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# The effect of high pressure on the luminescent properties of coumarin 153

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## Abstract

A dual-fluorescence emitting behaviour of coumarin 153 powder has been detected at high pressure while at ambient pressure the dye exhibits only single-band emission. Because of the strong electron-withdrawal group at site 7, these two fluorescent peaks can be ascribed to local excited state emission and charge transfer state emission, respectively.

## 1. Introduction

In recent years, applying high pressure to study the photophysical and photochemical properties of luminescent materials has been one of the most active research areas [1–4]. The purpose of high-pressure study is to obtain information about these properties by adding an extra degree of freedom in the field parameters other than temperature, electric field, and doping with impurities [5]. Furthermore, recent technical developments in high-pressure experiments have made it possible to perform various types of measurements such as Raman scattering, *in situ* x-ray, and time-resolved spectra, although the accuracy of the measurements is somewhat limited compared with that at atmospheric pressure [6]. Therefore, high pressure has proved to be a powerful tool for investigating and characterizing a wide variety of molecular and electronic phenomena [7].

Derivatives of 7-aminocoumarin are an important class of laser dyes in the blue–green region [8, 9]. The laser properties of these compounds depend on several factors, such as the molecular structure of the dye, temperature, and the nature of the solvent [10, 11]. The title compound, 2, 3, 6, 7-tetrahydro-9-(trifluoromethyl)-1H, 5H, 11H-[1] benzopyrano [6, 7, 8-*ij*]quinolizin-11-one (coumarin 153 (C153); see figure 1), is different from many other derivatives because it is a rigid coumarin and has a strong electron-withdrawal group. In this paper, we present the results of high-pressure luminescence measurements on C153 powder carried out with a view to understanding its photophysical properties more deeply.

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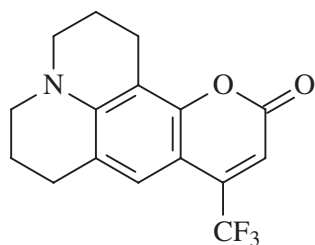


Figure 1. The structure of C153.

## 2. Experimental details

C153 was purchased from Aldrich and used without further purification.

All of the photophysical experiments were performed in a Merrill–Bassett diamond anvil cell (DAC). The stainless steel gasket had a hole 0.31 mm in diameter and 90  $\mu\text{m}$  in thickness. The sample and a tiny ruby chip were placed in the hole, and light mineral oil (Aldrich 33077-9) was used as the pressure medium. The pressure was calibrated with the ruby fluorescence shift [12].

Crystals were irradiated by means of the 441.6 nm line of a He–Cd laser (Model 3056, Omnicrome Inc.) in conjunction an interference filter and colour filters to cut off extraneous radiation from the emission path and to control the intensity of the excitation light. For the absorption measurement a Xe lamp was used as the light source and the light was dispersed with a 0.3 m monochromator. Two optical fibres were connected to the DAC and their other ends were connected to the monochromator and a photomultiplier tube (PMT), respectively. A NCL (ARC Inc.) electronics interface and computer were used to record the spectra and control the system.

## 3. Results

The absorption spectra of C153 have been measured in the range of pressure from 1 atm to 6.2 GPa (shown in figure 2(A)). With increase of pressure the absorption shifted to lower energy and the main maximum decreased, but the shapes of the absorption spectra at different pressures did not vary significantly.

Typical emission spectra of C153 ( $\lambda_{ex} = 441.6 \text{ nm}$ ) at different pressure are presented in figure 2(B). Emission spectrum in ambient pressure exhibited a broad band with maximum at 514.0 nm. With pressure increasing, the intensity of the emission dropped considerably and the peak position shifted to the red side. Up to 1.7 GPa, the emission band divided into two peaks with maxima at 534.0 and 474.0 nm. At higher pressure, the intensity of the emission peak at longer wavelength dropped sharply and the peak position moved clearly to the red side. However, the intensity of the emission peak at shorter wavelength dropped slowly and the peak position did not alter, as shown in figure 2(B). The emission spectrum detected was the same as the original at 1 atm when pressure was released after about 7.0 GPa.

