Supplementary Information

Electronic state of a fluoranthene-urea compound and the kinetics of its emissive tautomer state in the presence of acetate anions

*Mahiro Okada and Yoshinobu Nishimura**

Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1

Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

Experimental

Synthesis

3FU. 3-Aminofluoranthene (104 mg, 0.478 mmol) and phenylisocyanate (120 μL, 1.11 mmol) were stirred in dry tetrahydrofuran (THF; 5 mL) at 80 °C under N_2 for 21 h. The pure desired product was obtained by recrystallization of the residue from dimethyl sulfoxide to produce a light-yellow solid (70 mg, 45%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.02 (1H, t, J = 7.4 Hz), 7.34 (2H, dd, J = 7.4 Hz, J = 8.5 Hz), 7.36-7.41 (2H, m), 7.54 (2H, d, J = 8.5 Hz), 7.79 (1H, dd, J = 7.4 Hz, J = 8.4 Hz), 7.97 (1H, d, J = 7.4 Hz), 8.04 (1H, d, J = 6.9 Hz), 8.06 (1H, d, J = 7.8 Hz), 8.18 (1H, d, J = 6.9 Hz), 8.19 (1H, d, J = 8.4 Hz), 8.33 (1H, d, J = 7.8 Hz), 9.14 (1H, s), 9.16 (1H, s). Anal. Calcd for $C_{23}H_{16}N_2O$: C, 82.12; H, 4.79; N, 8.33; found: C, 82.01; H, 4.87; N, 8.34.

Apparatus

^{1}H NMR spectra were obtained on a Bruker AVANCE-400 (400 MHz) spectrometer using DMSO-d_6 as the solvents and tetramethylsilane as the internal standard. Absorption and fluorescence spectra were measured using a Shimadzu UV-1600 and a Hitachi F-7000 fluorescence spectrometer, respectively. Fluorescence decay measurements were performed using the time-correlated single-photon-counting method. Laser excitation measurements at 375 nm were conducted using an LDH-P-C-375 diode laser (PicoQuant) with a PDL 800-B power control unit (PicoQuant) at a repetition rate of 2.5 MHz. The temporal profiles of the fluorescence decays were detected via an R3809U microchannel plate photomultiplier (Hamamatsu) equipped with a TCSPC computer board module (SPC630, Becker and Hickl GmbH). The full width at half-maximum (fwhm) value of the instrument response function was 51 ps. The values of χ^2 and the Durbin−Watson parameters were used to determine the quality of the fit obtained by nonlinear regression. DMSO (spectroscopic grade, Wako Pure Chemical Industries, Japan) was used as solvent without further purification. The acetate ion was provided in the form of TBAAc, which contains the tetrabutylammonium cation (Sigma-Aldrich, Japan). DBU was purchased from TCI and used as received. Fluorescence spectra and fluorescence lifetime measurement were conducted at room temperature under Ar atmosphere. The concentration of 3FU was adjusted so that the absorption maximum of the excitation wavelength was about 0.1 for each sample.

Results

Absorption spectra in the absence of TBAAc

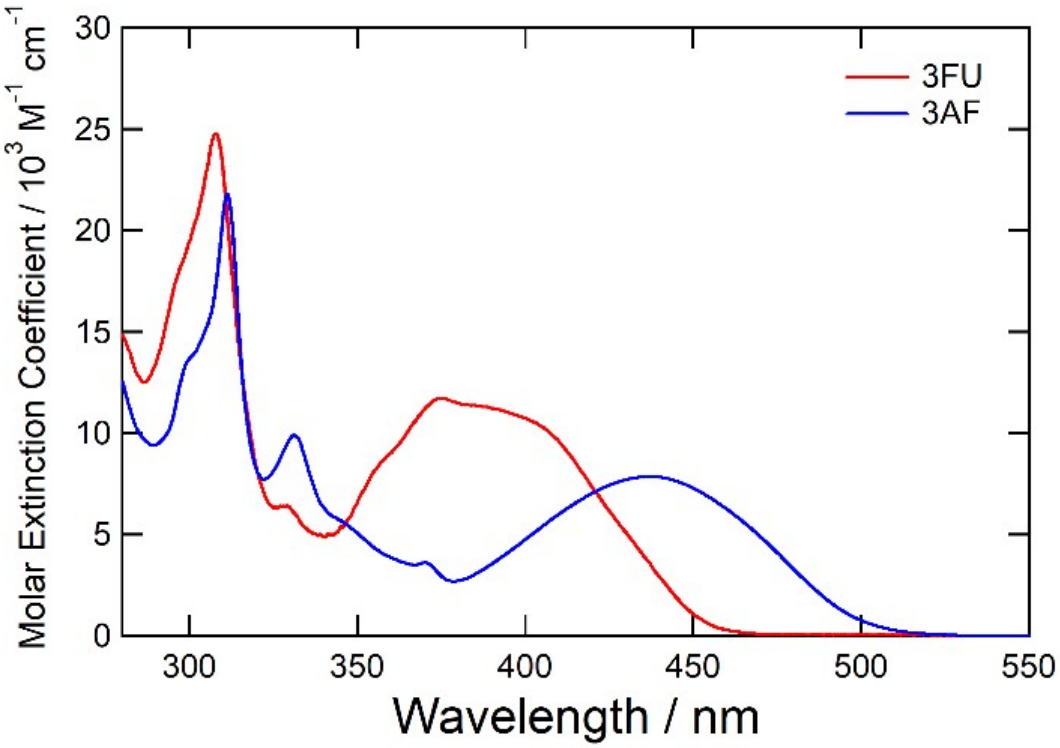

Fig. S1. Absorption spectra of 3FU and 3AF in DMSO.

