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Original article

Metal-free phthalocyanine single crystal: Solvothermal synthesis and near-infrared electroluminescence

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ABSTRACT

A metal-free purple H_2Pc single crystal was synthesized by a facile solvothermal method, and its solubility and near-infrared (NIR) optical properties were also investigated due to its potential applications as a light-emitting layer for OLEDs. The H_2Pc single crystal is insoluble in 1-chlorine naphthalene and other organic solvents. It gives a wide absorption in the range from 620 nm to 679 nm and a wide emission in near 922 nm. As an active light-emitting layer, H_2Pc was employed to fabricate electroluminescent (EL) devices with a structure of ITO/NPB (30 nm)/Alq_3:H_2Pc (30 nm)/BCP (20 nm)/Alq_3 (20 nm)/Al. The emission center is at 936 nm when the H_2Pc doping concentration is 20 wt%. The doping concentration strongly governs the emission intensity. When doping concentration decreases from 10 wt% to 1 wt%, the emission intensity remarkably fades, and simultaneously the emission center undergoes a blue shift.

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1. Introduction

Phthalocyanine and phthalocyanine complexes have a special two-dimensional conjugated π electronic structure and strong π–π electronic interactions caused by their conjugate ring structures, giving this variety of compounds their characteristic optical, electrical, and magnetic properties. Thus, they have potential applications in nonlinear optical materials [1], optical limiting complex materials [2,3], molecular electronic components [4,5], electrochromic materials [6,7], liquid crystal display materials [8,9] and optical dynamic anticancer treatment drugs [10–12]. Phthalocyanine complex single crystals are accessible and have been extensively used in OLEDs as the hole injection layer material [13,14] or as a hole buffer layer located between the ITO anode and the hole transport layer to improve device half-life. Yoshino *et al.* studied the near-infrared (NIR) emission spectroscopy of several phthalocyanine complex single crystals and their corresponding evaporation deposited films [15]. Zinc phthalocyanine single crystal has fluorescence peaks at 760 nm and 1000 nm, and a sharp phosphorescent peak at 1150 nm. Copper phthalocyanine single crystal has only a sharp phosphorescent peak around 1120 nm.

The photoluminescence properties in near-infrared region of phthalocyanine indicated that it could be used in organic NIR electroluminescent (EL) devices as the light-emitting layer material. Assour *et al.* have examined the fluorescence of phthalocyanine (H_2Pc) in 1-hydrogen chloride naphthalene solution [16], and observed three peaks located at 699 nm, 735 nm, and 778 nm. Fujii *et al.* reported single-layer H_2Pc light-emitting devices with emission of near-infrared light at 920 nm [17]. Despite these advances, phthalocyanine (H_2Pc) single crystals are difficult to obtain, and their corresponding fundamental solubility and optical properties have until now not been rigorously investigated.

Here, we reported a facile solvothermal synthesis to prepare single-crystalline H_2Pc. It gives poor solubility in various organic solvents, such as 1-chlorine naphthalene. UV–vis spectroscopy and PL spectroscopy of solid-state H_2Pc single crystals show wide absorption in the range from 620 nm to 679 nm and a wide emission near 922 nm. The strong aggregations of H_2Pc single crystals weaken fluorescence intensity due to concentration quenching. Thus, H_2Pc was doped with Alq_3 as a light-emitting layer to fabricate multilayer EL devices by a vacuum deposition method with a structure of ITO/NPB/Alq_3:H_2Pc/BCP/Alq_3/Al. The emission center is at 936 nm when the H_2Pc SC doping

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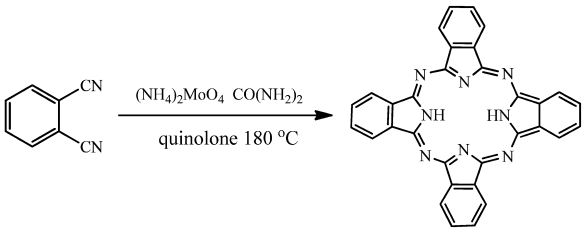

Scheme 1. Synthesis of H_2Pc single crystal.

concentration is 20 wt%. The H_2Pc doping concentrations influence emission intensity and blue shift the emission center.

2. Experimental

2.1. Materials and equipments

Solvents were purified according to standard procedures. All chemicals were obtained commercially and used without further purification.

Absorption spectra were taken on a UV-3600 230 VCE recording spectrophotometer (Shimadzu, Japan). Versus voltage (V) measurements were obtained using a Keithley 2400 current–voltage source. NIR PL spectra were measured on a PL 9000.

Photoluminescence System (Bio-Rad Micromeasurements Ltd., UK); the NIR EL signals were focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques. All the measurements were performed in air at room temperature.

