

## Aggregation-induced Emission and Solid-State Fluorescence of 2-(4-(*N,N*-diphenylamino)phenyl)tryptanthrin

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### Abstract

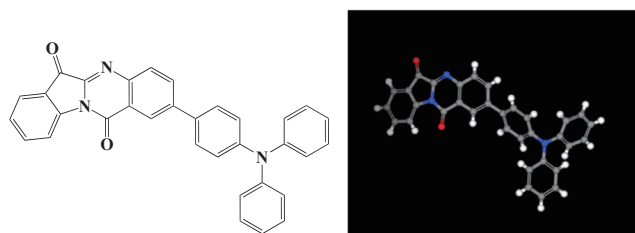
2-(4-(*N,N*-diphenylamino)phenyl)tryptanthrin (**T2PhNPh<sub>2</sub>**) was synthesized and its photophysical properties were examined. Among the seven examined solvents of various polarities, **T2PhNPh<sub>2</sub>**, which is non-planar only showed weak red fluorescence in non-polar toluene and 1,4-dioxane. This was assumed to be due to thermal deactivation as a result of the rotation of the phenyl groups' stimulation of internal conversion in calculation using the density functional theory. Although **T2PhNPh<sub>2</sub>** was non-fluorescent in tetrahydrofuran (THF), aggregation-induced emission was shown to cause fluorescence in water/THF solutions with more than 65 vol% water content. Additionally, fluorescence was observed at *ca.* 650 nm in the solid state.

**Key-words:** Fluorescence, Aggregation-induced emission, Mechanochromic luminescence, Tryptanthrin

### 1. Introduction

Fluorescent analysis reagents, including fluorescent chemosensors and probes that are based on organic fluorescent dyes, are simple and highly versatile. In particular, these molecular tools have proven indispensable for studying biological phenomena in life sciences<sup>1,2)</sup>. However, under some conditions, such as those that result in aggregation-caused quenching (ACQ), the advantageous properties of these fluorescence analysis reagents can be somewhat limited<sup>3)</sup>. Many organic fluorescent dyes have a planar structure, and their fluorescence is dependent on how the HOMO–LUMO gap changes when the region of the  $\pi$ -conjugated plane increases or decreases. For instance, the typical organic fluorescent dye pyrene efficiently emits fluorescence in a dilute solution. As the concentration increases, however, the pyrene molecules are arranged in a sandwich-type structure that shows excimer fluorescence at a longer wavelength than that corresponding to the monomer, and the intermolecular distance increases from 3 to 4 Å<sup>4)</sup>. Furthermore, in high concentration solutions, the  $\pi$ - $\pi$  stacking interaction becomes stronger, and the molecules form a layered structure that leads to fluorescence quenching. Thus, planar organic fluorescent dyes can be used only in dilute solutions, preventing their use in high concentration conditions or the solid state. To address the issues in detection sensitivity and quantification associated

with ACQ, the development of novel methodologies for the construction of fluorescent analysis reagents is highly desirable. In 2001, B. Z. Tang and coworkers reported a new aggregation-induced emission (AIE) type of organic fluorescent dye, in which the fluorescence intensity rises upon aggregation<sup>5)</sup>. Meanwhile, the competition between the radiative process of light emission and the non-radiative process of thermal release leads to consumption of excitation energy. Tetraphenylethylene, a typical AIE dye undergoes a non-radiative process with thermal release favored by the phenyl group's rotational movement in a dilute solution and exhibits no fluorescence. Nevertheless, in high concentration solutions, the rotational movement of the phenyl group is suppressed, favoring a light-emitting radiative process that leads to the emission of fluorescence. The introduction of an electron-donating group at the 2-position of tryptanthrin<sup>6,7)</sup>, an antimicrobial substance extracted from plants like indigo, is known to result in outstanding fluorescent properties<sup>8-20)</sup>. However, in highly concentrated solutions,  $\pi$ - $\pi$  stacking interactions in fluorescent tryptanthrin compounds with planar structures cause fluorescence quenching. Thus, for



**Fig. 1** Structural formula and X-ray crystal structure of **T2PhNPh<sub>2</sub>**<sup>21)</sup>.

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