## 4. Discussion

As mentioned above, the emission spectra were divided into two peaks with pressure increasing. The behaviour of the luminescence of C153 versus pressure can be elucidated as follows:

It has been reported that derivatives of 7-aminocoumarin could be described as two resonance forms (figure 3) [13]. The resonance structure ‘a’ is predominantly in the  $S_0$  ground state whereas the statistical weight of the resonance form ‘b’ increases with excitation. Therefore,

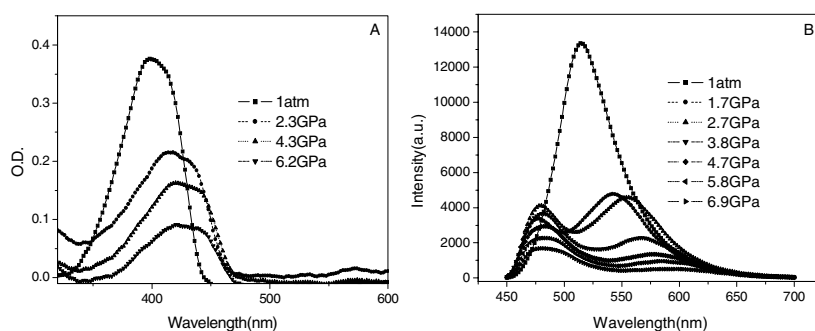


Figure 2. Absorption (A) and emission (B) spectra of C153 at different pressures.

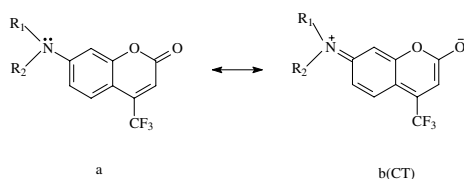


Figure 3. Resonance forms of the 7-aminocoumarin derivatives.

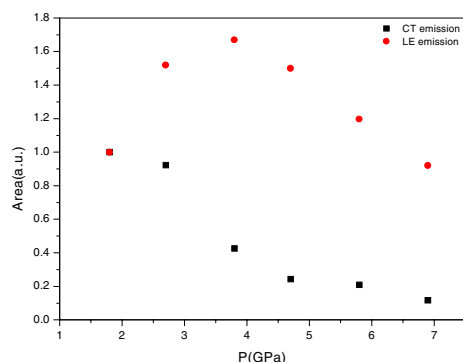
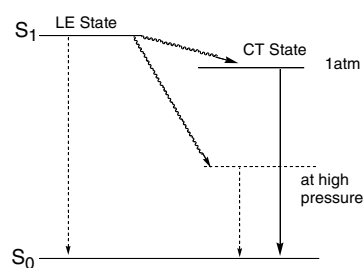


Figure 4. Band area (normalized) of the CT state and the LE state versus pressure for C153 powder.

the  $S_1$  singlet excited state of these dyes could be identified as a state with local excited (LE) character and a state with charge transfer (CT) character. Because  $-\text{CF}_3$  is a strong electron-withdrawal group, the  $S_1$  singlet excited state of C153 could be identified mainly as a CT state.

According to this mechanism, At 1 atm, the broad band is ascribed to the CT state emission; at higher pressure, the short-wavelength emission is described as LE state emission while the longer-wavelength emission is described as that of a CT state which is affected strongly by the pressure. By means of the program Peakfit 4.0 the emission spectra can be decomposed into LE state and CT state emission. The pressure dependence of the emission area of the two excited states (the CT state and the LE state) is presented in figure 4.

From 1.7 to 4.0 GPa, the area of the LE band increased while the area of the CT state emission dropped strongly. In this range, with pressure increasing, the CT state was stabilized due to increased interactions between the molecules. So the emission from the CT state shifted to the lower-energy side. With the CT state stabilized, the energy gap between the LE state and the CT state became greater, the internal conversion from the LE state to the CT state was restrained with the result that the emission from the LE state was observed, while the emission from the CT state shifted in the lower-energy direction. This process can be expressed by an energy level diagram: figure 5.



**Figure 5.** The energy level diagram of C153 at different pressures.

With pressure increasing further ( $>4.0$  GPa), the sample became partially amorphous. Therefore, the fluorescence was quenched because defects in the crystal lattice were increased. So, the area of each emission peak was decreased (shown in figure 4).

In general, photoreaction may occur at a different pressure when a laser irradiates the sample. However, this is not taken into consideration, because the emission spectra detected were similar to each other after the sample was irradiated at different times by a laser at particular pressure. On the other hand, if the photoreaction did indeed occur, a new emission peak ought to locate at a higher-energy position because of the conjugated structure being destroyed. Furthermore, the change of the spectra is reversible, the original form being recovered when the pressure is released. So, the photoreaction is negligible in this work.

In conclusion, photophysical properties of C153 were studied at high pressure. Because the energy gap between the LE state and the CT state became greater at high pressure, the emission of C153 was divided into two bands, LE and CT. The property of two-state fluorescent emission of C153 at a particular pressure is likely to have potential technological and commercial applications for both monochrome and bichrome dyes.

### Acknowledgments

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