2.2. Synthesis of H_2Pc single crystal

The mixture of phthalonitrile (0.051 g, 0.4 mmol), ammonium molybdate (0.022 g, 0.1 mmol), and urea (0.024 g, 0.4 mmol) in quinoline (20 mL) was kept at 180 °C in the autoclave for 8 h, and then cooled back to room temperature (Scheme 1). After removing the solvent, the target product of H_2Pc single crystal (0.0246 g, 48.24% yield) was obtained as a purple crystal.

2.3. H_2Pc electroluminescent devices

Organic film was prepared by a multiple source organic molecule vapor deposition system, and the instrument was produced by the Shenyang institute of Sida vacuum technology. The gas was pumped with a vacuum pump at a pressure of 4×10^{-4} Pa. For the evaporation of organic materials, the vacuum needs to be maintained at less than 1×10^{-3} Pa. The evaporation rate and film thickness were monitored in real-time through a quartz vibrator film thickness gauge.

The samples were stimulated by a He–Cd laser UV light with emission wavelength at 325 nm. Emitted light was focused by two lenses, passed through the slit of a grating monochromator, then detected by a photomultiplier tube to be recorded by the data acquisition system. The signal was enlarged by using standard phase-locked amplifier technology. When the near infrared electroluminescence spectrum of the device was tested, a JT-1 transistor characteristic tracer generated a 100 Hz saw tooth wave to launch 100 Hz pulse light. The light was aimed at the optical grating monochromator slits, and the signal was detected by liquid nitrogen cooling germanium detectors after passing through a monochromator spectrometer, and the data was recorded by a characteristic X–Y recorder after a phase-locked amplifier. When the sample was tested in the near-infrared range, 532 nm Nd YAG green laser was used as the excitation light source, and chopped into 25 Hz pulses of light. The light emitted by the samples was focused by two lenses, passed through the slit of a grating monochromator, and detected by a liquid nitrogen cooled germanium detector. The data was recorded by characteristic X–Y recorder after a phase-locked amplifier finally. *I–V* characteristic of the device was tested on Keithley 2400 current–voltage source.

Metal aluminum electrode was evaporated in a vacuum deposition machine of DM-300B type, which was produced in Beijing scientific instrument factory. We usually evaporate aluminum film when the vacuum reaches 2×10^{-3} Pa, and its thickness was also monitored by quartz vibrator film thickness gauge.

3. Results and discussion

3.1. Synthesis and structure determination

Quinoline is a high boiling point solvent which can be used as both the solvent for solvothermal synthesis and the culture solution for single crystal growth. Here, the H_2Pc single crystal was synthesized with phthalonitrile as the original material.

The single crystal with size of 0.08 mm × 0.02 mm × 0.01 mm was chosen for test by four-circle X-ray single crystal diffractometer. H_2Pc single crystal belongs to monoclinic system with formula of $N_8C_{32}H_{16}$, space group of $P2(1)/n$, and crystal cell parameters as follows: $a = 14.768(3)$ Å, $b = 4.7209(9)$ Å, $c = 17.331(3)$ Å, $\alpha = 90°$, $\beta = 104.240(3)°$, $\gamma = 90°$, $V = 1171.2(4)$ Å^3, $R1 = 0.0468$, $wR2 = 0.1209$.

The structure of H_2Pc is shown in Fig. 1. The central 16-member ring consists of eight N atoms and eight C atoms, and the C–N bonds range from 1.320(2) Å to 1.370(2) Å, which are similar to those observed in other H_2Pc structures. In H_2Pc ring, the distances between two relative N1 atoms is 3.928(3) Å and the distances between two N3 atoms is 3.926(3) Å. The packing diagram of H_2Pc is shown in Fig. 2, the H_2Pc rings are stacked in a herringbone fashion, similar to that of the unsubstituted phthalocyanine. It is found that the intermolecular π–π stacking is present between two H_2Pc molecules with central-to-central distances of 4.721(2) Å

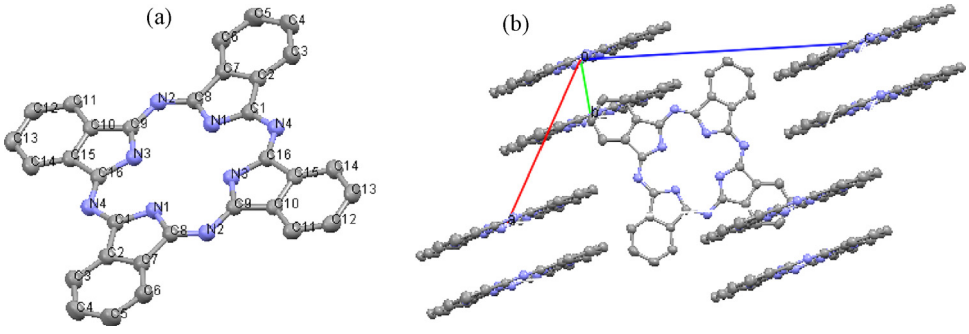

Fig. 1. Structure of H_2Pc single crystal (a) and crystal-packing diagram of H_2Pc (b).

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