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Self-assembled multilayer films containing 1,8,15,22-tetrakis (8-quinolineoxy-5-sulfonic acid)-phthalocyanine copper: Preparation, and third order nonlinear optical properties

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ABSTRACT

Composite film with alternating layers containing anionic 1,8,15,22-tetrakis (8-quinolineoxy-5-sulfonic acid)-phthalocyanine copper and cationic polydiallydimethylammonium chloride was fabricated by electrostatic self-assembled layer-by-layer (LBL) technique. The microstructure of the film was characterized by a series of techniques. The third-order nonlinear optical properties of the film were measured using 4f coherent imaging system with phase object (NIT-PO) with laser duration of 20 ps at the wavelength of 532 nm. The film exhibited excellent nonlinear absorption and self-focusing effect. The second-order molecular hyperpolarizability γ value of the film reaches as high as 1.54×10^{-29} esu.

1. Introduction

Phthalocyanine complexes have attracted much research attention owing to its potential applications in all-optical switching, signal processing, and ultrafast optical communications [1–4]. Especially, phthalocyanine complexes have been studied in the field of the third-order optical nonlinearities on account of π-conjugated systems. The research results demonstrate that the kinds of complexes behave the outstanding nonlinear absorption effect and refraction effect because of the macrocycle system of delocalized π-conjugation [5–8]. The third-order optical nonlinearities of organic compounds with enlarged π-delocalized conjugation system can be enhanced because π electrons could move freely within the extended π system to produce a large NLO effect [9]. Especially, the Pc systems could offer tremendous opportunities for tailoring the optical properties through aggregation of supramolecular structures which usually display outstanding properties.

Many solid film of phthalocyanine complexes display large third-order optical nonlinearities [10–15]. The orderly solid films have been fabricated through the electrostatic layer-by-layer (LBL) self-assembled technique [16,13] and Langmuir–Blodgett technique in order to obtain the the large second-order molecular hyperpolarizability γ value, and eventually put them into use in an optical device. Several kinds of electrostatic LBL self-assembled films of pthalocyanines have been prepared and their optical nonlinearities have been reported [17,18]. Our aim of this study is to synthesize the phthalocyanine with larger π-conjugated system, and to prepare the orderly ultrathin film with excellent third-order optical nonlinearities.

In the present study, 1,8,15,22-tetrakis (8-quinolineoxy-5-sulfonic acid)-phthalocyanine copper [CuPc($QnSO_3H$)$_4$] with larger π-conjugated system was synthesized, and the homogeneously composite films consisting of 1,8,15,22-tetrakis (8-quinolineoxy-5-sulfonic acid)-phthalocyanine copper [CuPc($QnSO_3H$)$_4$] and PDDA using the electrostatic LBL self-assembled technique were prepared. The third-order NLO properties of CuPc($QnSO_3H$)$_4$/PDDA film were investigated using the 4f coherent imaging system with phase object (NIT-PO).

2. Experimental

2.1. Materials

1,8,15,22-Tetrakis (8-quinolineoxy-5-sulfonic acid) phthalocyanine copper [CuPc($QnSO_3H$)$_4$] was synthesized according to the

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published paper (Fig. 1) [13]. 3-(5-Sulfonic quinoline-8-oxy) phthalonitrile is the starting materials for $CuPc(QnSO_3H)_4$ [19], and the synthetic method of 3-(5-sulfonic quinoline-8-oxy) phthalonitrile was also refered to the literature [19]. The synthetic method of $CuPc(QnSO_3H)_4$ is stated as follows. A mixture of 3-(5-sulfonic quinoline-8-oxy) phthalonitrile (0.4 mmol), $CuCl_2$(0.1 mmol), and 1.8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.7 ml) were dissolved in freshly distilled 1-hexanol (15 ml). And then, the mixture was refluxed for 24 h under a nitrogen atmosphere. After the reaction completed, the mixture was cooled to ambient temperature. The organic solvent was removed through vacuum distillation. Small amount of dimethylformamide (50 ml) was added into the reaction mixture, and the crude product was dissolved dimethylformamide. The obtained product was purified by column chromatography (silica gel, MeOH). The green eluant was collected and was concentrated to 2 ml via rotary evaporation method. And then a mount of CH_2Cl_2 was added into the concentrated solution to the solid product precipitated, and it was filtered off to yield 0.21 g (67%) of $CuPc(QnSO_3H)_4$ as dark green solid. IR [(KBr) νmax (cm.1)]: 3414 (S—O—H), 3087 (Ar—H), 1607, 1545 (C=N, C=C), 1189 (Ar—O—Ar), 1183 (O—S—O), 1043 (C—S). UV/Vis (DMSO): λ_{max} = 695 (5.85 × 104), 322[1.76 × 104]. MALIDI TOF-MS Found (Calcd): 1469.1 (1468.9).

