

ELECTRONIC SUPPLEMENTARY INFORMATION

Multiple Prototropicism of Fisetin in Sodium Cholate and Related Bile Salt Media

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Figure S1

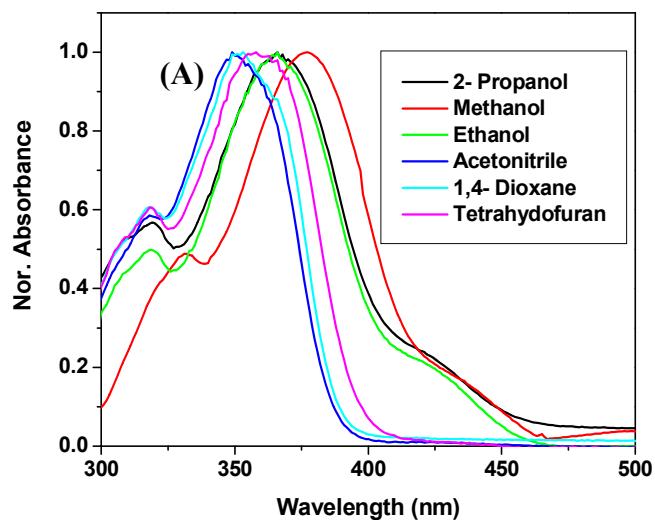


Figure S1. Absorption spectra of fisetin in different solvents. The neutral peak shifts to the blue end of absorption spectra with decreasing polarity and there is an appearance of a shoulder at ~ 418 nm in the alcoholic solvents.

