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Trapping Copper Phthalocyanine in a Silica Sono-Xerogel

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Abstract. A copper phthalocyanine (CuPc) has been encapsulated in silica. The trapping effects were studied comparing the UV-Vis absorption spectra of some CuPc solutions and composites prepared under different conditions. The trapped organic molecules' stability was monitored during the gelation and drying processes. Leachability test have been carried out with the aim of checking the trapping efficiency. Hydrolysis water of $pH = 2$ and a molar ratio $R_w = 6$ mol acid H_2O/mol TMOS leads to a higher CuPc stacking angle homogeneity. The increase of Pc induces a narrower mesopore distribution and helps the stabilization of the composite.

Keywords: copper phthalocyanine, sono-gel, UV-Vis absorption spectra, composite, mesopores

1. Introduction

It is known that organic materials with a π-conjugated system show relatively large third order nonlinear susceptibility, $\chi^{(3)}$, and ultrafast response times, which are due to delocalized π-electrons [1, 2]. Pthalocyanines and metallophthalocyanines are centrosymetric planar organic and metallo-organic molecules, respectively, with an extensively delocalized two dimensional conjugated π-electron system [3, 4]. Consequently, these molecules show a relatively large third order optical nonlinearity, that varies depending on the metal atom substitution. Other attractives of this molecule and many of its derivative products are their versatility, architectural flexibility and high environmental stability, very important requirements to implement optoelectronic applications [5–8].

Outstanding nonlinear optical properties of phthalocyanines have been measured in films on silica substrate or in solution. Encapsulating phthalocyanine molecules in bulk materials is interesting for nonlinear integrated optics applications. The sol-gel method provides a route for that. It allows the preparation of composites with different phthalocyanine concentrations modifying the material optical behaviour and the textural properties of these composites.

This work deals with the preparation of silica sono-xerogels doped with commercial copper tetrasulfonated phthalocyanine (CuTSPc). The ability of sono-xerogel for effective organic molecules encapsulation is well known, resulting in a transparent and homogeneous hybrid material with appropriate optical quality [9]. However, optical applications require an effective trapping of organic molecules to avoid any possible molecule-matrix interactions that would reduce their nonlinear perfomance. CuPc absorption changes during the composite processing give valuable information in order to monitor the organic-silica matrix interaction.

In the present paper diverse preparation conditions have been analyzed in order to optimize the composite performance in self-defocusing non-linear optical experiments [10].

2. Experimental

CuTSPc-silica-sono-xerogel composites have been prepared by hydrolysis and polycondensation of tetramethoxisylane (TMOS) from CuTSPc containing solutions. Formamide (FOR) was used as a drying control chemical additive (DCCA) in a proportion of 3 formamide/TMOS molar ratio, in order to get monolithic samples [11]. The hydrolysis water, previously adjusted with a H_2SO_4/H_2O vol. ratio $1:9$ (**A** samples) or $pH = 2$ (**B** samples), was added in molar ratio

$R_w = 6$ mol acid H_2O/mol TMOS. CuTSPc molecules were dispersed in the acid hydrolysis water, in concentrations, $10^{-4}M$, $5 \cdot 10^{-5}M$ and $10^{-5}M$ in the resulting sol.

Once formamide and hydrolysis water had been mixed with the alkoxide, the mixture was submitted to the action of ultrasound, as described elsewhere [9], leading to a transparent solution which was left to gel.

Then, when the resulting gels were aged for one week at room temperature, monolithic transparent blue pieces immersed in a colorless liquid are obtained. After three weeks at room temperature, dried composites result.

Matrix induced effects on organic molecules aggregation have been evaluated through UV-Vis absorption experiments carried out using a VARIAN Cary 31 spectrophotometer.

Composite pore size distribution, as well as specific surface and porous volume have been estimated by nitrogen adsorption isotherms.

Crystalline organic phases have been resolved using X-Ray powder diffraction obtained with a Philips diffractometer (PW 1830 of Cu Kα, fixed slits, graphite monochromator). Multiphase analysis of the trapped organic crystallites was performed from diffraction data by the WPF (Whole Profile Fitting) technique.

