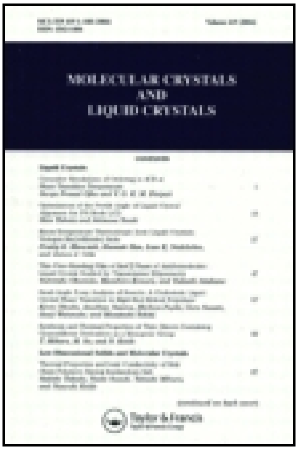

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Complex Formation and Its High Dispersion in the Simultaneous Vacuum Deposition of Copper and Phthalocyanine

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Version of record first published: 24 Sep 2006

To cite this article: Kazuhiro Tsuchiya, Satoru Takano & Katsuo Orihara (1998): Complex Formation and Its High Dispersion in the Simultaneous Vacuum Deposition of Copper and Phthalocyanine, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 149-154

To link to this article: http://dx.doi.org/10.1080/10587259808030214

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 149–154
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Complex Formation and Its High Dispersion in the Simultaneous Vacuum Deposition of Copper and Phthalocyanine

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Received 7 April 1998; revised 8 June 1998; accepted 14 June 1998

In the codeposition of Cu, Pc, and third component substance by means of simultaneous evaporation from different sources in vacuum, The formation of CuPc complex was observed. Later, a method to disperse the CuPc complex CuPc in the codeposition was developed.

Keyword: Complex Formation; Aggregation Inhibitor; Third Component Substance; Phthalimide; Simultaneous Vacuum Deposition; Dispersion

INTRODUCTION

The third-order optical susceptibility ($\chi^{(3)}$) of metallo-phthalocyanine complex (MPc) is expected to increase by highly dense packing[1]. In order to pack molecules densely, various ways have been investigated[2]. For the enhancement of $\chi^{(3)}$, a composite of MPc and non-polar molecules as a matrix would be desirable. With regard to this molecular dispersion, Sakakibara et al. reported that CuPc was dispersed in a polyimide matrix which was polymerized during the codeposition of its monomer with CuPc in vacuum[3]. However, CuPc was in the microcrystal state in the film, and no effect on $\chi^{(3)}$ was observed.

Considering these points, we first developed a codeposition method of multi-components evaporated simultaneously from different sources. As a result, the method was found to be useful to form highly pure MPc because it is not a catalyst process. Later, it was also found that MPc was dispersed molecularly in the codeposited film[4],[5]. The solid structure of the Pc component in the codeposited film was analyzed by X-ray diffraction and by electron microscope, and it was found that the crystal size and crystallinity of the Pc, MPc, and metal decreased remarkably compared with those of only Pc deposition film[5]. This tendency increases largely by the addition of a third component, paraffin.

Since the simultaneous evaporation (SE) method does not require the use of a catalyst, then the improvement of the optoelectronic function may be expected because the function depends on its impurity. In this study the dispersion of CuPc formed by SE-method was examined with two parameters : the blending ratio of Cu and Pc and kind of component. In particular, the effect of third component substances used as aggregation inhibitors was investigated.

EXPERIMENTAL METHOD

Cu (purity 99 %) was purchased from Wako Junyaku. As third component substances, paraffin(Pa) of nonpolar molecule (melting point 68-70°C) from Kanto Chemicals, stearic acid(SA) of amphiphilic molecule from Tokyo Kasei, and phthalimide(Pi) from Kanto Chemicals were used. These reagents were used without further purification. Pc from Tokyo Kasei and commercial CuPc from Wako Junyaku were used. Both of them were used without further purification. A high vacuum vapor deposition system (Shinku Kiko VPC-260 type) was applied for fabrication of the codeposited films. The deposition rate of Cu and Pc was observed by a crystal oscillator. By changing the temperature of the third component substance (T_{3rd}) at evaporation source, as shown in Table. I , its deposition rate was changed within a range of 0.01-0.02 nm/s.

TABLE . I Experimental conditions of the SE-method.