Figure S2

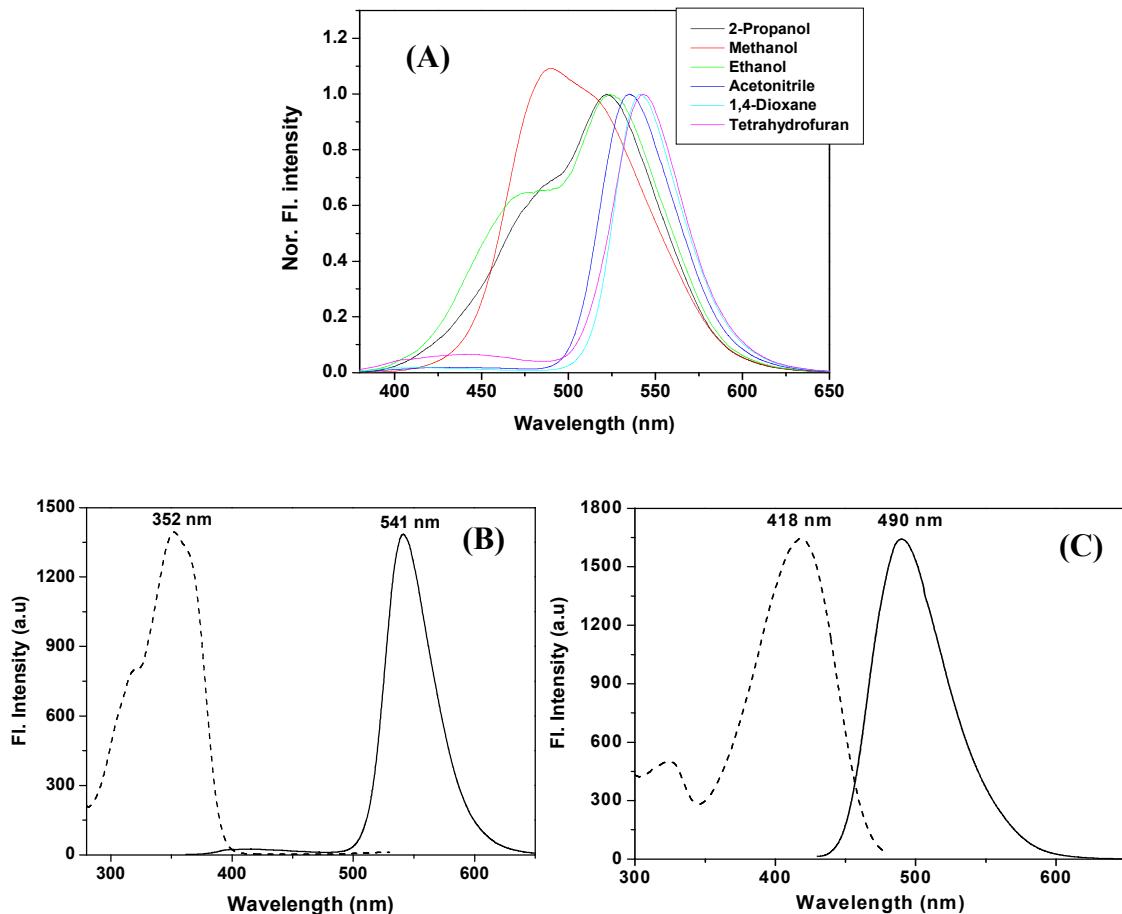


Figure S2. Fluorescence excitation and emission spectra of fisetin in (A) in different solvents, showing the shift in FT emission and presence of (FA)_{ES} (B) in HBA solvents (1,4-dioxane, acetonitrile, N,N-dimethylformamide, tetrahydrofuran), showing the FT emission at 540 nm (λ_{ex} 370 nm) and (C) in HBD-A solvents (methanol, ethanol, isopropanol), showing the (FA)_{GS} emission at 490 nm (λ_{ex} 418 nm).

Figure S3

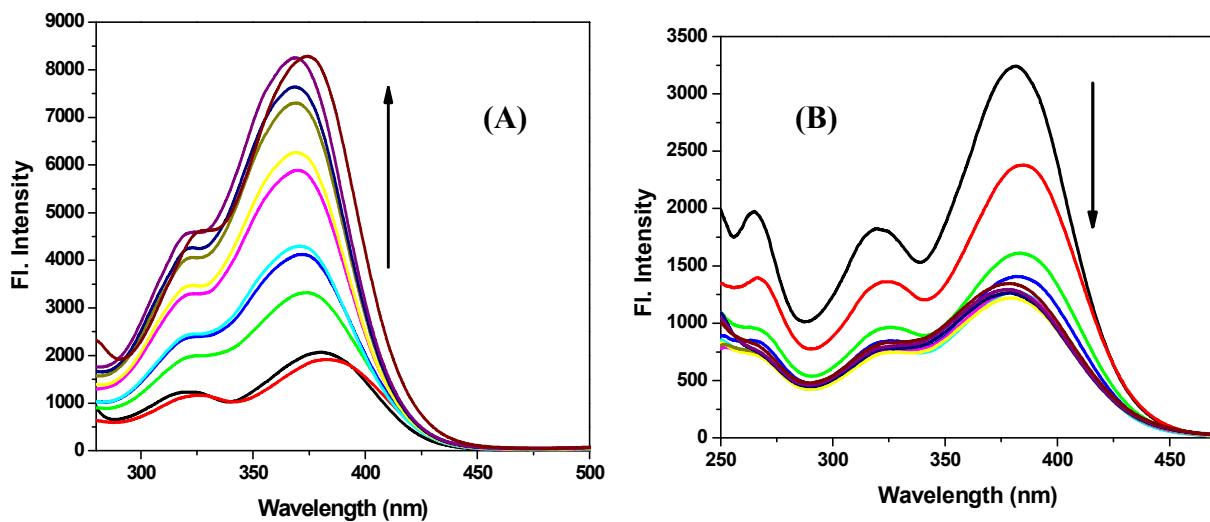


Figure S3 Excitation spectra of fisetin in different NaC concentrations ($[NaC] = 4.8 - 42.3\text{ mM}$), (A) Emission wavelength is 540 nm and (B) Emission wavelength is 490 nm.