Absorption spectra in the presence of TBAAc

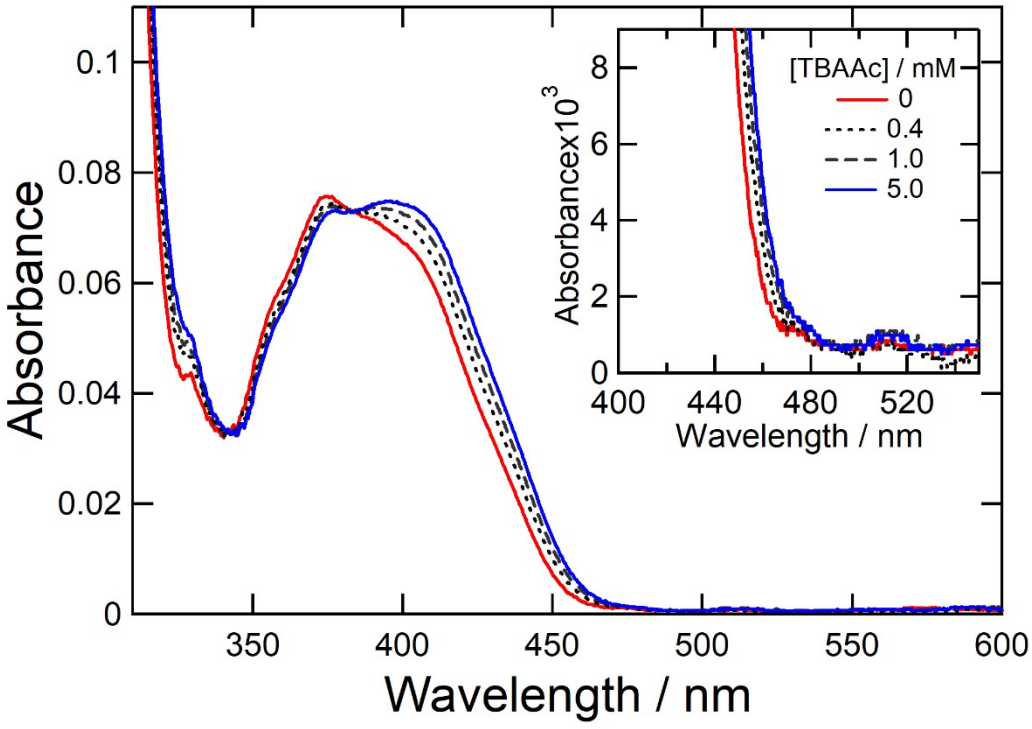

Fig. S2. Absorption spectra of 3FU upon the addition of TBAAc in DMSO.

