

Fluorescence Based on Excited-State Intramolecular Proton Transfer of 1-(2-Benzothiazolyl)-2-hydroxytryptanthrin

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Abstract

1-(2-Benzothiazolyl)-2-hydroxytryptanthrin (**T2OH1BT**) with benzothiazole as a proton acceptor at the 1-position of 2-hydroxytryptanthrin (**T2OH**) was synthesized and its photophysical properties were investigated. **T2OH1BT** was found to emit fluorescence at 630–670 nm in polar solvents due to proton dissociation of the hydroxy group, and 575–610 nm in low polar solvents due to excited-state intramolecular proton transfer. **T2OH1BT** emitted fluorescence in the solid state, thereby differentiating it from common tryptanthrin derivatives which cannot emit fluorescence in the solid state due to their planar structure.

Key-words: Fluorescence, Excited-state intramolecular proton transfer, Tryptanthrin

1. Introduction

Organic fluorescent dyes, which are employed in organic light-emitting diodes^{1–3}, dye-sensitized solar cells⁴, dye lasers⁵, fluorescent probes⁶, and conventional dye materials, have attracted increased research attention recently. We explored the photophysical properties of tryptanthrin derivatives as novel fluorescent dyes. Tryptanthrin is a weakly basic alkaloid present in several plant species⁷. Tryptanthrin shows antimicrobial activity against diverse pathogenic bacteria and fungi⁸. When an amino group or other electron-donating substituent is introduced at the 2-position of tryptanthrin, intramolecular charge transfer (ICT) occurs between the electron-withdrawing carbonyl group at its 6-position and the amino group, resulting in strong fluorescence and positive fluorescence solvatochromism^{9,10}. The fluorescence wavelengths of fluorescent solvatochromic dyes vary according to the surrounding environment (polarity difference); thus, various life phenomena can be observed via the fluorescent color change. The near-infrared (NIR) region (650–900 nm) is referred to as the “optical window” of cells and tissues because of the lack of efficient endogenous absorbers in this spectral range and the subsequent high penetration depth (in the order of a few millimeters) in most tissues¹¹. Organic fluorescent dyes that emit NIR fluorescence are preferable for application in biological systems because they can reduce autofluorescence and photodamage to living cells.

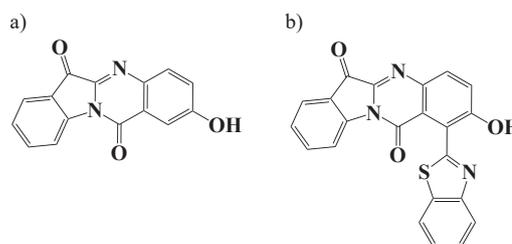


Fig. 1 Structures of (a) **T2OH** and (b) **T2OH1BT**.

Previously, we reported the photophysical properties of an ICT dye, 2-hydroxytryptanthrin (**T2OH**, Fig. 1a)¹². The absorption maxima ($\lambda_{a, \max}$) of **T2OH** in a dimethyl sulfoxide (DMSO)/H₂O (1/9, v/v) solution at a pH range from 1.3 to 7.2 and from 8.5 to 10.6 were at *ca.* 410 nm and *ca.* 495 nm, respectively. The fluorescence maxima ($\lambda_{f, \max}$) were at *ca.* 660 nm regardless of the pH. **T2OH** was soluble in polar solvents and showed two fluorescence peaks. One was derived from undissociated **T2OH** at *ca.* 530 nm and the second, which was not observed in nonpolar solvents, was derived from the proton-dissociated tryptanthrin-2-olate anion (**T2O⁻**) at *ca.* 660 nm. Therefore, we synthesized 1-(2-benzothiazolyl)-2-hydroxytryptanthrin (**T2OH1BT**, Fig. 1b) and investigated its photophysical properties, assuming that the introduction of a proton-accepting substituent into the molecule would allow it to exhibit only long-wavelength fluorescence.

2. Experimental

Proton nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL JNM-ECA 500 spectrometer with tetramethylsilane (TMS) as an internal standard. Ultraviolet-

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