Sample	Pressure / 10^{-3}Pa	Depo. rate of Cu / nm•s^{-1}	Depo. rate of Pc / nm•s^{-1}	Depo. thick. of Cu / nm	Depo. thick. of Pc / nm	Depo. time /s	T_{3rd}^{a}/ ℃
Cu*Pc	3.8	0.01	0.025	2.0	5.6	200	-
Cu*Pc	3.2	0.01	0.045	3.4	17.7	470	-
Cu*Pc	4.7	0.01	0.1	3.4	43.0	420	-
Cu*Pc*Pa	4.3	0.01	0.02	5.2	11.1	480	115
Cu*Pc*SA	4.3	0.01	0.02	5.0	10.0	480	70
Cu*Pc*Pi	16.0	0.02	0.04	7.4	15.5	400	120
Cu*Pc*Pi	12.0	0.03	0.04	9.8	13.0	300	120
Cu*Pc*Pi	20.0	0.02	0.05	8.7	18.8	360	120
Cu*Pc*Pi	15.0	0.01	0.1	3.8	42.0	400	120

a: Temperature at evaporation source of the third component substance

Substrate temperature was kept 13°C, and its distance from the evaporating source was 11.5 cm. As a substrate for deposition, a slide glass was used. Dispersion state and chemical structure of the Pc component in the codeposited film were analyzed by using a visible absorption spectrometer (Hitachi, 200-10). To analyze the chemical structure of Pc or MPc, a 1-chloronaphthalene dilute solution of the samples was used in similar manner as that described in our previous paper[5].

RESULT AND DISCUSSION

Visible absorption spectrum in solution

Visible absorption spectra of 1- chloronaphthalene dilute solution of the composite film deposited by three-source simultaneous evaporation, (Cu * Pc * Pa), (Cu * Pc * SA), and/or (Cu * Pc * Pi), are shown in Fig.1. For comparison, the spectra of dilute solution of Cu * Pc , Pc, and commercial CuPc were also shown in Fig.1.

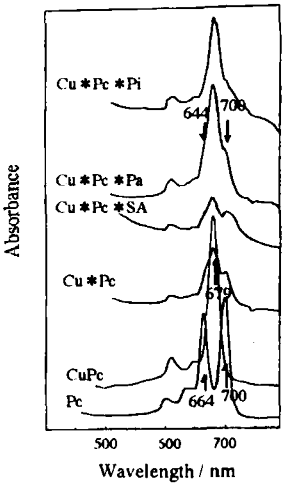

FIGURE.1 The visible absorption spectra of 1-chloronaphthalene dilute solution of each sample, CuPc and Pc as reference.

In the spectrum of Cu * Pc * SA, two peaks are observed at 664nm and 700nm. Such peaks also appear in the spectrum of pure Pc. Another peak, similar to that of commercial CuPc, is also observed at 679nm. As for the peak at 700nm in Cu * Pc * SA, the absorbance is larger than that at 700nm of Cu * Pc. From these results, a mixture of Pc and CuPc in Cu * Pc * SA was suggested. Fig. 2 shows the absorption spectra of 1-chloronaphthalene dilute solution of the Pc/CuPc mixture as a function of mixing ratio. The systematic change of spectra by increasing the CuPc ratio, for example, can

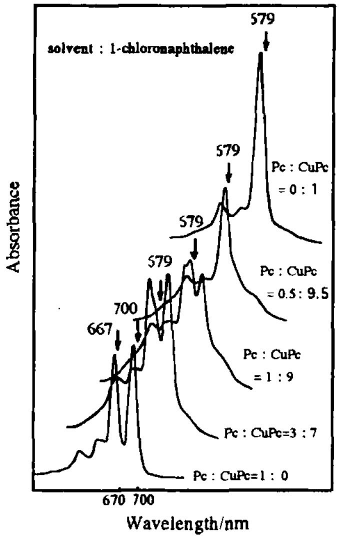

FIGURE.2 The visible absorption spectra of 1-chloronaphthalene dilute solution of the Pc/CuPc mixture at various mixing ratio.

be observed. Considering this tendency, we could conclude that the yield of CuPc formation in Cu * Pc * SA is less than that in Cu * Pc. On the other hand, the yield of CuPc formation in Cu * Pc * Pa seems to increase compared to that of Cu * Pc. Furthermore, in the spectrum of Cu * Pc * Pi, a shoulder at 700nm becomes slimmer compared to that of Cu * Pc * Pa. The profile is identical with the spectrum of commercial CuPc. Accordingly, almost 100% yield of CuPc formation was suggested in Cu * Pc * Pi.

