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Lead phthalocyanine incorporated in sol and gel

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Lead phthalocyanine (PbPc) was first successfully doped in organic-inorganic matrix by choosing proper alkoxy-silane containing amino-group by sol-gel processing. The characteristics of PbPc in sol and gel were studied using optical absorption spectroscopy. The results show that the presence of PbPc monomer in the sol and gel is strongly controlled by the pH value of sol, and the action of amino-group is an important factor for PbPc monomer able to exist in gel. © *1999 Kluwer Academic Publishers*

1. Introduction

Metallophthalocyanine (MPcs) has been focused on much attention because of their wide variety of remarkable properties such as photoconductivity, photochemical reactivity, bioinorganic and catalytic activity and electrochromism, and their possible application use in the field of color display technology and gas sensor [1, 2]. Recently, Perry *et al.* have shown that MPcs have large nonlinear absorption and can be used as optical limiters which can protect human eyes or optical sensors from optical damage [3, 4]. Transparent inorganic and inorganic-organic matrices with high laser damage threshold incorporating with these MPcs, if developed, show particular promise for practical application in optical devices, because of their significant chemical and thermal stabilities. So far, some MPcs such as CuPc, SnPc, GePc and $SiPcCl_2$ have been incorporated in SiO_2 gels using a sol-gel method [5, 6]. The sol-gel method is widely used to obtain inorganic glass and ceramics at low temperature. Generally, the limiting response of MPcs is increased as the weight of metal increases. Because of it, of all MPcs, lead phthalocyanine (PbPc) is most promising and is of particular interest to be incorporated in the inorganic matrix. However, PbPc molecule is very easy to dimerize and further agglomeration, which results in the reduced effect of optical limiting. Up to now, there are no reports for doping PcPc in the form of monomer into an inorganic and organic-inorganic matrix.

In this work, we report our first successful synthesis of PbPc monomer embedded in an organic-inorganic gel by the sol-gel process and demonstrate the existence of PbPc monomer in this matrix with optical absorption spectroscopy.

2. Experimental

Lead Phthalocyanine (PbPc) was available from Tokyo Kasei Organic Chemicals, Japan, and used without further purification. The molecule's structure of PbPc with a center-symmetic structure and the π-electron conjugated system is shown in Fig. 1. The reagent grade chemical of 3-(Diethoxymethylsily)propylamine ($NH_2(CH_2)_3Si(OC_2H_5)_2$-$CH_3$, DEMPA) and 3-Glycidyloxypropyltrimethoxysilane ($H_2COCHCH_2O(CH_2)_3$-$Si(OCH_3)_3$, GPTMS) were used as a matrix materials. In fabricating for PbPc/DEMPA solution, 5 mg PbPc was added into 30 ml DEMPA solution. The mixture was sonicated. A clearly green solution was obtained. There was some black PbPc deposition not dissolved with DEMPA solution in the bottom of beaker. The sedimentation was removed by filtering process. It was found that the maximum solubility for PbPc at room temperature was about 1.5 mg in every 40 ml DEMPA. The resultant solution was hydrolyzed with the mixture of C_2H_5OH and H_2O. The pH value of which was adjusted using HCl. Because of the very slow hydrolysis-rate of DEMPA, the GPTMS/DEMPA system was chosen as matrix for PbPc. In a typical run, 10 ml of above obtained PbPc/DEMPA solution was added into 12 ml GPTMS, and then added 15 ml C_2H_5OH. This solution was hydrolyzed by gradually dropping 1.8 ml distilled water, followed by stirring for 40 min. The resultant clear and homogeneous solution was gelled to form a stiff gel at room temperature for 2 weeks in a covered polystyrene container.

The optical absorption measurement of solution was carried out on the samples filled in 10 mm optical silica cuvette by a UV/Vis spectrophotometer (JASCO Ubest-50). The pH value of the solution was measured with Model HM-1 K pH meter.

3. Results and discussion

3.1. Incorporation of PbPc in DEMPA solution

Crystalline PbPc belongs to monoclinic and triclinic [7] and is dissolved as monomer, dimer, and aggregates in solution. In optical absorption spectra, the PbPc monomer has two absorption bands in the range of

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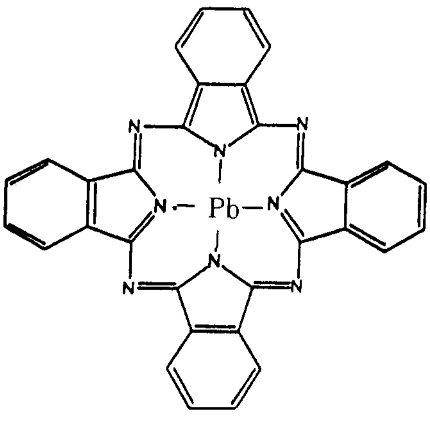

Figure 1 The molecular structure of PbPc.