3. Results and Discussion

In order to improve the ring system solubility in aqueous media, a sodium salt of a sulphonic substituted copper phthalocyanine has been chosen as the composite organic phase. Nevertheless, the CuTSPc spectra show, in many cases, the effect of molecule aggregation. Considering that most phthalocyanines dissolve in concentrated sulphuric acid, this solvent was firstly used as a reference in order to evaluate the influence of the Pc solubility on the absorption behaviour [12].

The experimentally determined phthalocyanine absorption spectra usually show five principal bands, referred to as Q, B, N, L and C. This study is focused on the Q-band analysis, found in the far red region of the spectrum, well separated from the others [12]. B, N, L and C-bands are very difficult to study because they are screened by the silica matrix ultraviolet absorption.

Figure 1 shows the absorption spectra of $10^{-4}M$ CuTSPc solution in different H_2SO_4/H_2O mixtures. The evolution of the Q-band profile and position with

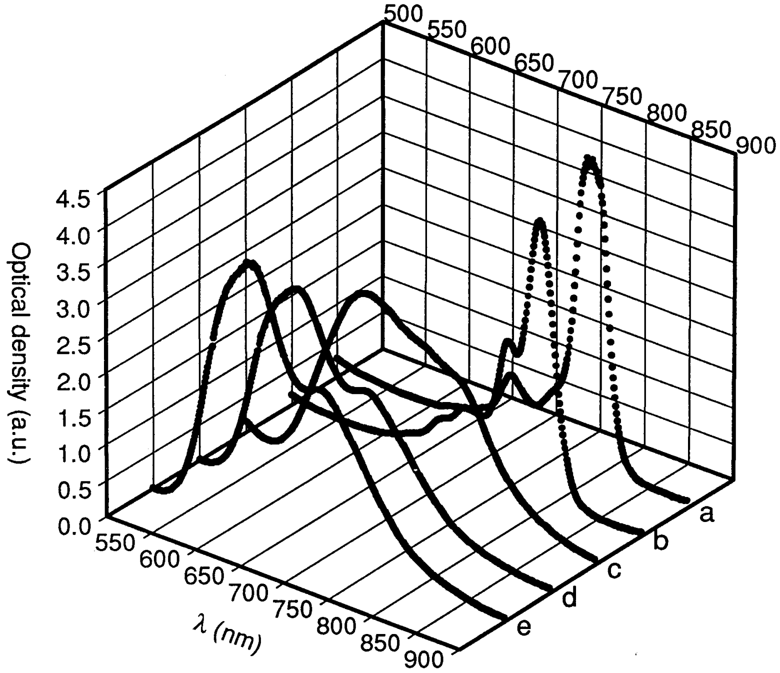

Figure 1. Visible absorption spectra for $10^{-4}M$ CuTSPc dissolved in different H_2SO_4 water solutions: (a) 95% vol.; (b) 75% vol.; (c) 50% vol.; (d) 10% vol.; (e) pH = 2.

water addition points out a solvent-induced aggregation process. The curve corresponding to the highest acid solution presents a Q-band (790 nm) with the typical red shift induced by the sulphuric acid, indicating the main contribution of the monomer species. When the water concentration is increased, the stronger intermolecular interactions lead to a higher degree of aggregation causing the replacement of the typical monomer Q-band structure by two broader bands and a blue shifted absorption band.

The close proximity of two or more rings can lead to coupling between the transition dipoles for two identical transitions. This interaction gives rise to two new energy levels; the separation between them is referred to as the exciton splitting energy. Thus, the molecular exciton theory predicts, for the fully cofacial arrangement, a blue-shift of the Q-band absorption with regard to the monomer, which is reduced when the alignment is not fully cofacial [13].

