FLUORESCENT PROPERTIES OF NATURAL INDIGO

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EXTENDED ABSTRACT

Key Words: Indigo; Fluorescence analysis; Fluorescence quenching; Pyrolysis

1. INTRODUCTION

Fluorescence analysis can reflect various properties of molecules and is a common method for substances analysis with the advantages of high sensitivity and ease of use.Indigo is a natural dye extracted from the plants *Indigofera tinctoria* and *Isatis* tentoria, which have been used to color textiles in India, China, and Egypt for 4000 years. Indigo exists at ambient temperature and pressure as dark blue–violet needles or leaves with a reddish bronze metallic appearance [1]. Two adjacent intramolecular hydrogen bonds are formed between the adjacent carbonyl group and the imino group in the indigo molecule, the hydrogen bond and the carbon-carbon double bond on the ring form a five-membered ring, which makes each atom in the indigo is in the same plane with the indoles ring. Therefore, indigo molecule is a rigid planar structure with strong conjugate effect, which can produce strong fluorescence.

In this study, the fluorescence characteristics of natural indigo were analyzed by measuring the excitation spectra and emission spectra of indigo standard solution of different concentrations with steady state/transient fluorescence spectrometer. In addition, the pyrolysis products of indigo were obtained at 350, 400, 450, 500 and 550℃ by using a synchronous thermal analyzer. The pyrolysis mechanism of indigo was discussed after measuring and comparing the fluorescence spectra of indigo and its pyrolysis products. The results can provide reference for the research of qualitative identification, quantitative analysis and thermal performance of indigo.

2. EXPERIMENTAL

2.1 Materials and Instrumentation

Indigo reference standard (Chengdu Plant Standard Chemical Co., Ltd.); Plant indigo dyes (Shanghai Huiran Biotechnology Co., Ltd.); N,N-dimethylformamide(DMF, Sinopharm Chemical Reagent Co., Ltd); QM/TM Steady State/Transient Fluorescence Spectrometer (PTI, USA); AL-104 Electronic Balance (Mettler Toledo, Switzerland); KQ-500DE CNC Ultrasonic Cleaner (Kunshan Ultrasonic Instrument Co., Ltd.); STA8000 (PerkinElmer, America)

2.2 Fluorescence spectroscopy

The fluorescence spectra of indigo solution in DMF were determined by fluorescence spectrometer. The excitation and emission slit width is 5 nm, and the excitation and emission wavelengths are measured in the range of 260-460 nm and 400 nm-680 nm.

3. RESULTS AND DISCUSSION

3.1 Fluorescence characteristics of indigo solution

A 50 g/ ml indigo solution was prepared in DMF, and the fluorescence spectrum was measured by the method of 2.2. The aromatic ring, carbon-carbon double bond, the carbonyl group in the indigo molecule are chromophores, and the imino group is a auxochrome. When energy is absorbed, the aromatic ring, carbon-carbon double bond produces $\pi\rightarrow\pi^*$ transition, the carbonyl group produces $n\rightarrow\pi^*$ transition, and the auxochrome is connected to the chromophore, so that the absorption wavelength shifts toward the long-wave direction. Therefore, indigo has three characteristic absorption peaks at 281 nm, 323 nm, and 397 nm in the ultraviolet region. However, the electrons in the π^* orbit are unstable and will quickly return to the ground state and emit fluoresce, with a fluorescence peak of 485 nm (Figure 2a).

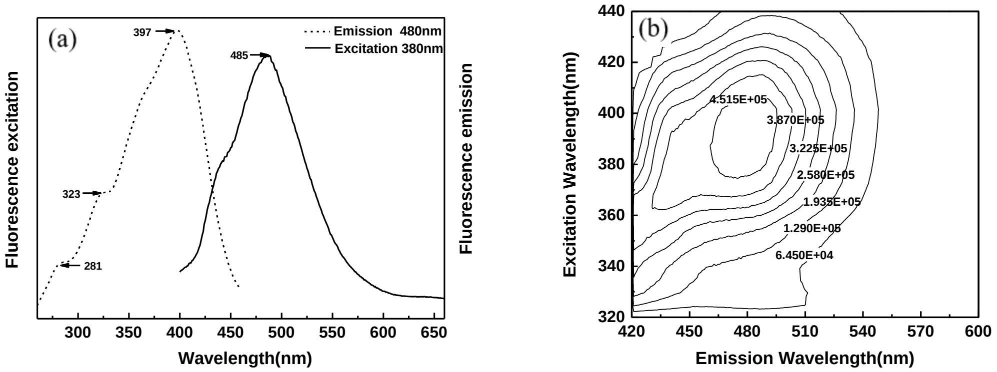

Figure 2. (a) Fluorescence spectrum of indigo. (b) Three-dimensional fluorescence spectrum of indigo