Absorption spectra in the presence of DBU

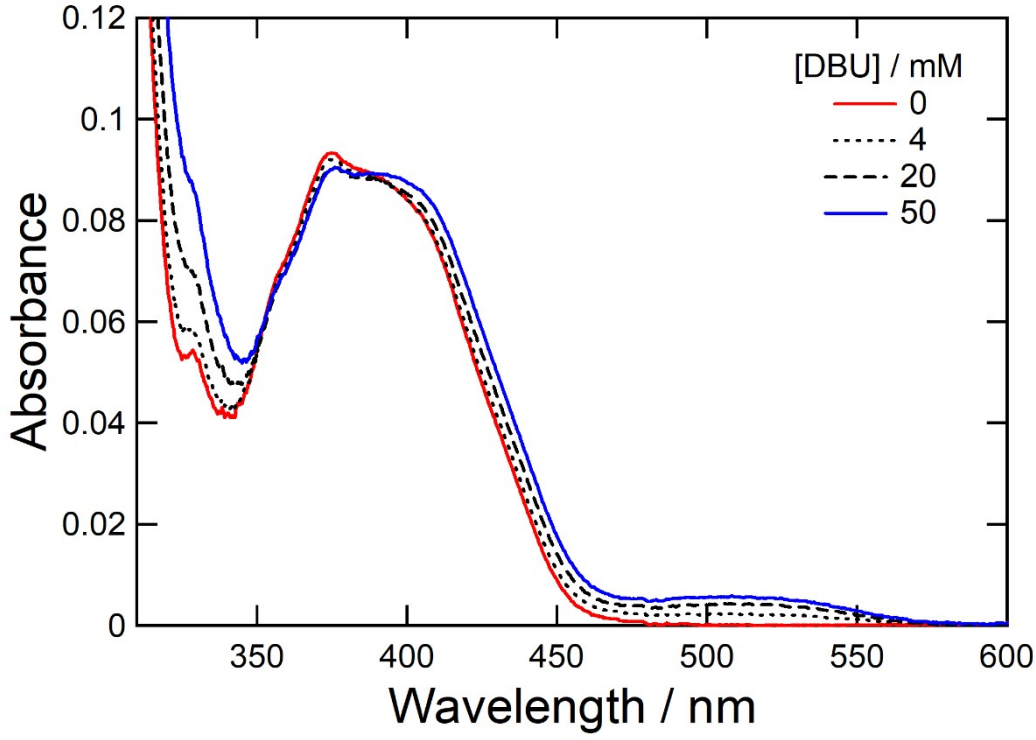

Fig. S3. Absorption spectra of 3FU upon the addition of DBU in DMSO.

^{1}H NMR spectra of 3FU in the absence and presence of TBAAc

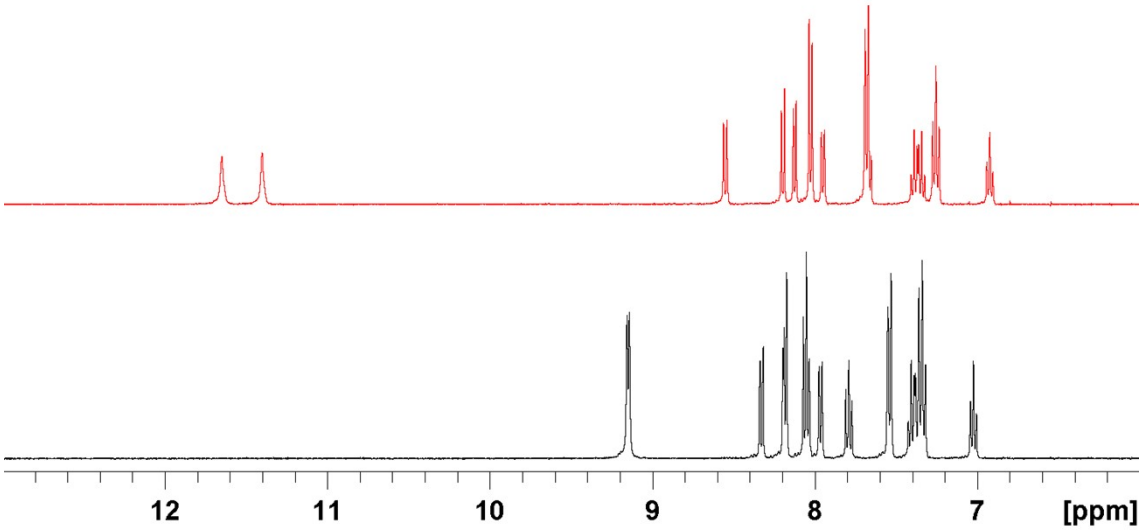

Fig. S4. ^{1}H NMR spectra of 3FU in the absence (bottom) and presence (top) of TBAAc in DMSO-d_6.

Fluorescence spectra of 3FU and 3AF

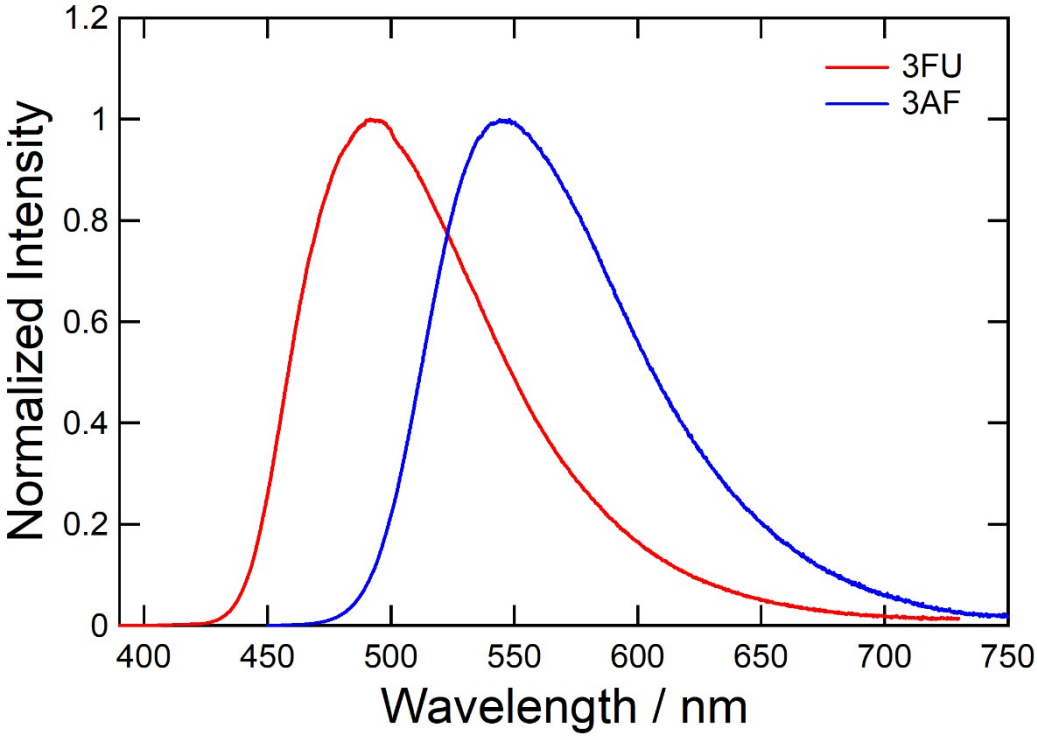

Fig. S5. Fluorescence spectra of 3FU and 3AF in DMSO.