The spectrum corresponding to molecules in solution at 75% in sulphuric acid presents the monomer peak at 786 nm and a less intense one at 750 nm indicating the presence of aggregated species. The broader band in the case of the solution at 50% in acid is due to the greater number of molecular environments produced by the combined water and sulphuric acid effects for this concentration. Spectra corresponding to solutions at the two weaker acid concentrations show the same profile, with a monomer peak at 692 nm and a high intensity aggregate peak at 614 nm.

It should be mentioned that these sulphuric acid solutions cause phthalocyanine decomposition pointed out by a sharp decrease of the band intensity speeding up as the sulphuric concentration is higher.

The two weaker acid solutions in Fig. 1 have been used to prepare CuTSPc-sonogel composites. Their corresponding UV-Vis absorption spectra, at different moments during gelation, ageing and drying, are shown in the graphs of Fig. 2 for the CuTSPc $10^{-4}M$ processed composite. All curves show the Q-bands at 692 and 614 nm, corresponding to the monomer and aggregated species, respectively. Despite observing no important changes in absorption band position, an increase of absorption intensity with time is noticeable, that is more pronounced after two weeks and for the **B** sample. This behaviour, probably due to the phthalocyanine concentration increase during sample shrinkage, indicates an effective molecular trapping in the matrix. In fact, the absorption intensity decrease when the A sol gels denotes that the aforementioned degradation effect takes place only before molecule encapsulation in the solid matrix. On the other hand, UV-Vis absorption spectra of the leachability test liquid, without any evidence of Pc-Q band, confirms crystallite confinement in the matrix [14, 15].

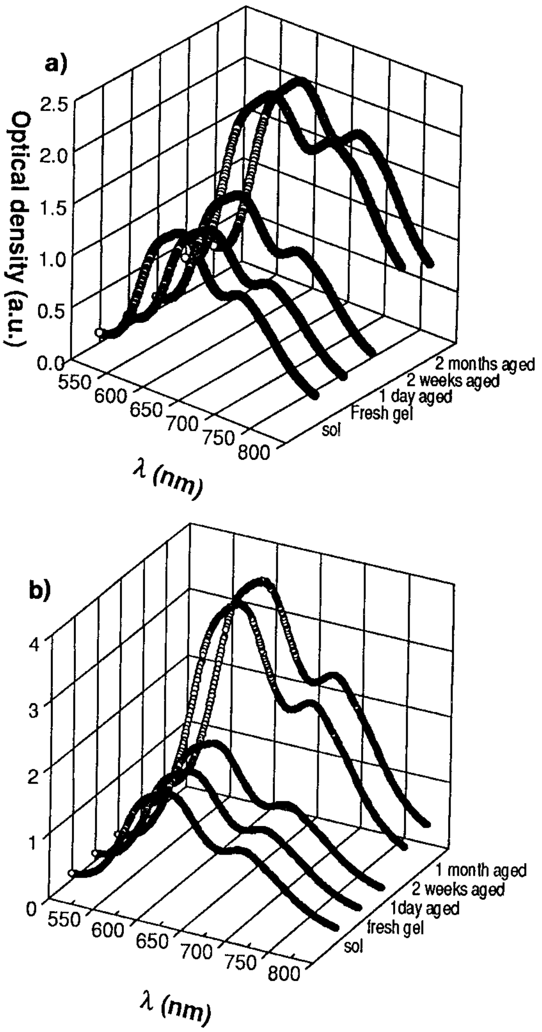

Figure 2. Visible absorption spectra of CuTSPc-composite at different processing steps: (a) A-composites and (b) B-composites. Phthalocyanine concentration in the starting sol was $10^{-4}M$.

Comparison of spectra of both aged gels from Figs. 2(a) and 2(b) reveals a broader absorption band for the A composite. This fact can be interpreted, under the molecular exciton theory, as a spreading of the molecular stacking angle distribution in this composite with regard to the **B** sample.

Table 1 shows composite textural parameters, evaluated from nitrogen adsorption isotherms and Hg

Table 1. Composite textural parameters, obtained from nitrogen adsorption isotherms and Hg picnometry, for several CuTSPc concentrations.