3.2 Fluorescence spectra of indigo solutions with different concentrations

The indigo solution was respectively prepared at a concentration of 10~100 μg/ml using DMF as a solvent, the fluorescence spectrum was measured by the method of 2.2. The intensity of the fluorescence peak of indigo gradually increases with the concentration of the solution, and the fluorescence peak changes from 440 nm to 488 nm (Figure. 3). When the concentration increases to 80 μg/ml, the fluorescence peak intensity begins to decrease. Due to its rigid molecular structure, indigo has a strong π-π interaction in the aggregate state, which causes the decay of the excited state to be dissipated in a non-radiative relaxation mode, thereby producing fluorescence quenching. When the concentration increased to 100 μg/ml, the fluorescence intensity at the wavelength of 660 nm began to increase, because in the aggregated state, the steric hindrance of the indigo molecule increases to suppress intramolecular rotation, which promotes radiation transition and leads to fluorescence enhancement. Therefore, indigo may have two different luminescence phenomena, aggregation-caused quenching and aggregation-induced emission, in the aggregate state.

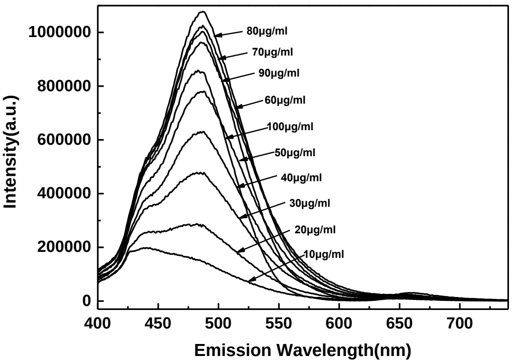

Figure 3. Fluorescence emission spectra of indigo solutions with different concentrations.

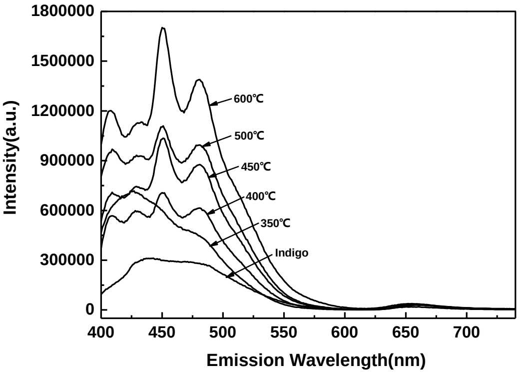

Figure 4. Fluorescence spectra of indigo solutions with different pyrolysis temperature

3.3 Fluorescence spectra of indigo solutions with different pyrolysis temperature

Indigo sublimes at about 300°C and decomposes at 390°C[2]. Indigo and its pyrolysis products were obtained at 350, 400, 450, 500 and 550°C, respectively, by using a synchronous thermal analyzer. The products were dissolved in DMF to obtain five solutions with 50 ug/ml concentration, and their fluorescence spectra were measured by 2.2 method. When the cracking temperature is below 400 °C, the position of the fluorescence peak of the indigo solution shifts slightly; when the cracking temperature reaches 400 °C, the indigo molecules begin to decompose, at which time the carbon-carbon double bond is broken, the nitrogen heterocycle is opened, and the fluorescent emission group are destroyed, causing four fluorescence emission peaks to appear in the solution (Figure 4).

4. CONCLUTIONS

The indigo molecular structure is a rigid plane and contains a conjugated structure, which can produce strong fluorescence. When energy is absorbed, the aromatic ring, carbon-carbon double bond produces $\pi \rightarrow \pi^*$ transition, the carbonyl group produces $n \rightarrow \pi^*$ transition, so that the fluorescence peak of indigo was 485nm. As the concentration of the solution increases, indigo may have two different luminescence phenomena, aggregation-caused quenching and aggregation-induced emission, in the aggregate state. At about 300 ° C, the indigo can be purified by sublimation; above 390 ° C, the fluorescent base group of indigo is destroyed and the fluorescence spectrum are beginning to change.

5. REFERENCES

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