Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Non-Crystalline Solids 333 (2004) 327–332

JOURNAL OF
NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

# Aggregation effects in non-linear absorption of CuPc–$SiO_2$ sono-xerogels

R. Litrán *, E. Blanco, M. Ramírez-del-Solar

*Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz,*
*Campus Universitario del Río San Pedro s/n, 11510 Puerto Real (Cádiz), Spain*

Received 19 October 2002

## Abstract

It is known that aggregation effects in metallophthalocyanine/$SiO_2$ composites play an important role in the optical properties of these materials. With the aim to avoid phthalocyanine dimer and oligomer formation induced in aqueous solution, alternative processing methods for trapping the organic in the matrices have been tested. The combination of ultrasonic energy used to promote the reactions and the methanol used as solvent, makes it possible to obtain monolithic xerogels under extremely acid conditions, preserving their homogeneity and transparency. Textural parameters and pore size distribution of the composites and the optical absorption features have been evaluated. Finally, the effects of molecular self-association degree on the non-linear absorption of the samples have been analyzed. All the samples studied exhibit reverse saturable absorption behavior but the figure of merit is strongly determined by the aggregation state of the active phase in the composite.

## 1. Introduction

In the last years, the increasing number of applications using high power lasers has demanded the development of methods for limiting exposure to laser radiation in order to provide passive sensor and eye protection from these sources [1]. In the practice, organometallic molecules exhibiting reverse saturable absorption (RSA) are one of the most promising materials for optical limiting. This non-linear optical mechanism, increasing optical absorption with increasing optical intensity, requires the existence of excited states [2] with a higher absorption cross-section ($\sigma_{ex}$) than the ground-state cross-section ($\sigma_g$). The figure of merit of RSA cromophores as optical limiters [3] is mainly determined by the ratio of this cross-section $\sigma_{ex}/\sigma_g$.

Metallophthalocyanines (MPc) have attracted strong interest because the large non-linearities associated to the extended conjugation of the 2D delocalized electronic molecular system [4,5].

For practical purposes, the sol–gel method offers a soft route, well suited for incorporation of phthalocyanine molecules without thermal damage, leading to solid non-linear materials, with improved mechanical properties and stability, more convenient for the use as optical components [6–8].

Several authors have demonstrated that reverse saturable absorbers preserve their properties when they are confined into the pores of a xerogel matrix [6]. Nevertheless, MPc molecules have shown a propensity to self-associate that is enlarged due to the low solubility of phthalocyanine compounds in the common solvents of the sol–gel process [9]. Molecules aggregation is readily detected on the UV–Visible spectra, particularly in the Q-band region where the coupling between electronic states leads to a blue shift of the maximum absorbance and an overall broadening of the Q-envelope. As the close proximity of two or more rings leads to a higher aggregation degree, this typical monomer Q-band is replaced by a blue shifted broader structure. This behavior involves cofacial association of π-electron system, as described by molecular exciton theory [10–12].

The importance of molecular aggregation on non-linear optical properties has been widely demonstrated. In a previous paper we have reported about the

---

* Corresponding author. Tel.: +34-956 016 324; fax: +34-956 016 288.
*E-mail address:* rocio.litran@uca.es (R. Litrán).

0022-3093/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2003.10.003

dispersion of non-linear absorption for a CuPc/silica sonogel composite and pointed out the need to increase the monomer to aggregate ratio in the material in order to improve the RSA magnitude and spectral characteristics [13].

Diverse processing conditions, including Pc covalently bonded to the gel matrix, have been proposed in order to produce materials with a reduced aggregation [14]. In the present paper, we analyze the effect of different processing conditions on the aggregation of CuPc trapped in a sonogel matrix by the evaluation of their non-linear absorption. For comparison, the same evaluation is made with a CuPc sulfuric acid solution in which monomeric species mainly exist.

