Tryptanthrin (T, Fig. 1a) is a weak basic alkaloid formed in a number of plant species. This compound possesses antibacterial activity against a variety of pathogenic bacteria. However, the optical absorption and fluorescence properties of T and its derivatives have never been reported. Recently, we investigated the optical absorption and fluorescence properties of T and its derivatives. As results of measurements of their UV-vis absorption and fluorescence spectra, we found that 2-aminotryptanthrin (T2NH2, Fig. 1b) had excellent photophysical properties, such as wide-wavelength absorption and emission, and a high fluorescence quantum yield (Φf = 0.5 in acetonitrile). T2NH2 will become a good energy acceptor for FRET (fluorescence resonance energy transfer), compatible with an energy donor having a wide excitation wavelength range of over 300 nm.

Tryptanthrin was synthesized as a fluorescent chemosensor for Al3+. Excited at 325 nm, corresponding to absorption of the pyrene unit of T2NH2, emission at 600 nm from the 2-aminotryptanthrin unit has been observed, indicating that intramolecular fluorescence resonance energy transfer (FRET) occurs in T2NH2. However, when Al3+ is added to a solution of T2NH-P5P, the fluorescence of 2-aminotryptanthrin is quenched (FRET-off), whereas that of the pyrene group is revived. Such a FRET “on-off” behavior of T2NH-P5P is not observed for other metal cations (Ca2+, Ba2+, and Zn2+).

The titration of T2NH-P5P ([T2NH-P5P] = 1 μM, M = mol dm−3) against metal-ion solutions was performed in a spectrophotometric cell of 1-cm path length. The UV-vis spectra (between 200 and 600 nm) of the resulting solutions were recorded at room temperature with a JASCO V-670 spectrophotometer after the addition of each metal salt: Ca(ClO4)2, Ba(ClO4)2, Zn(ClO4)2, and Al(ClO4)3. The fluorescence spectra were measured between 350 and 700 nm with an excitation wavelength of 325 nm. Titrations were performed with metal ions (10 – 1000 μM) as a titrant and T2NH-P5P (1 μM) as a titrate. The metal-ion sources were identical to those used to

Fig. 1 Structural formulas of a) T, b) T2NH2, c) T2NH-P5P, d) T2NH-CH2COOEt, and e) 1EP.
perform UV-vis studies. The UV-vis absorption spectrum of T2NH-P5P is essentially identical to an equimolar mixture of ethyl (2-tryptanthrinylamino)acetate (T2NH-cH2COOEt, Fig. 1d) and ethyl pyrene-1-carboxylate (1EP, Fig. 1e).

In contrast, the fluorescence spectrum of T2NH-P5P showed differences from that of the equimolar mixture of T2NH-cH2COOEt and 1EP (Fig. 2). Although an equimolar mixture of T2NH-cH2COOEt and 1EP showed strong emission from the pyrene chromophore, excited at 325 nm corresponding to the absorption of pyrene unit (energy donor) of T2NH-P5P, emission at 600 nm from the 2-aminotryptanthrin unit (energy acceptor) was observed, indicating that intramolecular fluorescence resonance energy transfer (FRET) occurred in T2NH-P5P.

We examined the change in the fluorescence spectra after adding metal ions to a solution of T2NH-P5P. When Al³⁺ is added to a solution of T2NH-P5P, the fluorescence of 2-aminotryptanthrin is quenched (FRET-off), whereas that of the pyrene group is revived (Fig. 3). Such a FRET “on-off” behavior of T2NH-P5P is not observed for other metal cations (Ca²⁺, Ba²⁺, and Zn²⁺). The association constant (K) was determined from the fluorescence change at 395 nm using the program NMRIT.⁹ The value of log K of the T2NH-P5P-Al³⁺ complex was 4.8. The detection of Al³⁺ is of great interest because of the potential toxicity and the widespread presence of this ion.¹⁰ T2NH-P5P will become a good fluorescent chemosensor for Al³⁺.

We have reported on the preliminary results of our studies of aluminum ion recognition by T2NH-P5P. Further studies are now in progress.

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References

6. T2NH-P5P: ¹H NMR (500 MHz, CDCl₃) δ 3.50 - 4.02 (16H, m, –CH₂O(CH₂CH₂O)₃CH₂–), 4.03 (2H, d, –CH₂CO–, J = 5.2 Hz), 4.35 (2H, t, –COOCH₂–, J = 4.6 Hz), 4.66 (2H, t, –COOCH₂–, J = 4.8 Hz), 5.19 (1H, t, –NH–, J = 5.2 Hz), 6.80 - 8.70 (16H, m, tryptanthrin and pyrene rings); ESI-MS m/z (M+H) calcd. 770.2714 found 770.2614.
7. T2NH-cH2COOEt: ¹H NMR (500 MHz, CDCl₃): δ 1.34 (3H, t, –CH₃, J = 7.0 Hz), 4.07 (2H, d, –CH₂CO–, J = 5.0 Hz), 4.31 (2H, q, –OCH₂–, J = 7.0 Hz), 5.04 (1H, t, –NH–, J = 5.0 Hz), 7.00 - 8.80 (7H, m); ESI-MS m/z (M+H) calcd. 350.1141 found 350.1151.
8. 1EP: ¹H NMR (500 MHz, CDCl₃): δ 1.34 (3H, t, –CH₃, J = 7.0 Hz), 4.07 (2H, d, –CH₂CO–, J = 5.0 Hz), 4.31 (2H, q, –OCH₂–, J = 7.0 Hz), 5.04 (1H, t, –NH–, J = 5.0 Hz), 7.00 - 8.80 (7H, m); ESI-MS m/z (M+H) calcd. 275.1072 found 275.1041.