CuPc-concentration	Bulk density ($g \cdot cm^{-3}$)	Specific surface ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)
$10^{-5} M$	1.32	683	0.94
$5 \cdot 10^{-5} M$	1.37	500	0.85
$10^{-4} M$	1.43	523	0.83

picnometry, shown for several CuTSPc concentrations. It should be noticed that the pore volume decreases and the bulk density increases as phthalocyanine concentration increases. The origin of that lies on the progressive pore occupation by the organic phase crystallites. Nevertheless, specific surface area values do not follow a similar trend as would be expected. In consequence, pore filling is phthalocyanine concentration dependent. Thus, for low CuPc concentration, the minor radius pores are mainly occupied whereas if the concentration is high, big pores are preferentially filled, leading to a high specific surface area with a low pore volume.

Figure 3 shows the pore radius distribution obtained from the isotherm desorption branches for the same organic phase concentration presented in Table 1. These curves show how the increase in phthalocyanine content leads to a narrower mesopore size distribution, favoring the composite homogeneity and stability.

A quantitative analysis of the experimental X-Ray pattern for the commercial CuTSPc and for the trapped molecule has been carried out by the WPF technique [16, 17]. Figures 4(a) and 4(b) show the results of Pseudo-Voight function fitting. These results indicate that the trapped organic phase recrystallizes differently than commercial phthalocyanine, leading to a distinct distribution of the crystals. The proportion of β-CuTSPc in the xerogel precipitated phthalocyanine is greater than in the commercial near pure α-CuTSPc (Fig. 4).

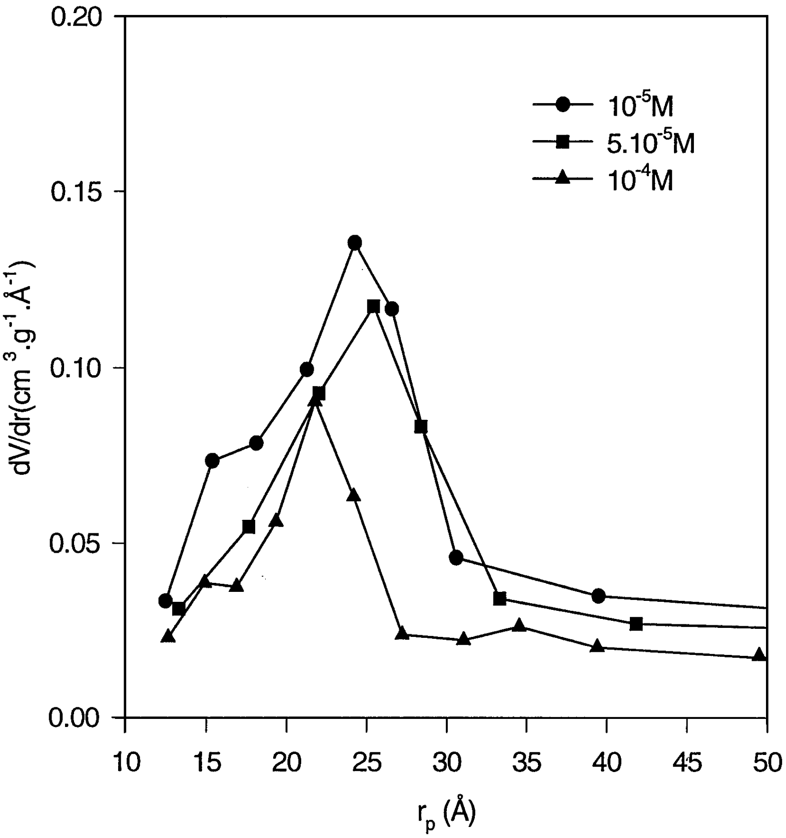

Figure 3. B-composite pore radius distributions calculated from isotherms desorption branch. Notice that increasing CuPc concentrations modifies the composite pore size distribution.

