of 368 nm (absorption λ_{max}), in Figures 4(a) and (b). No exciplex was observed there. When Cu^{2+} is added to the solution, the system exhibits enhancement in fluorescence intensity. Cu^{2+} -promoted enhancement of fluorescence intensity with increasing number of the metal equivalents in methanol solution *is observed*, if the number is higher than 0.5 (Figure 5). Most other transition metal ions from the first transition series (such as Co^{2+} , Fe^{2+} , Ni^{2+} and Zn^{2+}) also cause this increase in fluorescence but the concentration required to achieve a similar effect to that observed with Cu^{2+} are much higher.

The emission spectra of the chemosensor and its Cu^{2+} complex encapsulated in silica xerogel (Figure 6) resemble the spectra for the species dissolved in methanol but due to encapsulation is observed a slight shift to red. As in methanol solution, the metal complex causes an increase in fluorescence.

4. Conclusion

The results presented in this study suggest that there is a possibility to prepare a recognition device based on the fluorescent chemosensor and porous silica support for an optical chemical sensor detecting Cu^{2+} ions in solutions.

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