Figure S4

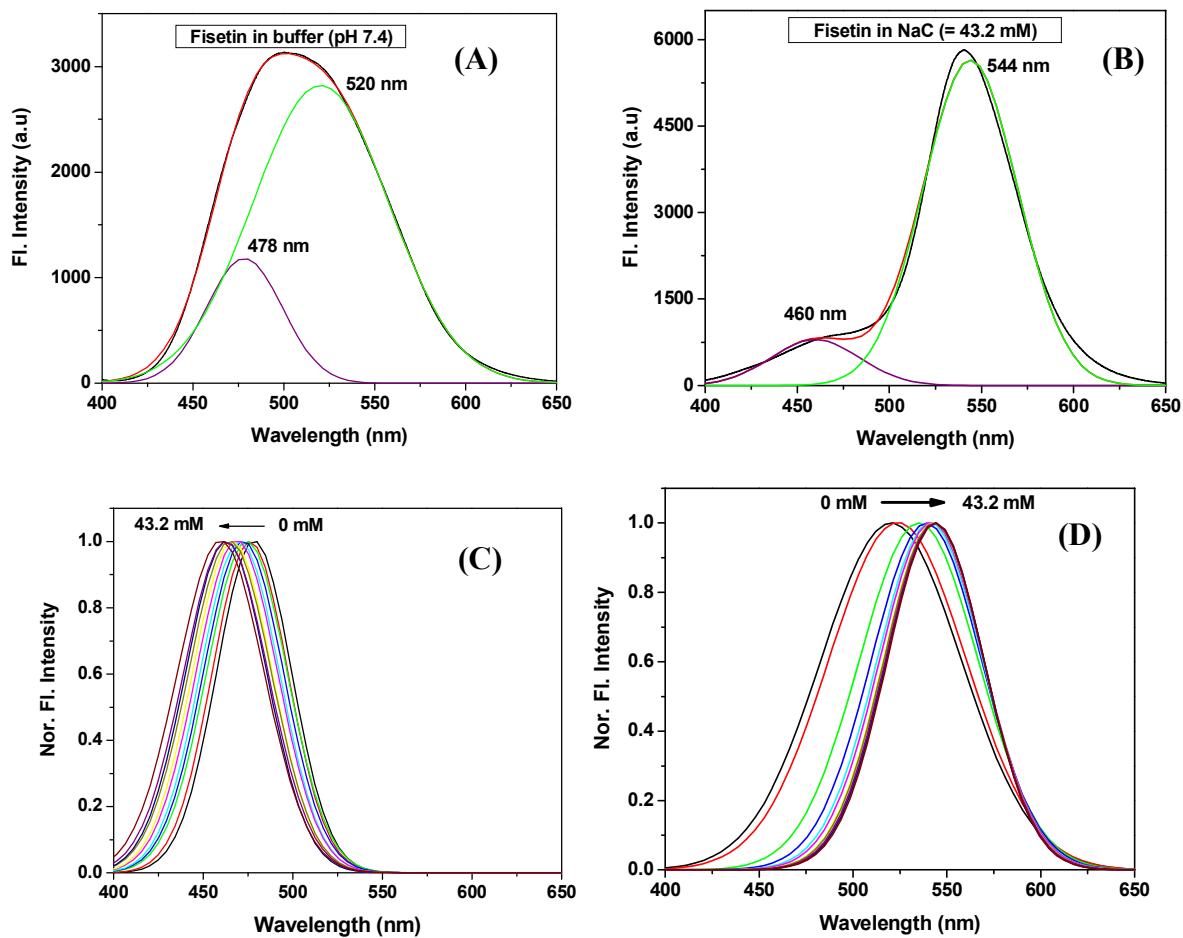


Figure S4. Deconvoluted emission spectra of FN ($\lambda_{\text{ex}} 369 \text{ nm}$) in (A) pH 7.4 buffer (B) NaC micellar solution ($[\text{NaC}] = 43.2 \text{ mM}$). (C) Blue shift of $(\text{FA})_{\text{ES}}$ emission peak and (D) red shift of FT emission peak in the deconvoluted emission spectra of FN in different concentrations of NaC. ($T = 25 \text{ }^{\circ}\text{C}$, $\text{pH} = 7.4$)