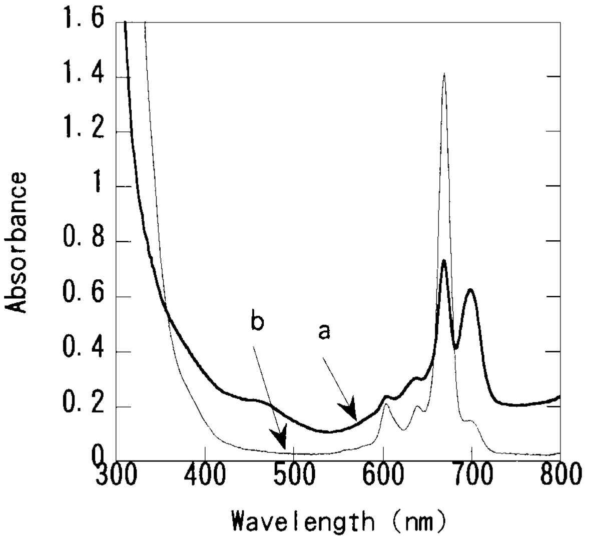

Figure 2 UV/Vis absorption spectra of PbPc in DEMPA solution: (1) sonicated for 15 minutes; (2) sonicated for 2 hours.

300–400 nm and 600–800 nm wavelength which are assigned to Q- and B-band, respectively [8, 9]. In general, the formation of dimer and aggregation of PbPc molecules quenches the optical limiting effect and changes their other optical properties. Therefore, for the optical limiting effect, it is the crucial issue to prevent the dimer and aggregation formation from PbPc monomers in the sol-gel process.

In our preliminary experiments to dissolve PbPc in solvents, some solvents such as CH_3OH, TMOS and TEOS were chosen but failed to dissolve PbPc. Optical absorption spectra of PbPc-dissolved DEMPA (5 mg PbPc in 30 ml DEMPA), measured after sonicating for 0.25 and 2 hours are shown in Fig. 2. It is apparent that both spectra consist of the Q and B-bands in the range of 600–800 nm and 300–400 nm wavelength, respectively. In the Q-band region, four bands are observed at 604, 639, 669 and 702 nm wavelength, which are assigned to the dimer, monomer and aggregation, respectively. Because of the strong absorption of DEMPA at the range of 200–400 nm, the another monomer band of PbPc at 350 nm disappears.

One can notice in Fig. 2 that by the ultrasonic treatment for long period the intensity of monomer band peaking at 669 nm significantly increases, instead for the decreases in the band intensity of the aggregation of PbPc. This result strongly indicates that the PbPc can be dissolved in the monomer former in DEMPA solvent. The PbPc molecule is a π-electron conjugated system and is liable to be surrounded by amino-groups of DEMPA molecule. By choosing alkoxy-silane containing amino-group, the hydrolysis and condensation of $-OCH_3$, or $-OC_2H_5$ can take place which helps PbPc molecules get entrapped along with $-NH_2$ group in the growing covalent gel network. We also found that the solubility of other soluble MPcs such as $SiPcCl_2$ was much higher in DEMPA than that in other common solvents such as CH_3OH and tetrahydrofuran (THF).

3.2. Effects of solvent and pH value on sol

The obtained PbPc/DEMPA solution was hydrolyzed with H_2O and different quantity of C_2H_5OH, the optical spectra of which are shown in Fig. 3. Four absorption bands at 605, 642, 670 and 702 nm indicate the formation of dimer, monomer and micro-crystal, respectively. The intensity corresponding to the respective absorption bands reduces gradually with increasing the amount of C_2H_5OH. However, the relative optical intensities of monomer and dimer show almost no changes, indicating that the quantity of alcohol solvent does not influence the state of PbPc, and the C_2H_5OH just dilutes the sol solution.

The PbPc/DEMPA solution hydrolyzed with H_2O show high pH value around 12. Fig. 4 shows the optical spectra of PbPc/DEMPA solution hydrolyzed using HCl with $pH = 4$ and 8. It is evident that the bands at 607, 642 and 671 nm wavelength disappear in solutions of pH 4 and 8. It is well known that, when HCl is introduced into sol solution, the amino-group (NH_2-) can easily react with HCl. As amino-group gradually depleted by the HCl, the environment of PbPc surrounded by amino-groups no longer equilibrates and then is broken. The PbPc monomers are aggregated again.

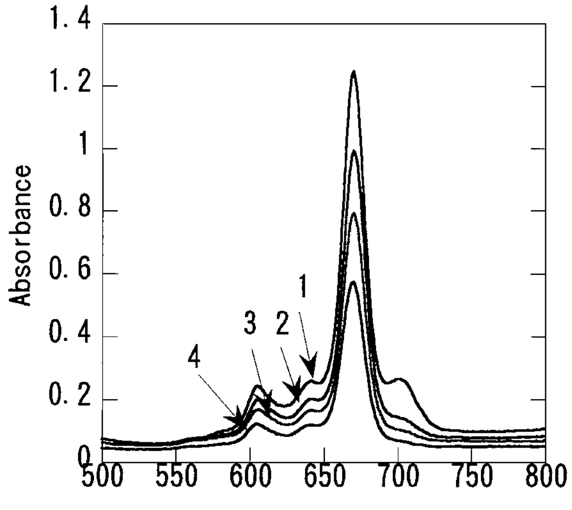

Figure 3 UV/Vis spectra of PbPc in DEMPA sol hydrolyzed with H_2O and different quantity of alcohol: (1) 3 mlDEMPA/0.6 mlH_2O; (2) 3 mlDEMPA/0.6 mlH_2O/0.6 mlC_2H_5OH; (3) 3 mlDEMPA/0.6 mlH_2O/1.6 mlC_2H_5OH; (4) 3 mlDEMPA/0.6 mlH_2O/3.6 mlC_2H_5OH.