## 2. Experimental

Studied composites are silica xerogels doped with copper phthalocyanine, used as active optical phase. With the aim to evaluate the dye aggregation state influence, on the non-linear optical behavior, we have prepared three different silica sono-xerogels [15] following the procedure described elsewhere [16]. As we detail before, we have obtained the called MET samples, adding in this case methanol as solvent [9]. In the second case, the methanol is replaced by formamide [12], used as drying control chemical additive, and the resulting composites have been refereed by code FOR. Finally, for the third kind of samples, it is the pH = 2 hydrolysis water what is replaced by a 2/3 volume proportion of $H_2SO_4/H_2O$ solution, obtaining the called ACD xerogels [16]. In all the cases, tetrasulfonated copper phthalocyanine (CuTSPc) has been used as the optically active phase, previously dissolved in the hydrolysis water leading to nominal concentrations of $5\times10^{-5}$ M (adding the code 2 to the xerogel code for sample identification) and $10^{-5}$ M (code 1) in the resulting sol.

As described in [16], after three weeks of aging and drying at room temperature, transparent monolithic CuPc–silica xerogels are obtained, which are blue when MET and FOR route is followed, but green in the case of ACD samples. The final thickness is about 3 mm for FOR and ACD xerogels and 2 mm for MET samples. The larger shrinkage in MET samples, gives place to a final volume for dried samples approximately 1/4 of the initial volume in the case of FOR and ACD samples, and 1/10 the initial volume for MET samples. This fact, leads to different final phthalocyanine concentration for composites with the same nominal dye proportion but with different chemical processing. Table 1 shows the initial nominal concentration of CuPc in the sol, as well as the estimated final concentration for each xerogel.

In order to evaluate the molecular aggregation effect on the non-linear behavior, and knowing that phthalocyanines keep as monomer species when solved in $H_2SO_4$ [10,12] we have also prepared a reference CuTSPc/$H_2SO_4$ solution with the lower molecular concentration.

Table 1
Initial nominal CuPc concentrations and their corresponding final concentrations for each prepared composite

| Sample | Nominal CuPc concentration in the sol ($\mathrm{mol\,l^{-1}}$) | Final CuPc concentration in the xerogel ($\mathrm{mol\,l^{-1}}$) |
|---|---|---|
| MET2 | $5\times10^{-5}$ | $\sim5\times10^{-4}$ |
| FOR2 | $5\times10^{-5}$ | $\sim10^{-4}$ |
| ACD2 | $5\times10^{-5}$ | $\sim10^{-4}$ |
| ACD1 | $10^{-5}$ | $\sim5\times10^{-5}$ |
| Reference solution | $5\times10^{-5}$ | $5\times10^{-5}$ |

Linear optical absorption of composites, and matrix induced effects on organic molecules aggregation, have been evaluated from UV–Visible absorption spectra.

Textural characteristics of composites, such as, pore size distribution, specific surface area and pore volume, have been estimated from nitrogen physical adsorption isotherms [17], performed in commercial equipment with accuracy in the pressure measurement of 0.5% of reading [16], at the liquid nitrogen temperature. In order to remove the liquid from the pores without provoking the alteration of the material textural features, composites were previously degassed at 75 °C. Completed adsorption–desorption isotherms have been analyzed and pore size distributions have been evaluated from the desorption branches data, using the Dollimore–Heal method [18].

Non-linear absorption measurements have been performed with a frequency doubled Q-switched Nd:YAG (532 nm wavelength) laser of 6 ns pulse. The laser pulses have been focused on the sample surface with a spot size of approximately 0.4 mm diameter using a 10 cm focal-length. The transmitted fluence after the sample has been measured by a power meter, for different input energy values by changing a set of neutral density filters before the sample to attenuate the input energy.

## 3. Results

Fig. 1 shows the absorption spectra corresponding to different CuTSPc–$SiO_2$ xerogel composites, as well as that for a similar concentration CuTSPc/$H_2SO_4$ solution used as reference, and that corresponding to the xerogel matrix without organic dye doping. We have already reported [12] about changes in the typical phthalocyanine Q-band profile when this molecule is trapped in the gel, due to the presence of common sol–gel processing solvents. The $H_2SO_4$ solution is used as reference, knowing that phthalocyanine keeps monomer when solved in this acid. This is the reason for preparation of the ACD composites, containing the highest $H_2SO_4$