Figure S5

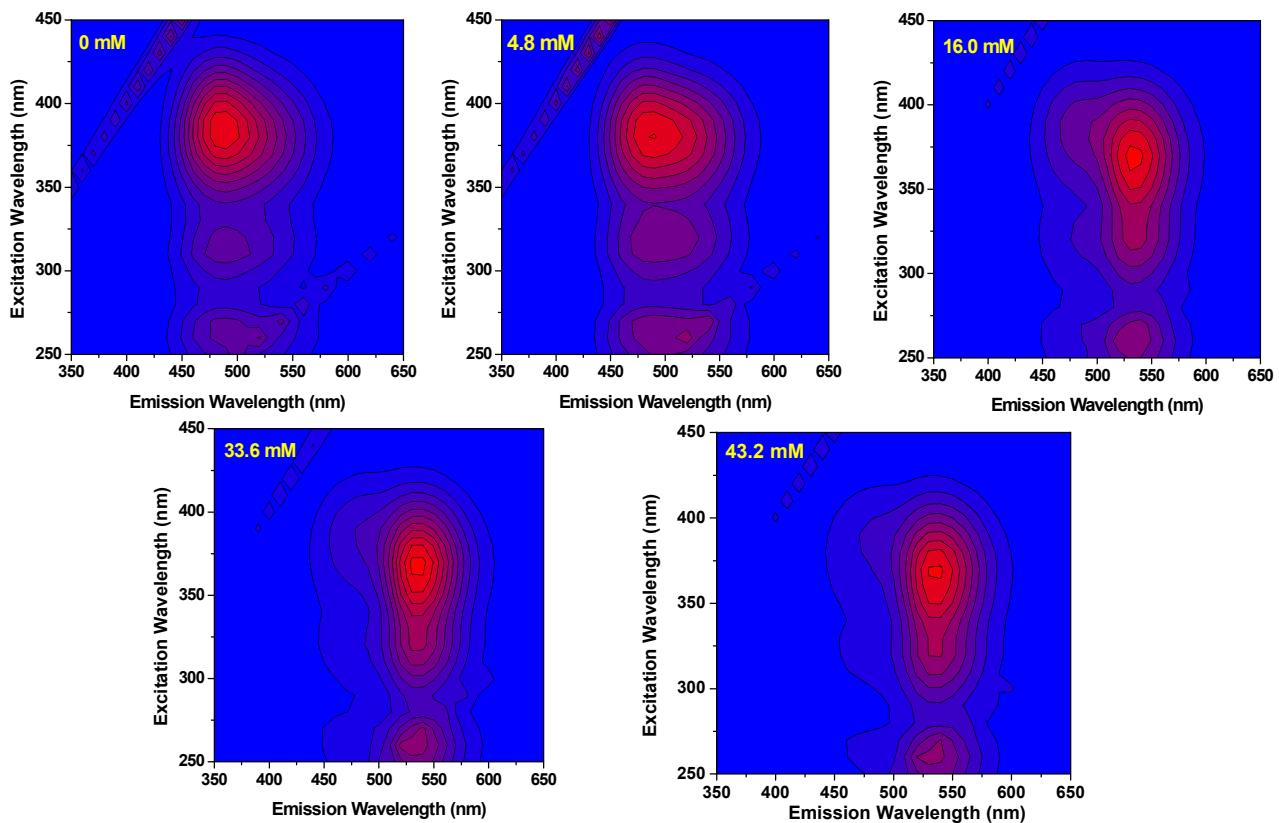


Figure S5. Excitation Emission Matrix Fluorescence (EEMF) of fisetin in buffer medium and different concentrations of NaCl at 25 °C