2.2. Preparation of the layer-by-layer films

The tetrasodium salt of $CuPc(QnSO_3H)_4$ was obtained through the reaction of $CuPc(QnSO_3H)_4$ with sodium hydroxide solution, and the concentration of $CuPc(QnSO_3Na)_4$ aqueous solution is 1 mg/ml. PDDA (polydiallydimethyldiallylammonium chloride, MW ca. 100,000–200,000 Aldrich) for the preparation of Pc/PDDA was diluted to 5 wt% aqueous solution. Then, the processing method of the substrates for the films was described in the published method (Fig. 2(A)) [16,13]. Three layers of PDDA/PSS (Fig. 2(B)) were firstly deposited on the surface of the pre treated substrates. And then the substrate was dipped into the $CuPc(QnSO_3Na)_4$ aqueous solution and PDDA aqueous solution sequentially. The recycling fashion was repeated until the desired number of bilayers was obtained.

2.3. Measurements

Small angle X-ray diffraction (XRD) patterns of the film were measured using an X-ray diffractometer model D8 with Cu Kα radiation at the wavelength of 1.5406 Å. The linear refraction coefficient of the 50-bialyer film was 1.5348 measured on an optical ellipsometer (JOBIN YVON UVISEL). The total thickness of the 50-bilayer film is 30.68 nm obtained through the step profiler (Dektak 150). The multilayer growth process was monitored with Perkin–Elmer Lambda 900UV/Vis/NIR spectrometer. Atomic force microscopic (AFM) image was taken in air at room temperature with nanoscopic III instrument (digital instrument) operating in tapping mode. The nonlinear optical properties of $CuPc(QnSO_3H)_4$ film were investigated using the setup of 4f coherent imaging system with phase object (NIT-PO) at 532 nm with a repetition rate of 10 Hz, pulse width of 20 ps. The third-order optical properties of phthalocyanine aqueous solution were measured using the Top-hat Z-scan measurements with the same laser source as that of in the 4f nonlinear imaging with phase object measurements.

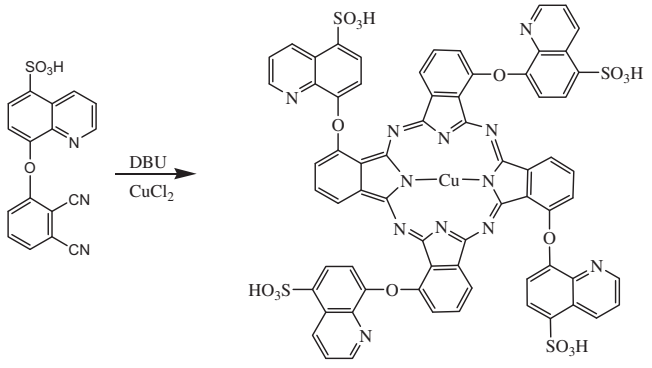

Fig. 1. The synthetic route of $CuPc(QnSO_3H)_4$.

3. Results and discussion

3.1. UV–Vis spectra

Fig. 3 shows the UV–Vis spectra of $CuPc(QnSO_3H)_4$ aqueous solution and the film from 5 bilayer to 40 bilayer every other five bilayers deposited on the quartzs substrate. The Q bands of $CuPc(QnSO_3H)_4$ exist whether in UV–Vis spectra of the film or that of aqueous solution. The absorption maximum for Q-band of the film is red-shifted by 10 nm relative to the aqueous solution of Pc, suggesting that face to face aggregation occurred in the film [20]. The same amount of $CuPc(QnSO_3H)_4$ molecules deposited on the surface of the substrate, which can be deduced from that the absorbance at both the Soret-band and Q-band increases linearly with the number of layers.

3.2. Small angle XRD

More information about the surface of the film can be provided by the small-angle X-ray diffraction study. Fig. 4 shows diffraction curve of the 20-bilayer film consisting of $CuPc(QnSO_3H)_4$/PDDA on the quartz substrate. The surface of the film deposited on the substrates is very flat because the well-defined Kiessig fringes up to scattering angles $2\theta = 2^\circ$ occurs in Fig. 4 [21]. It is further confirmed that the growth of $CuPc(QnSO_3H)_4$ molecules on the surface of the substrates is uniform.

3.3. Atomic force microscopy (AFM)

Figs. 5 and 6 provide the morphology details of 20-bilayer and 50-bilayer $CuPc(QnSO_3H)_4$/PDDA films deposited on the silica slides. The morphologies of the 20-bilayer film present dispersed nanoparticles with an average diameter of about 15.259 nm, and the mean interface roughness is 3.418 nm. Similarly, the nanosize particles with a uniform spherelike shape were seen obviously to be packed on the 50-bilayer film surface. The bulk of the nanosize particles with the average diameter of 24.451 nm in the 50-bilayer film was larger than that of 20-bilayer film. But, the mean interface roughness of 50-bilayer film is 2.926 nm, meaning that the surface of 50-bilayer film is more smooth and uniform than that of 20-bilayer. Obviously, either the area of nanosize particles in 20-bilayer film or in 50-bilayer film is much larger than that of Pc molecules [22], displaying that the Pc molecules aggregate in the films.

These experiment results, including AFM measurement, UV–Vis spectra and small-angle X-ray diffraction study suggest that the self-assembly of highly ordered ultrathin films is rather uniform and in good homogeneity.

3.4. Optical nonlinearities measurements

The setup of 4f coherent imaging system with phase object (NIT-PO) is shown in Fig. 7. All of the 4f measurements were performed in the same manner detailed in reference [22]. The output laser beam was first expanded by two convex lenses and spatially filtered by a pinhole to obtain a near Gaussian beam profile. Then