Excitation spectra of 3FU in the presence of TBAAc

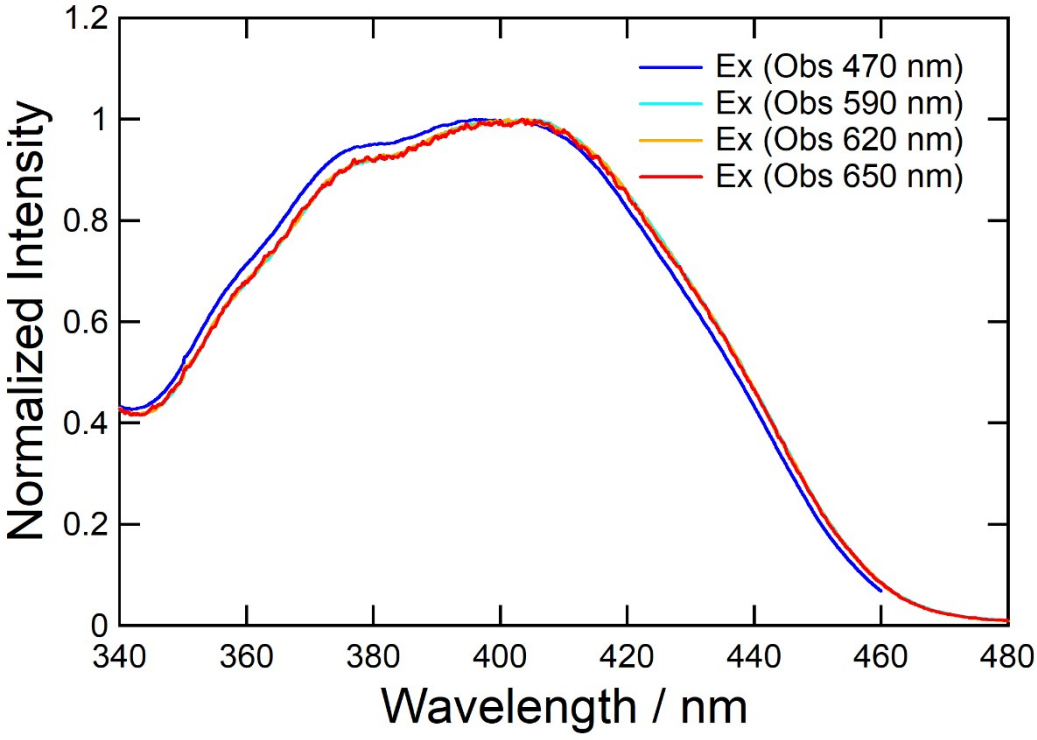

Fig. S6. Excitation spectra of 3FU in the presence of TBAAc in DMSO.