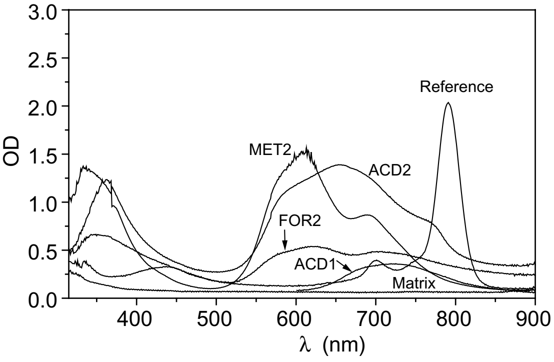

Fig. 1. UV–Visible absorption spectra for different CuPc–$SiO_2$ composites. The spectrum for a $5\times10^{-5}$ M CuTSPc/$H_2SO_4$ solution as well as the corresponding to the matrix, have been also plotted for comparison.

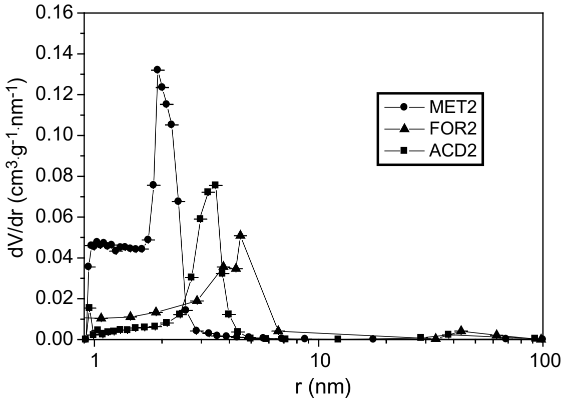

Fig. 2. Pore size distributions for CuTSPc/$SiO_2$ composites obtained from the desorption branch of complete nitrogen isotherms.

concentration compatible with the sol–gel processing. As expected, the typical phthalocyanine Q-band for CuTSPc in $H_2SO_4$ solution appears redshifted compared to spectra for solutions in organic solvents [10,12]. No important absorption is found in this region for xerogel matrix. In all the cases, the composite spectra show a blue shifted and broader structure for Q-band than the spectrum corresponding to the solution, pointing out the presence of aggregate species [12]. The same absorption profile, with a maximum at 692 nm and a higher intensity peak, characteristic of aggregated species, around 614 nm appears for samples MET2 and FOR2. This clearly split Q-band does not appear in the case of ACD2 composite, showing a broad band, typical of a wide dispersion of species, centered at 665 nm, with a shoulder around 800 nm. Moreover, in this case, there is not a defined blue shifted maximum (614 nm), characteristics of aggregates species, probably due to the proportion of $H_2SO_4$ used in the processing, which contributes to a larger ratio of monomer to aggregates. This kind of sample presents a narrower absorption band when concentration decreases (ACD1).

Pore size distributions for the composites are plotted in Fig. 2. As we described in previous works, these distributions have been obtained from adsorption–desorption isotherms, which can be considered as IUPAC type IV isotherms, presenting a hysteresis loop due to capillary condensation in the mesopores [16]. The largest pore sizes and widest size distribution correspond to FOR sample, while MET composite shows the smallest average sizes with a significant contribution of small size pores. ACD sample, presents the narrowest pore radio distribution centered around 3 nm.

From the analysis of textural parameters obtained from the adsorption experiment (Table 2) the lowest surface area values are found for type ACD samples, pointing out that there is not a significative contribution of smaller pores to the surface. This value drastically increases for MET samples in which the proportion of small pores is considerably more important.

Table 2
Composites textural parameters, obtained from nitrogen adsorption isotherms, for samples with different processing and different CuTSPc concentrations

| Sample | Specific surface ($m^2\,g^{-1}$) | Pore volume ($cm^3\,g^{-1}$) |
|---|---|---|
| ACD2 | $248 \pm 1$ | $0.702 \pm 4\mathrm{E}^{-3}$ |
| MET2 | $1200 \pm 6$ | $1.261 \pm 6\mathrm{E}^{-3}$ |
| FOR2 | $373 \pm 2$ | $1.112 \pm 6\mathrm{E}^{-3}$ |
| ACD1 | $102.2 \pm 0.5$ | $0.353 \pm 2\mathrm{E}^{-3}$ |