Figure S6

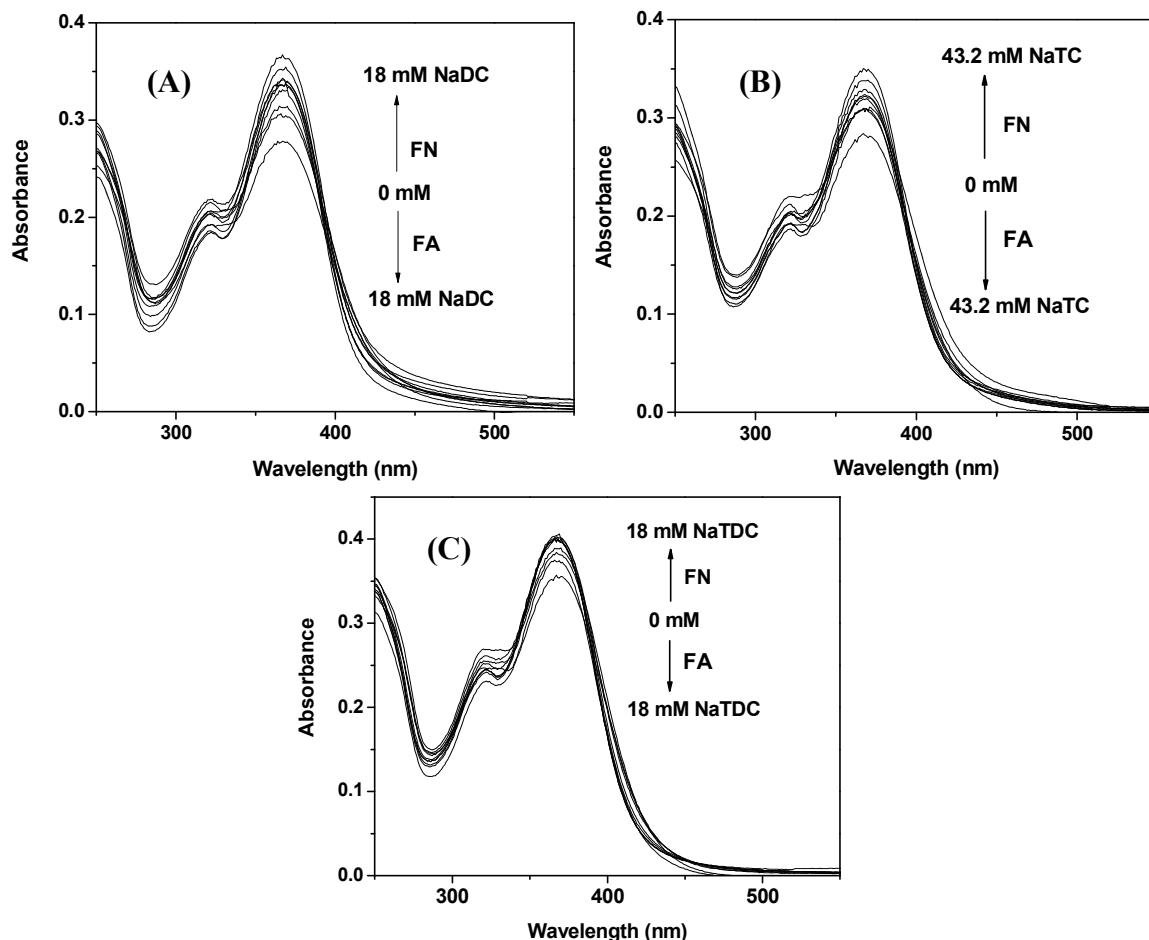


Figure S6. Absorption spectra of fisetin in different bile salt concentrations, showing an enhancement of FN at 369 nm and a decrease in FA peak (~ 418 nm).