Fluorescence spectra of 3FU upon the addition of DBU excited at 360 nm

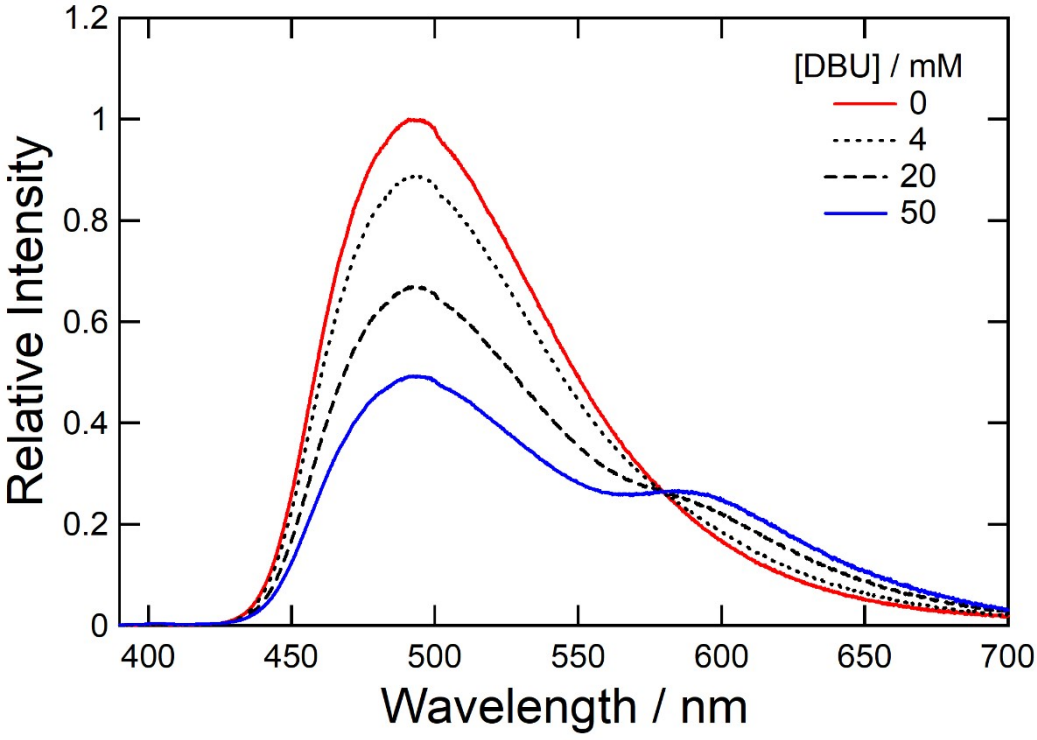

Fig. S7. Fluorescence spectra of 3FU upon the addition of DBU excited at 360 nm in DMSO.

Fluorescence spectra of 3FU upon the addition of DBU excited at 480 nm

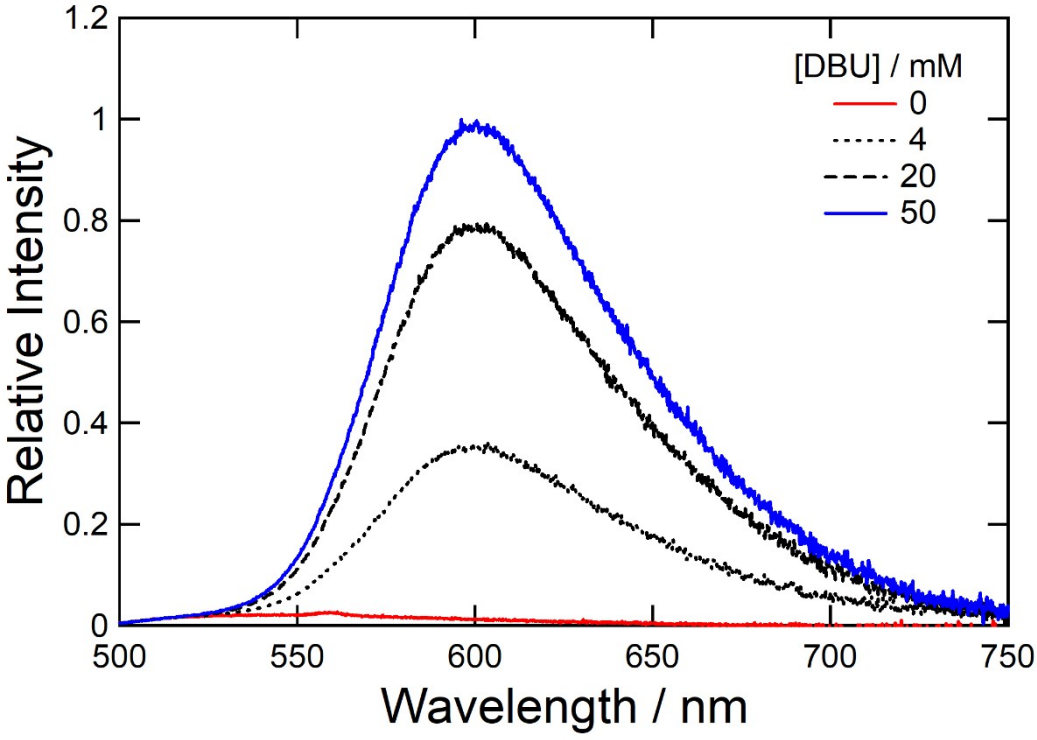

Fig. S8. Fluorescence spectra of 3FU upon the addition of DBU excited at 480 nm in DMSO.