Fig. 3 shows the transmittance fluence of different CuTSPc–$SiO_2$ composites as well as of reference solution, as a function of the incident fluence. The points correspond to experimental data and the solid lines are their numerical fitting. The $SiO_2$ xerogel without

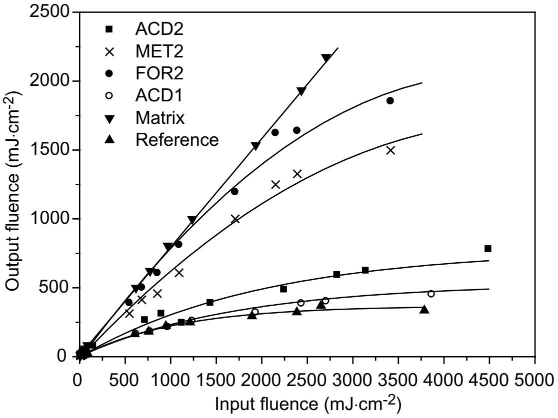

Fig. 3. Optical limiting results for different CuTSPc–$SiO_2$ composites. The transmittance data for the CuTSPc/$H_2SO_4$ solution as well as those for sono-xerogel matrix have also been plotted as reference of the non-linear phenomena for disaggregated Pc and for the linear behavior, respectively.

Table 3
$\sigma_{ex}/\sigma_{gr}$ ratio at 532 nm estimated from transmittance data obtained by the optical limiting experiments

| Sample | $T_l$ | $T_S$ | $\sigma_{ex}/\sigma_g$ |
|---|---|---|---|
| ACD2 | 0.62 | 0.34 | 2.25 |
| ACD1 | 0.82 | 0.29 | 6.20 |
| MET2 | 0.74 | 0.67 | 1.33 |
| FOR2 | 0.80 | 0.78 | 1.14 |
| Reference | 0.72 | 0.10 | 6.98 |
| Matrix | 0.84 | 0.83 | 1.05 |

phthalocyanine presents a linear behavior, showing a constant transmittance when the incident laser energy is increased. However, for samples containing CuTSPc, this feature keeps linear only for low incident fluence. At these low input fluences, the transmittance of samples fits with the linear transmittance obtained from the UV–Visible absorption spectra. As incident laser energy increases, the transmittance exhibits inverse fluence dependence, pointing out the existence of reverse saturable absorption (RSA) and, consequently, the optical limiting effect in these materials. Nevertheless, this change in transmittance does not occur at the same input fluence value for all samples. The strongest nonlinearity appears for ACD1 composite, for which the change takes place above 0.5 $\mathrm{J\,cm^{-2}}$. This non-linear absorption phenomenon is also high in the case of ACD2 composite, decreasing for MET and FOR composites, which are closer to the linear trend.

In order to obtain a magnitude of the RSA phenomena, the ratio between the excited absorption cross-section, $\sigma_{ex}$, and the ground absorption cross-section, $\sigma_g$, has been estimated using the optical absorption as $I_o/I_i = \exp(-\sigma NL)$, where $I_o$ and $I_i$ are the output and input laser intensities, respectively, and $L$ the length of laser pass [14,19]. $N$ is the concentration, calculated taking into account the final phthalocyanine concentration in the xerogel. This final concentration (Table 1) has been calculated considering the shrinkage and consequently the densities of the xerogels in each sample. For an ideal absorptive material, the ratio of $\sigma_{ex}/\sigma_g$ for 532 nm wavelength can be estimated from the expression $\ln T_s/\ln T_l$, where $T_l$ and $T_s$ are the linear and saturated transmittances, respectively. Table 3 shows the ratio of $\sigma_{ex}/\sigma_g$ estimated from data in Fig. 3, for different composites. In all cases, $T_s$ and $T_l$ have been corrected using the corresponding values for the matrix in order to obtain information of the molecule nonlinear effect.

