Original Technical Paper
J. Jpn. Soc. Colour Mater., **98**〔6〕, 168–172 (2025)

Fluorescence Resonance Energy Transfer and Aggregation-induced Emission of 2-(4-(*N*,*N*-diphenylamino)phenyl)-9-(1-pyrenyl)tryptanthrin

Jun Kawakami*,†, Junpei Kuji* and Takuma Kureha*

* *Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan*
†*Corresponding Author, E-mail: jun@hirosaki-u.ac.jp*

(Received March 7, 2025; Accepted April 21, 2025; published June 20, 2025)

Abstract

2-(4-(*N*,*N*-diphenylamino)phenyl)-9-(1-pyrenyl)tryptanthrin (**T2PhNPh$_2$9Py**), which has pyrene introduced at the 9-position of 2-(4-(*N*,*N*-diphenylamino)phenyl)tryptanthrin (**T2PhNPh$_2$**), where aggregation-induced emission (AIE) is observed, was synthesized and its photophysical properties were investigated. The aggregation properties of **T2PhNPh$_2$9Py** were studied using a mixture of THF (good solvent) and water (poor solvent) to create an aggregate state by increasing the water content. When excited at 340 nm in the pyrene absorption band of the energy donor (**D**) in fluorescence resonance energy transfer (FRET), at 0% water content, weak **D**-derived pyrene fluorescence was observed near 450 nm, but with increasing water content, the pyrene fluorescence gradually disappeared and the energy acceptor (**A**)-derived **T2PhNPh$_2$** fluorescence increased near 650 nm. Therefore, **T2PhNPh$_2$9Py** was observed to have a combination of intra- and intermolecular FRET and AIE properties.

Key-words: *Fluorescence resonance energy transfer, Aggregation-induced emission, Tryptanthrin, Pyrene*

1. Introduction

Fluorescent analytical 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 the study of biological phenomena in the life sciences$^{1,2)}$. However, under certain conditions, such as those that lead to aggregation-caused quenching (ACQ)$^{3)}$, the advantageous properties of these fluorescence analysis reagents can be somewhat limited$^{4)}$. Many organic fluorescent dyes have a planar structure, and their fluorescence depends on how the HOMO–LUMO gap changes as the area of the π-conjugated plane increases or decreases. For example, the typical organic fluorescent dye pyrene emits fluorescence efficiently in a dilute solution. However, as the concentration increases, the pyrene molecules are arranged in a sandwich-like structure that exhibits excimer fluorescence at a longer wavelength than that of the monomer, and the intermolecular distance is 4 Å to 3 Å$^{5)}$. Furthermore, at high concentrations, the π–π stacking interaction becomes stronger, and the molecules form a layered structure, leading to fluorescence quenching. Thus, planar organic fluorescent dyes can only be used in dilute solutions, preventing their use at high concentrations or in the solid state. To address the detection sensitivity and quantification issues associated with ACQ, the development of novel methodologies for the construction of fluorescent analytical 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 increases upon aggregation$^{6)}$. The excitation energy is consumed by the competition between the radiative process of the emission of light and the non-radiative process of the emission of heat. Tetraphenylethylene, a typical AIE dye, undergoes a non-radiative thermal release process favored by the rotational motion of the phenyl group in a dilute solution and shows no fluorescence. However, in high concentration solutions, the rotational motion 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$^{7,8)}$, an antimicrobial substance extracted from plants such as indigo, is known to result in excellent fluorescence properties$^{9\text{-}21)}$. However, in highly concentrated solutions, π-π stacking interactions cause fluorescence quenching in fluorescent tryptanthrin compounds with planar structures. Therefore, in 2023, we synthesized 2-(4-(*N*,*N*-diphenylamino)phenyl)tryptanthrin (**T2PhNPh$_2$**, **Fig. 1**a), with a bulky electron-donating substituent 4-(*N*,*N*-diphenylamino)phenyl group at the 2-position of tryptanthrin and AIE expression was confirmed$^{22)}$. Here, we synthesized

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