Theoretical plot for association constant

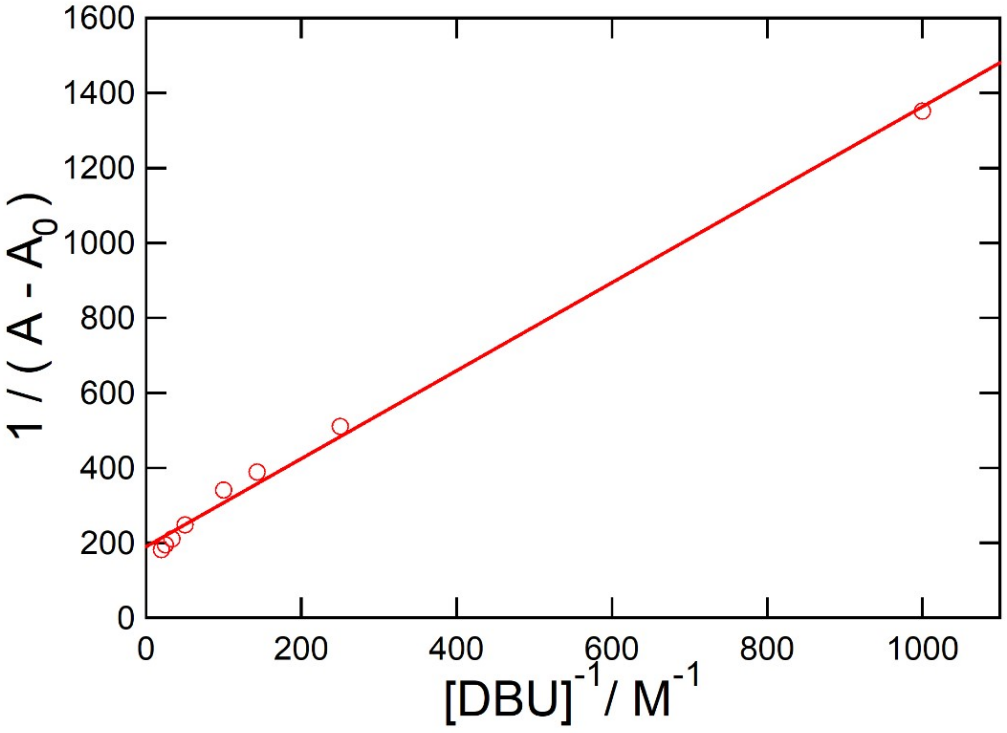

Fig. S9. Theoretical plot for association constant.

Time-resolved fluorescence spectra of 3FU

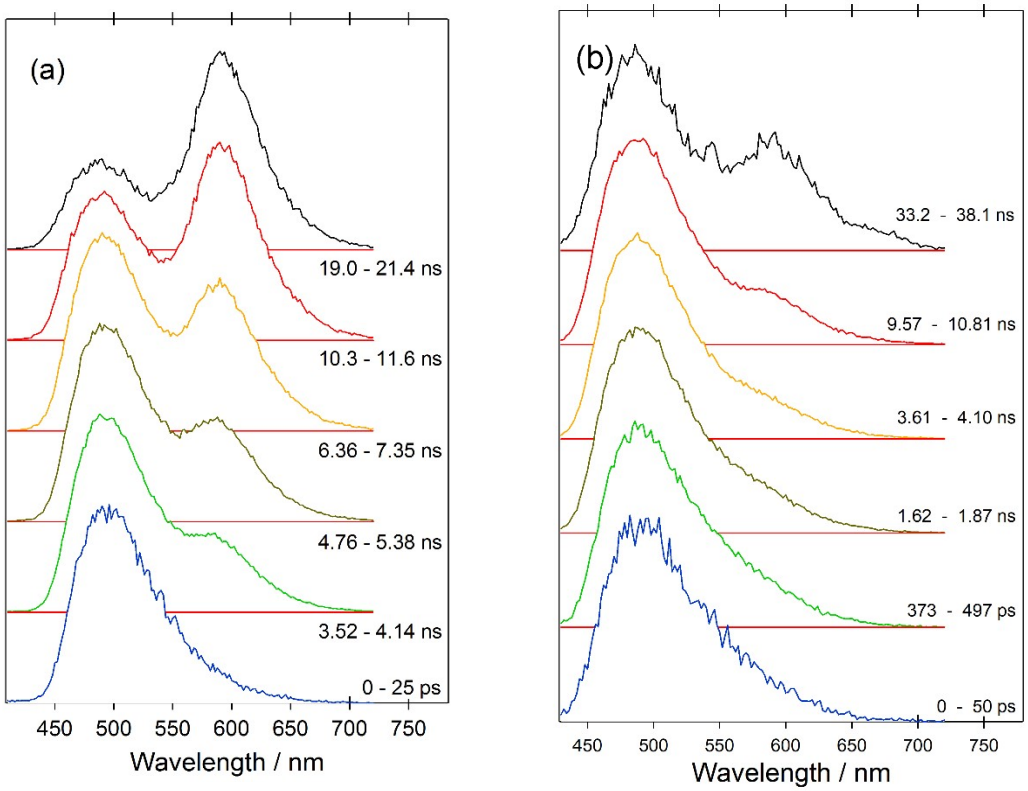

Fig. S10. Time-resolved fluorescence spectra of 3FU excited at 375 nm in (a) the presence of 13 mM TBAAc and in (b) the presence of 60 mM DBU in DMSO under Ar.