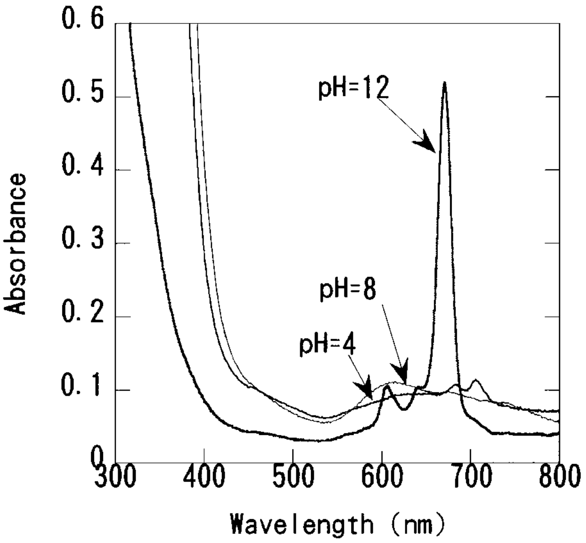

Figure 4 UV/Vis spectra of PbPc in solution hydrolyzed with aqueous HCl solution at pH = 4, 8 and 12.

3.3. Existence of PbPc monomer in ormosil

It was found that the hydrolysis rate of PbPc/DEMPA solution was very slow and it is necessary to keep more than two months to form gel. In order to accelerate the hydrolysis rate of solution. GPTMS was added into PbPc/DEMPA solution and hydrolyzed with the mixture of H_2O and C_2H_5OH. Fig. 5 shows the optical absorption spectrum of thus obtained gel of $\sim$0.8 mm thick. The bands at 608, 628, 672 and 716 nm are clearly observed, and spectrum feature is very similar to that measured in PcPb/DEMPA solution. The optical spectrum and green color of the gel strongly indicate that the PbPc monomers are entrapped in the gel network.

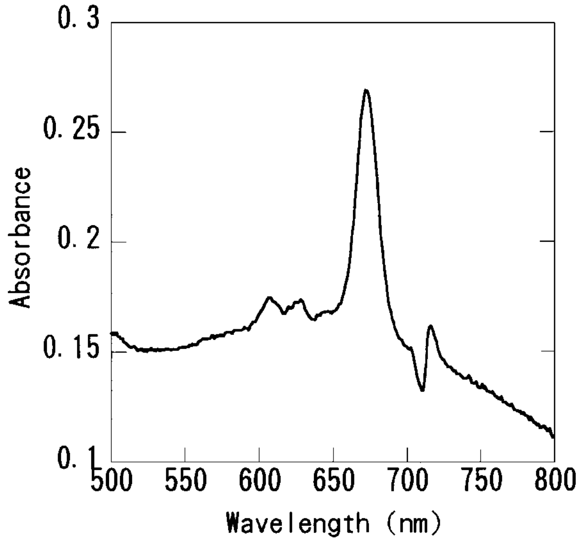

Figure 5 UV/Vis spectra of PbPc-doped dried gel.

Comparing the monomer bands of PbPc in DEMPA solution, DEMPA/C_2H_5OH/H_2O sol and DEMPA/DPTMS gel, peaking at 669, 670 and 672 nm respectively, only a 3 nm red-shift for the monomer is observed from DEMPA solution (669 nm) to gel (672 nm). In our related study for $SiPcCl_2$ doped in SiO_2 matrix, a 14 nm red-shifted from sol to gel was observed. This is attributed probably to the soft environment of PbPc surrounded by -NH_2 groups. The influence of ormosil matrix on the dopant is weak compared with SiO_2 gel.

From these results, it is evident that the existence of PbPc monomer in sol and gel greatly depend on the high pH value of sol due to the presence of amino-groups. However, the quantity of C_2H_5OH has no effect on the existence of PbPc monomer. Hence, we conclude that the monomer and dimer of PbPc are located in the chemical environment surrounded by the amino-groups of DEMPA.

4. Conclusion

Uniform composite of lead phthalocyanine doped ormosil by the hydrolysis of GPTMS and DEMPA can be synthesized by selecting suitable alkoxy-silane containing aminogroup. PbPc monomer is restricted within the network of the gel matrixes. The PbPc monomers can be hold in sol and gel under the chemical condition with high pH value due to the action of -NH_2 group with H_2O. The states of dimer and aggregation changing from PbPc monomers in the sol and gel do not take place in an abundance of aminogroups. Such composite containing PbPc is expected to find application as limiter and optical electric device, which will be reported in future papers.

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