## 4. Discussion

The analysis of UV–Visible absorption data from Fig. 1, allows obtaining information about the aggregation degree of phthalocyanine species present in composites. In the case of composites type MET2 and FOR2, the split Q-band indicates a larger ratio of aggregated species to monomer. Although for both samples the Q-band is specially wide, it is even broader for FOR2 than for MET2, probably indicating a spreading of associate species in FOR2 samples regarding to MET2 composites. This decrease of aggregation degree for samples prepared with methanol/water solution (MET samples) is attributed to the lower protonation of sulfonate groups, responsible of dye solubility [9]. As we have already reported [16], the lower pore size average of MET2 samples (Fig. 2) can contributed to limit the self-association of molecule into the network porosity. The intensity of Q-band is especially higher for MET2 samples, due not only to the higher final phthalocyanine concentration during the sample shrinkage, but also to the less aggregation level of MET2, induced by the presence of methanol. The Q-band profile is particularly different for composite ACD2. The absence of the peak at 614 in the case of ACD2 composite possibly indicates a larger ratio of monomer species to aggregate, than in MET2 and FOR2 cases. Despite only one main maximum is observed for ACD2 composite, the band is quite broader compared to the one for the reference. Nevertheless, the Q-band for this composite shows a shoulder at the position of the reference peak pointing out the bigger contribution of monomeric species in this sample. In this case, the second blue shifted maximum, characteristics of aggregates species is less pronounced than for MET2 and FOR2 samples, as we have explained, probably due to the influence of $H_2SO_4$ presents in this kind of samples. The absorption band is narrower for ACD1 than for ACD2 composite, due to the lower probability of self-association when phthalocyanine concentration decreases.

The analysis of pore size distributions plotted in Fig. 2, shows the highest pore size average for FOR2 sample, due to the influence of formamide in the polycondensation rate [20]. In the case of MET sample, the initial processing pH value combined to the methanol effect gives place to the formation of small mesopores, due to the mechanisms involve in the network formation [21]. As we have already reported [16], the extremely acidic processing conditions of ACD2 sample, gives place to a less fine porosity that it could be expected, presenting pore size average larger than MET2 composite, but with a more homogeneous texture. The acid conditions drastically modify the condensation mechanism, even provoking the network collapse [16]. The presence of dye aggregates avoids this collapse, allowing to the cluster to grow around organic aggregates.

From the analysis of textural parameters obtained from the adsorption experiment (Table 2), the lowest surface area values are found for type ACD samples, because there is not a significative contribution of smaller pores to the surface. This value drastically increases for MET samples in which the proportion of small pores is considerably more important.

The difference in the RSA effect, observed in Fig. 3, for composites with different processing conditions can be related with the molecular aggregation state of phthalocyanine. The sample showing the highest non-linear absorption is the reference which, as is known, is largely composed of monomeric material. The non-linear behavior is almost the same for ACD1 composite than for reference solution. The non-linear effect can be directly compared between these two samples, due to the final CuPc concentration in the xerogel ACD1 is the same than in reference solution. As has been explained, the ACD processing involves a lower phthalocyanine aggregation level in the xerogel, and consequently, higher number of monomeric species contributes to the non-linear effect. The RSA behavior is also important but decreases in ACD2 sample regarding to ACD1. Although the ACD samples do not preserve the proportion of monomeric species obtained in reference solution, these composites present an considerably RSA effect at the studied wavelength, especially for the lower CuPc concentration. Composites with processing type MET2 and FOR2 present a lower RSA effect, due to the large ratio of aggregate species to monomer, according to the broad and split profile of Q-band in the absorption spectra, especially for FOR2 type sample.

The highest ratio, 6.98, is found for the reference, although a close value, 6.20, is obtained for ACD1 composite. Nevertheless, the higher the CuTSPc concentration in the composite the lower the $\sigma_{ex}/\sigma_g$ ratio for the same processing type pointing to a concentration-induced aggregation.

For samples MET2 and FOR2, the $\sigma_{ex}/\sigma_g$ parameter reaches values closer to the unity, indicating the low magnitude of RSA effect at the studied wavelength. However, these materials have been previously studied, showing efficiently non-linear optical behavior compared with the same molecules in solution, for different phenomena [7,8]. This fact reveals the influence of the aggregation state on the RSA magnitude.

For ACD samples, we have found, for lower CuPc concentration, RSA figure of merit comparable with those obtained by other authors [14,19], but in our case without chemical bonding of phthalocyanine to the gel network. In order to increase the RSA magnitude, using higher CuPc concentrations, the covalent bonding of organic phase to the network would be necessary [22].