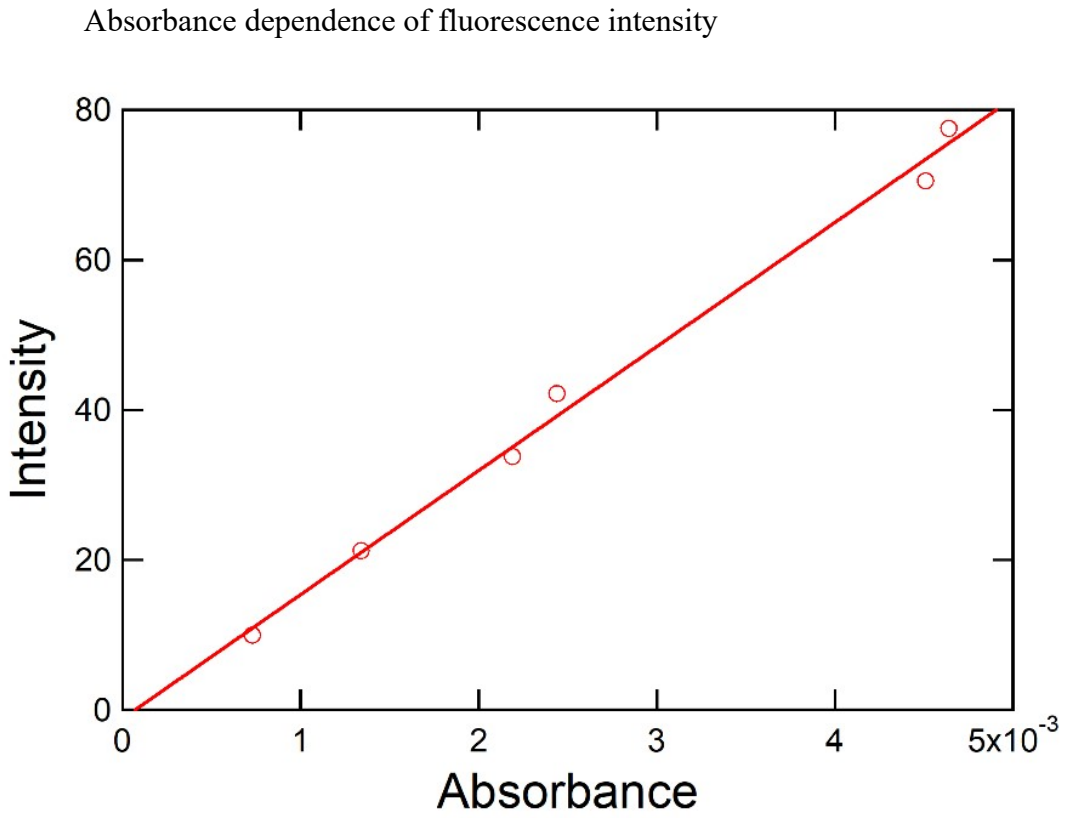

Fig. S11. Absorbance dependence of fluorescence intensity excited at 480 nm.

Fluorescence spectra of 3FU in the presence of DBU

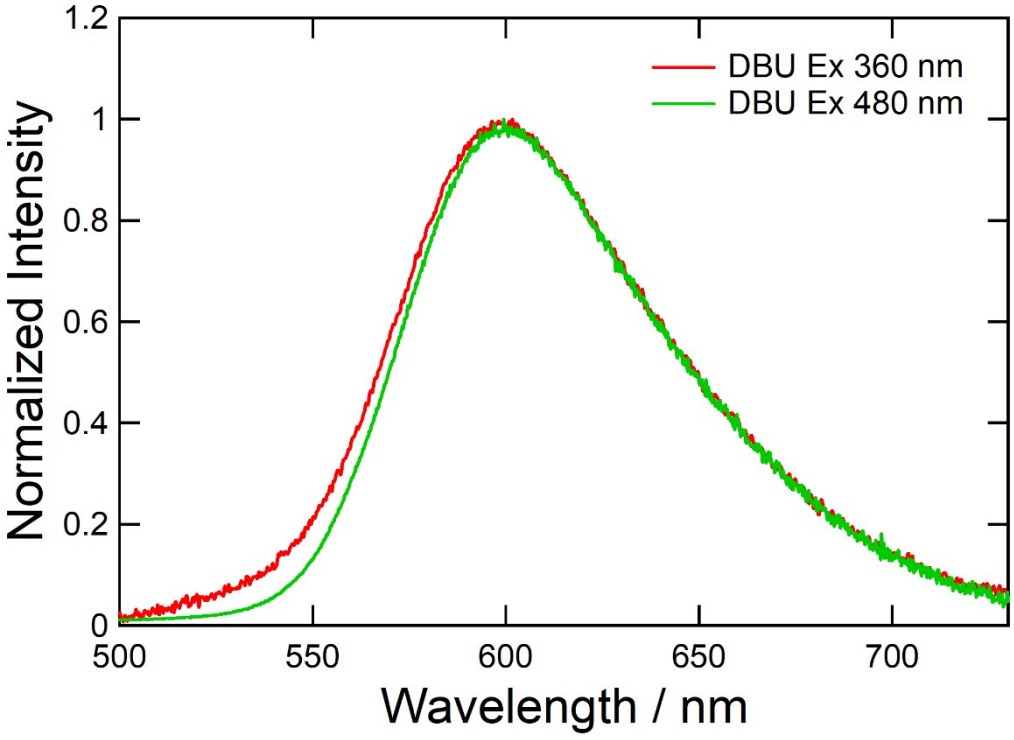

Fig. S12. Fluorescence spectra of 3FU in the presence of DBU excited at 360 and 480 nm.