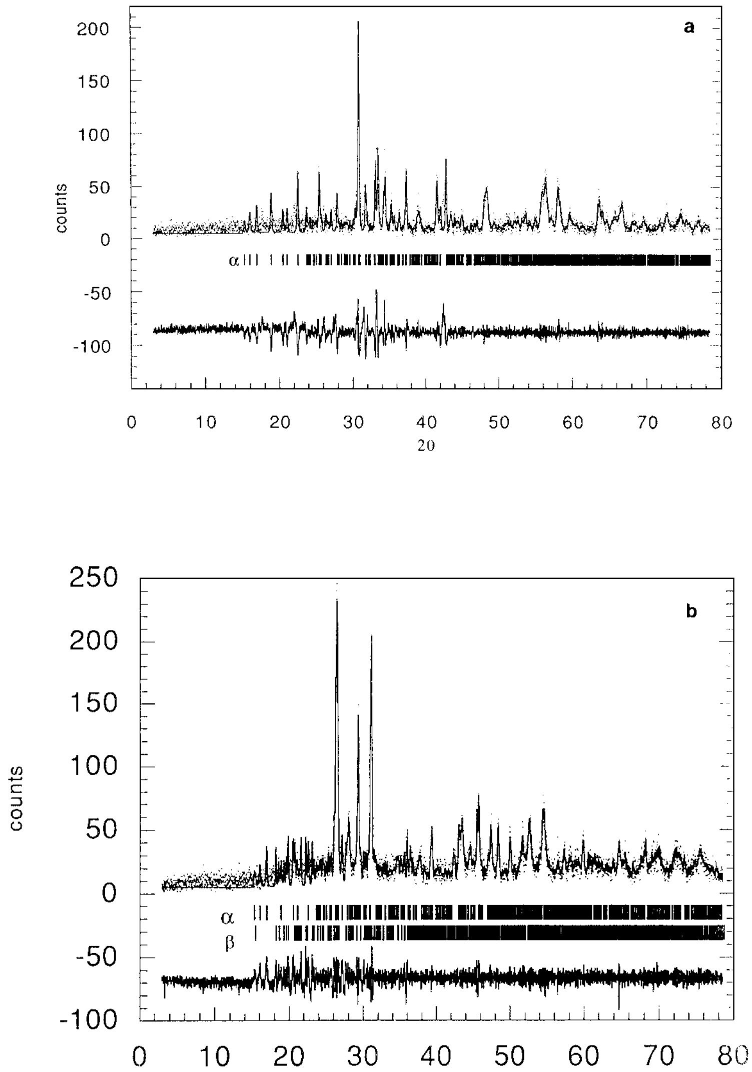

Figure 4. XRD pattern (dotted line) of starting CuPc salt (a) and xerogel trapped phthalocyanine (b). Continuous line corresponds to Pseudo-Voight function calculated by WPF, considering the crystalline phases indicated on the bottom.

Some evidence about the phase composition of the nanocrystals could be obtained from absorption spectra. It is known α and β forms show an absorption to both the red and the blue of the Q-band transition in the solution phase spectra. For the α form, the red shifted peak appears at the lowest intensity one or as a shoulder, but for the β form it is the highest intensity absorption. Nevertheless, composite spectra in Fig. 2 merely point out, in agreement with the WPF results, the major contribution of the α form, mainly in **B** samples. Processing effects on the organic crystalline phases composition and its influence on the composite's nonlinear optical behaviour will be the subject of future papers [10, 18].

4. Conclusions

Transparent blue monolithic pieces of CuPc-silica composites have been obtained by the sonocatalytic sol-gel method. The hydrolysis water pH utilized in the sol-gel process affects the final composite microstructure mainly in two ways: the molecules aggregation level, depending on their solubility in the aqueous media, and the gelling process. A compromise between these factors leads to two pH values being used for the composites processing. UV-Vis absorption spectra of the composite show that the organic phase remains effectively trapped in the sonoxerogel porous network. This has been confirmed by different stability tests. B composite processing leads to a higher CuPc stacking angle homogeneity. The increase in Pc content induces a narrower composite mesopore size distribution, helping the composite stabilization.

Acknowledgments

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