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Langmuir-Blodgett Films and Second-Order Nonlinear Optical Property of a Phthalocyanine-Fullerene Dyad

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The Langmuir-Blodgett films of a new copper phthalocyanine-fullerene dyad were fabricated. Its second harmonic gernation property from the films were studied.

Keywords: phthalocyanine; fullerene; Langmuir-Blodgett film; second harmonic generation (SHG)

INTRODUCTION

Phthalocyanines (Pcs) have attracted much attention in recent years because of their good optical and electronic properties as well as excellent thermal and chemical stability. Pcs have been used in many fields, such as chemical sensors[1], photovoltaic cells, electrochomic display devices[2] *etc*. Pcs' unique properties come from their extensive delocalized large two-dimensional 18π-electron system. Which also makes Pcs as the good candidates for organic nonlinear optical materials[3]. Both of the second and third order NLO properties of the Pcs have been studied extensively. Fullerene (C_{60}) has been a new functional material since its discovery in 1985. C_{60} has special three-dimensional π-conjugated system and there are many papers about the third-order NLO properties of C_{60}. Furthermore, C_{60} can serve as useful electron

acceptor moiety.

In this paper, a Pc linked C_{60} Compound (Pc-C_{60}) was synthesized[14] with the Pc being used as donor and C_{60} as acceptor. It is interesting to study the interaction between two large π-conjugated systems, i.e C_{60} and Pc. The larger and complicated system of Pc-C_{60} will lead to the different NLO properties compared with single Pc or C_{60}. If noncentro-symmetric film of Pc-C_{60} can be obtained, we can measure the second harmonic generation (SHG) behavior of the film and study the second-order NLO properties of this new material for the first time.

EXPERIMENTAL

The chemical structure of Pc-C_{60} was shown in Figure 1. Pc-C_{60} is stable and soluble in common organic solvents, such as toluene and chloroform.

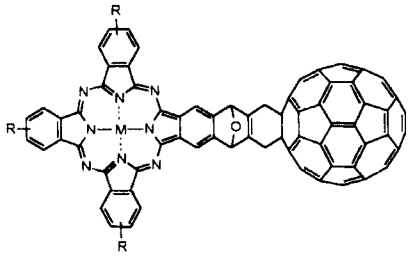

Figure 1 Chemical structure of Pc-C_{60} dyad, R = t-Butyl, M = Cu.

Langmuir-Blodgett (LB) films of Pc-C_{60} were fabricated on KSV-5000 Instrument (KSV, Finland). A chloroform solution of Pc-C_{60} was spread onto the pure water surface at 20±0.5 °C. The condensed film on the subphase was transferred onto hydrophilic quartz substrate at a constant surface pressure of 25mN/m with the best transfer ratio of 0.61. Fabrication of 1, 3 and 7 layers LB films of Pc-C_{60} were performed under same condition.

The SHG measurements of 1, 3, 7-layer LB films of Pc-C_{60} were carried

out in a transmission geometry using 1064 nm output from an Nd:YAG model-locked laser[15]. An infrared blocking filter and a 532 nm interference filter were used to ensure that only SHG signal was detected. The SHG signal of standard Y-cut quartz substrate was also measured under same condition.

RESULTS AND DISCUSSION

Figure 2 shows the π-A isotherm of Pc-C_{60}. It indicates that Pc-C_{60} can form stable condensed film at the air-water interface. The limiting molecular area is determined to be 0.54 nm^2.

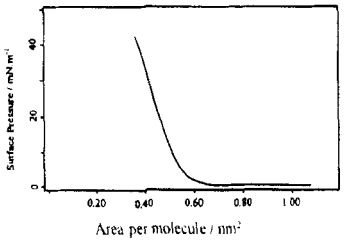

Figure 2 The π-A isotherm of Pc-C_{60}.

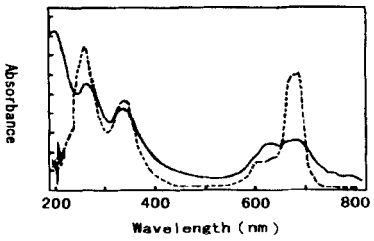

Figure 3 The UV-Visible pectra of Pc-C_{60} (a) in toluene (- - - -), (b) 6-layer LB film (——)

The UV-Visible spectra of Pc-C_{60} in toluene and 6-layer LB film mainly have two bands, i.e. Q and B band, as shown in the figure 3. The absorption of Pc part in Pc-C_{60} is so strong that it almost covers the absorption of C_{60}. Both of the two spectra exhibit little character of the existence of C_{60}. Furthermore, The Q band of LB film becomes wider and weaker than that in solution because of the stronger interaction between the molecules in solid state.

In experiment, the p-polarized second harmonic (SH) intensities $I_{2\omega}^{p\to p}$ of the LB films were measured under p-polarized fundamental light. The $I_{2\omega}^{p\to p}$ of

the standard Y-cut quartz substrate is 7.55×10^5, written as I_{SiO_2}, and its $\chi^{(2)}$ is known to be 1.2×10^{-9} esu. Then, the measured SH intensities of the samples were compared with that of standard quartz substrate. The results shown in table 1 indicate that the SH signals increase with the number of layers according to a subquadratic dependence. It proves the existence of the second-order nonlinear optical property of the material.

Table 1 The SH intensities of 1, 3 and 7 layers LB film of Pc-C_{60} and the comparing results with the referring quartz substrate.

The number of layers of LB films	1	3	7
$I_{2\omega}^{p\to p}$ of the samples	1.76	5.90	31.59
$\frac{I_{2\omega}^{p\to p}}{I_{SiO_2}}\times10^5$	2.33	7.81	41.84

In summary, the LB films of a novel phthalocyanine linked C_{60} dyad Pc-C_{60} was fabricated successfully and its NLO property was studied for the first time. The further study of the interaction between C_{60} and Pc is ongoing.

Acknowledgements

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