## 5. Conclusions

Two procedures of CuPc–silica composite processing have been tested for improvement of the non-linear optical behavior already studied in previous results (samples FOR). One of them was focused on the possibility of a textural control of the phthalocyanine aggregates size, leading to composites (samples MET) where the organic is trapped in small pores avoiding further molecules self-association. This fact confers a better NLO response than samples FOR but it is still far away from the expected for monomers species.

As a second strategy, a novel high acidic conditions processing has been developed leading to optically transparent monolithic pieces (samples ACD) with suitable mechanical properties. This method, based on the optimization of the monomer/aggregate ratio in the doping solution, gives rise to samples with pore network controlled by the organic phase size in the solution which preserves a lower aggregation state in the composite. An RSA figure of merit close to the reference one is reached by this second procedure with a concentration-limited behavior.

## Acknowledgements

This work is supported by Ministerio de Ciencia y Tecnología (proj MAT2000-0468P402).

## References

[1] G.L Wood, A.G. Mott, E.J. Sharp, SPIE 1692 (1992) 2.

[2] R.L. Sutherland, Handbook of Non-linear Optics, Marcel Dekker, 1996.

[3] J.W. Perry, K. Mansour, S.R. Marder, K.J. Perry, D. Alvarez, I. Choong, Opt. Lett. 19 (9) (1994) 625.

[4] T.H. Wei, D.J. Hagan, M.J. Sence, E.W. Van Stryland, J.W. Perry, D.R. Coulter, Appl. Phys. B 54 (1992) 46.

[5] F.H. Mose, A.L. Thomas, The Phthalocyanines, CRC, Boca Raton, FL, 1992.

[6] F. Bentivegna, M. Canva, P. Georges, A. Brun, F. Chaput, L. Malier, J.P. Boilot, Appl. Phys. Lett. 62 (15) (1993) 1721.

[7] R. Litrán, E. Blanco, M. Ramírez del Solar, A. Hierro, M.A. Díaz-García, A. García-Cabañes, F. Agullo-López, Synth. Met. 83 (1996) 273.

[8] R. Litrán, P.M. Petersen, P.M. Johansen, L. Linvold, M. Ramírez-del-Solar, E. Blanco, J. Appl. Phys. 81 (1997) 7728.

[9] P.D. Fuqua, B. Dunn, J.I. Zink, J. Sol–Gel Sci. Tech. 11 (1998) 241.

[10] M.J. Cook, in: R.J.H. Clark, R.E. Hester (Eds.), Spectroscopy of New Materials, John Wiley, 1993, chapter 3.

[11] E. Ortí, J.L. Bredas, C. Clarisse, J. Chem. Phys. 92 (2) (1990) 1228.

[12] R. Litran, E. Blanco, M. Ramírez del Solar, L. Esquivias, J. Sol–Gel Sci. Tech. 8 (1997) 985.

[13] E. Blanco, D. Narayana Rao, F.J. Aranda, D.V.G.L.N. Rao, S. Tripathy, J.A. Akkara, M. Ramirez-del-Solar, J. Appl. Phys. 83 (6) (1998) 3441.

[14] H. Xia, M. Nogami, Opt. Mater. 15 (2000) 93.

[15] L. Esquivias, J. Zarzycki, in: J.D. Mackenzie, R. Ulrich (Eds.), Ultrastructure Processing of Advanced Ceramics, John Wiley, New York, 1987.

[16] R. Litrán, M. Ramírez-del-Solar, E. Blanco, J. Non-Cryst. Solids 318 (2003) 49.
[17] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 3827.
[18] D. Dollimore, G.R. Heal, J. Appl. Chem. 14 (1964) 109.
[19] H. Xia, M. Nogami, T. Hayakawa, D. Imaizumi, J. Mater. Sci. Lett. 18 (1999) 1837.
[20] L.L. Hench, in: L.L. Hench, D.R. Ulrich (Eds.), Science of Ceramics Chemical Processing, John Wiley, New York, 1986.
[21] C.J. Brinker, G.W. Scherer, in: . In: Sol–Gel Science, Academic Press, San Diego, 1990.
[22] A.O. Ribeiro, J.C. Biazzotto, O.A. Serra, J. Non-Cryst. Solids 273 (2000) 198.