Separation of fluorescence spectra of N* and T*

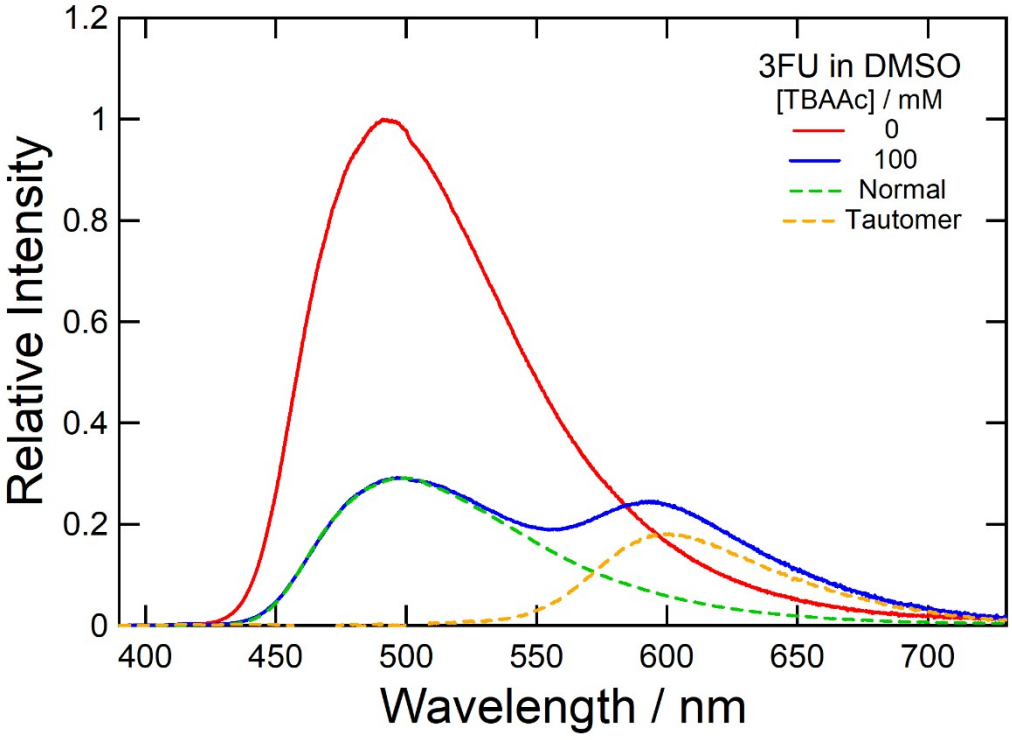

Fig. S13. Separation of fluorescence spectra of N* and T*.

Plot of the area of the fluorescence spectrum against the absorbance

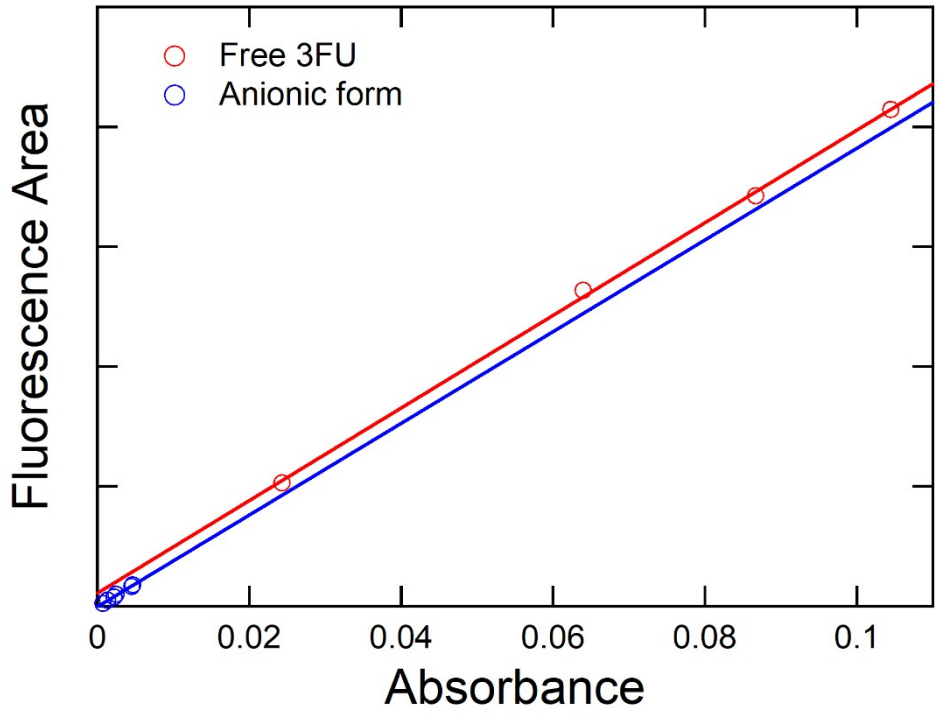

Fig. S14. Plot of the area of the fluorescence spectrum against the absorbance