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Spectroscopic Properties of Porphyrin-doped Silica Films by the Liquid Phase Deposition Method

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Silica films doped with water soluble porphyrin, 5,10,15,20-tetrakis[4-(N-trimethyl)ammonio]phenylporphyrin (TTMAPP), were deposited on the surface of a glass slide at 25-35°C by the liquid phase deposition (LPD) method from saturated hydrofluorosilicic acid or fluorosilicate solutions containing TTMAPP. It was doped as protonated (cationic) or neutral forms depending on the deposition condition. Two forms are reversibly converted by heat treatment or environments. The lifetime of excited triplet state of TTMAPP in silica films was more than ten times longer than that in aqueous solutions used for deposition. Fairly strong molecular interaction of excited triplet states in aqueous solutions was almost eliminated in silica films. The LPD method is useful to fix firmly organic dyes in silica at high concentrations without undesirable molecular interactions.

Keywords: silica films; liquid phase deposition; porphyrin; excited triplet state

INTRODUCTION

Organic compounds have attracted much interest in view of their potential applicability to future electronics and photonics, because their electronic state can be easily controlled by molecular structure, assembling, or external stimulation. We have shown that unique and ultrafast linear and nonlinear photoresponses can be achieved in various organized systems [1]. Many efforts have also been made to utilize their superior properties stably for a long period. The fixation of organic compounds into inorganic materials like silica will be one of the most promising approaches especially in photonic applications. The sol-gel method is most popular in preparing silica thin films containing organic dyes and has contributed a great deal to increase the stability and the physical properties of organic compounds. But there remain some problems such as micro pores, less etching

resistance, organic impurities, or a heating process. Recently the liquid phase deposition (LPD) method has been developed for preparation of organic dye-doped silica with highly dense structure and very low impurities. We reported this method will be useful for preparing new hybrid materials containing organic dyes for future photonics [2]. In the present paper, preparation of porphyrin-doped silica by this method and control of its excited triplet state will be reported.

EXPERIMENTAL

Silica films doped with water soluble porphyrin, 5,10,15,20-tetrakis[4-(N-trimethyl)ammonio]phenylporphyrin (TTMAPP), were deposited on the surface of a glass slide at 25 - 35°C by immersing it for appropriate times in saturated hydrofluorosilicic acid solution as previously reported [2] or fluorosilicate and boric acid solutions at relatively higher pH. These films were characterized by absorption and fluorescence spectroscopies, transient absorption upon ns laser excitation at 532 nm.

RESULTS AND DISCUSSION

The absorption spectrum of TTMAPP doped in silica films by the LPD method from saturated hydrofluorosilicic acid solution showed the Soret band with a peak at 433 nm, which was assigned to protonated (cationic) TTMAPP. Deposition from fluorosilicate solutions increased the absorption at about 410 nm attributed to a neutral form. No spectral changes were observed after keeping TTMAPP-doped silica for 40 h in 25% ammonia solution. It confirmed again the much more dense structure of silica films by the LPD method than those by the sol-gel method as previously reported for malachite green doped systems [2]. It was converted to a neutral form TTMAPP with the Soret band at 410 nm and the Q-band with four peaks very slowly by heat treatment above 50°C as shown in Fig. 1 and also by evacuation. The neutral form was stable in dry atmosphere, in vacuo, or in a silica coated film. The fluorescence spectra clearly corresponded to such structural changes of TTMAPP. The protonated form was regenerated slowly but reversibly independent of environments as shown in Fig. 2. These results strongly suggested that protons are not removed away from silica films and also that they did not come from outside. Thermal activation or evacuation most probably caused only the displacement of protons from/to porphyrins inside of silica net-