TABLE. II Yield of CuPc formation in each sample calculated by comparing the spectra in Fig.1 and Fig.2.

Sample	CuPc Yield (CuPc / Pc + CuPc) / %
Cu * Pc	82
Cu * Pc * SA	79
Cu * Pc * Pa	89
Cu * Pc * Pi	95

The yield of CuPc formation in each sample can be estimated roughly by comparing the spectra in Fig.1 and Fig.2, summarized in Table. II. From Table. II, it was found that the CuPc yield is dependent on the kind of third component used.

Visible absorption spectrum in solid state

Fig. 3 shows visible absorption spectra of solid-state film by SE- method. To examine the effect of molecular species of the third component for dispersibility of CuPc formed on the codeposition, the ratio of deposition rate of Cu to that of Pc was kept about 2/1, and the deposition rate of third component was fixed in the range of 0.01-0.02nm/s too.

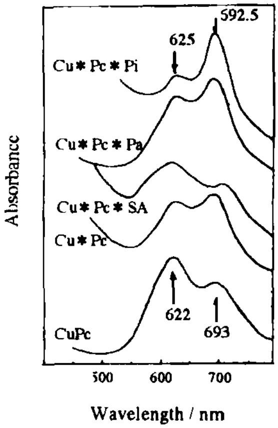

FIGURE.3 Visible absorption spectra of solid state codeposition films. The sample was deposited at same condition as that used in Fig.1

The absorption spectrum of CuPc deposition film shows two peaks assigned to π-π * transition at 622nm and 693nm[6]. Since this spectrum coincides with that of α type crystal of CuPc[6], the existence of α type crystal in the CuPc deposition film was suggested. Furthermore, the spectrum of Cu * Pc * SA agrees almost with that of CuPc. This agreement suggests that the Pc component in Cu * Pc * SA changed to CuPc almost completely. It is well known that the stronger absorption at longer wave length shows higher dispersion of CuPc[7]. Then, from the shape of each spectrum at long wave length of 692.5nm in Fig.3, the degree of CuPc dispersion is estimated as a following order: Cu * Pc * Pi> Cu * Pc * Pa> Cu * Pc> Cu * Pc * SA.

TABLE. Ⅲ Degree of dispersion of CuPc formed in the SE-method process of samples.

Sample	Dispersibility $A_{\lambda L}/A_{\lambda S}$
Cu ＊Pc	1.25
Cu ＊Pc ＊SA	0.8
Cu ＊Pc ＊Pa	1.3
Cu ＊Pc ＊Pi	4.3
CuPc[＊a]	5.7

a: Dilute solution in 1-chloronaphthalene

The quantitative degree of dispersion was evaluated from the absorbance ratio of two peaks ($A\lambda L/A\lambda S$) of the long wavelength side (692.5nm) and the short wavelength side (625nm) in Fig.3. The results are shown in Table Ⅲ. The dispersion of CuPc depends intensively on the third component substance. In particular, Cu * Pc * Pi shows the largest value among the samples examined here.

CONCLUSION

High degree of dispersion of the CuPc component formed in the codeposition of Cu and Pc was achieved by the simultaneous evaporation method. When the moler ratio of Cu and Pc was 38:1 and Pi was used as an aggregation inhibitor, the dispersion went up to almost the same level as that of the dilute solution of commercial CuPc. The application of Pi induced the yield increase of CuPc formation by the simultaneous evaporation of Cu and Pc in vacuum. These results seem to be useful to fabricate third-order non-linear optical materials with large susceptibility. When Pa was used as an aggregation inhibitor, the effect on the dispersion of CuPc formed was little. However, the yield of CuPc formation increased. When SA was used as an aggreration inhibitor, no effects were observed on the dispersion and on the yield of the CuPc formation.

ACKNOWLEDGMENTS

The author thanks Mr. K. Aoki, Mr. K. Ebe, and Mr. Y. Yamagata for their cooperation. The present work was supported by the Izumi Foundation for Science and Technology.

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