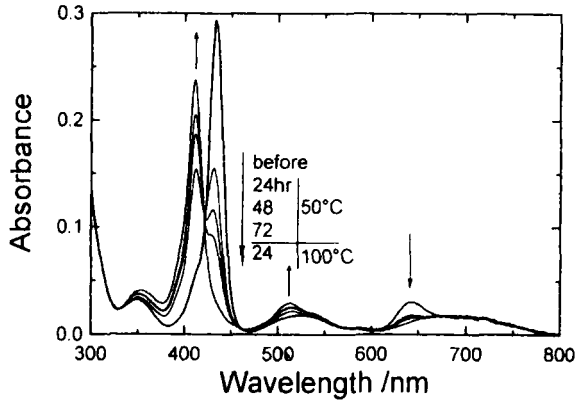

FIGURE 1 Spectral changes of TTMAPP-doped silica films prepared from saturated hydrofluorosilicic acid solution upon heating at 50 °C and 100 °C.

works. Two forms of TTMAPP in LPD silica films under various treatments and environments are schematically shown in Fig. 3.

Upon excitation of TTMAPP with a ns YAG laser at 532 nm, transient absorptions with a main peak at 490 nm in silica films and at 440 nm in aqueous solutions were observed. They are attributed to the excited triplet state of protonated and neutral TTMAPP, respectively. The lifetime of excited triplet state of TTMAPP doped in silica films (1.5 ms) was more than ten times longer than that in aqueous solutions (0.1 mM) used for deposition. The decay curves of excited triplet did not follow a single exponential decay in both cases. The decay in silica films was analyzed by a dispersive process, $I(t)= I_0\exp(-kt^{\alpha})$, where the dispersive parameter α is

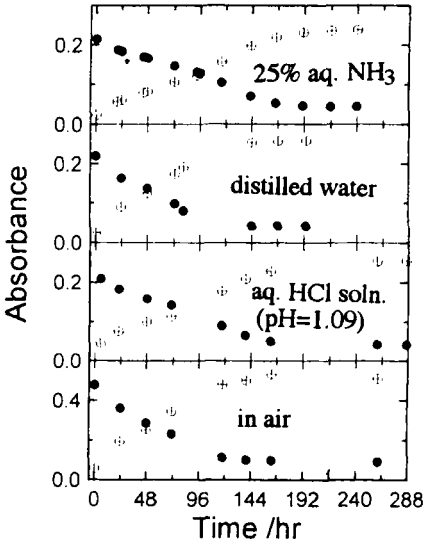

FIGURE 2 Time dependences of absorbance at 433 (○) and 410 nm (●) in various environments at room temperature for TTMAPP-doped silica films after heat treatment for 24 h at 100 °C.

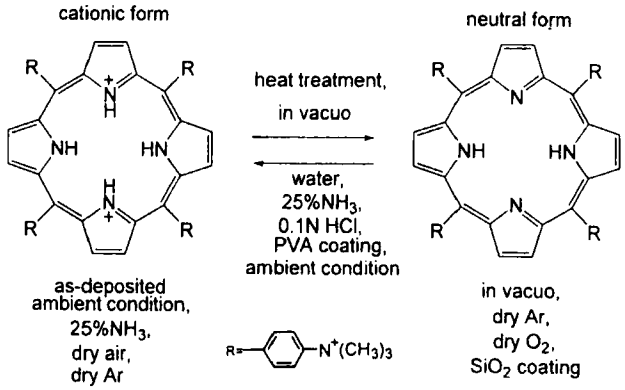

FIGURE 3 Two forms of TTMAPP in LPD silica films under various treatments and environments.

between 0 and 1. The α-value was 0.8 for TTMAPP doped in silica films deposited from 0.1 mM solutions, indicating fairly homogeneous distribution of chromophores. The decay in 0.1 mM aqueous solutions used for deposition did not follow a dispersive process neither, which indicated very strong intermolecular interactions. Such strong interaction of excited triplet TTMAPP in aqueous solutions was almost eliminated in silica films as suggested by $\alpha = 0.8$.

CONCLUSION

TTMAPP was fixed firmly in silica films by the LPD method as either a protonated or a neutral form at high concentrations without undesirable molecular interactions. Porphyrin-doped LPD silica films are expected as one of the promising hybrid materials for linear and nonlinear photonics.

Acknowledgments

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