Figure S7

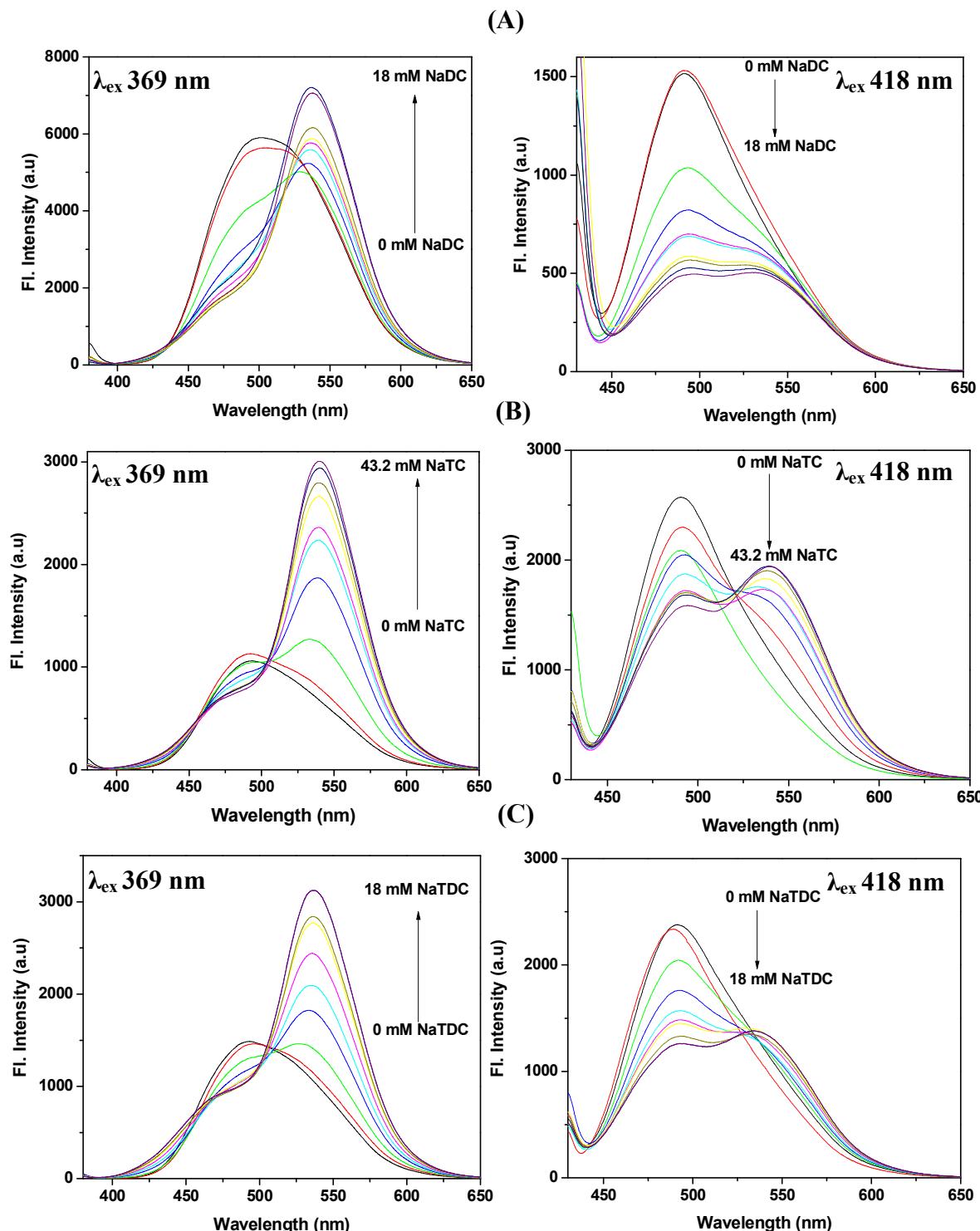


Figure S7. Emission spectra of FT ($\lambda_{\text{ex}} 369 \text{ nm}$) and (FA)_{GS} ($\lambda_{\text{ex}} 418 \text{ nm}$) in different concentrations of bile salts. (A) NaDC (0 – 18 mM), (B) NaTC (0 – 43.2 mM) and (C) NaTDC (0 – 18 mM)

Figure S8

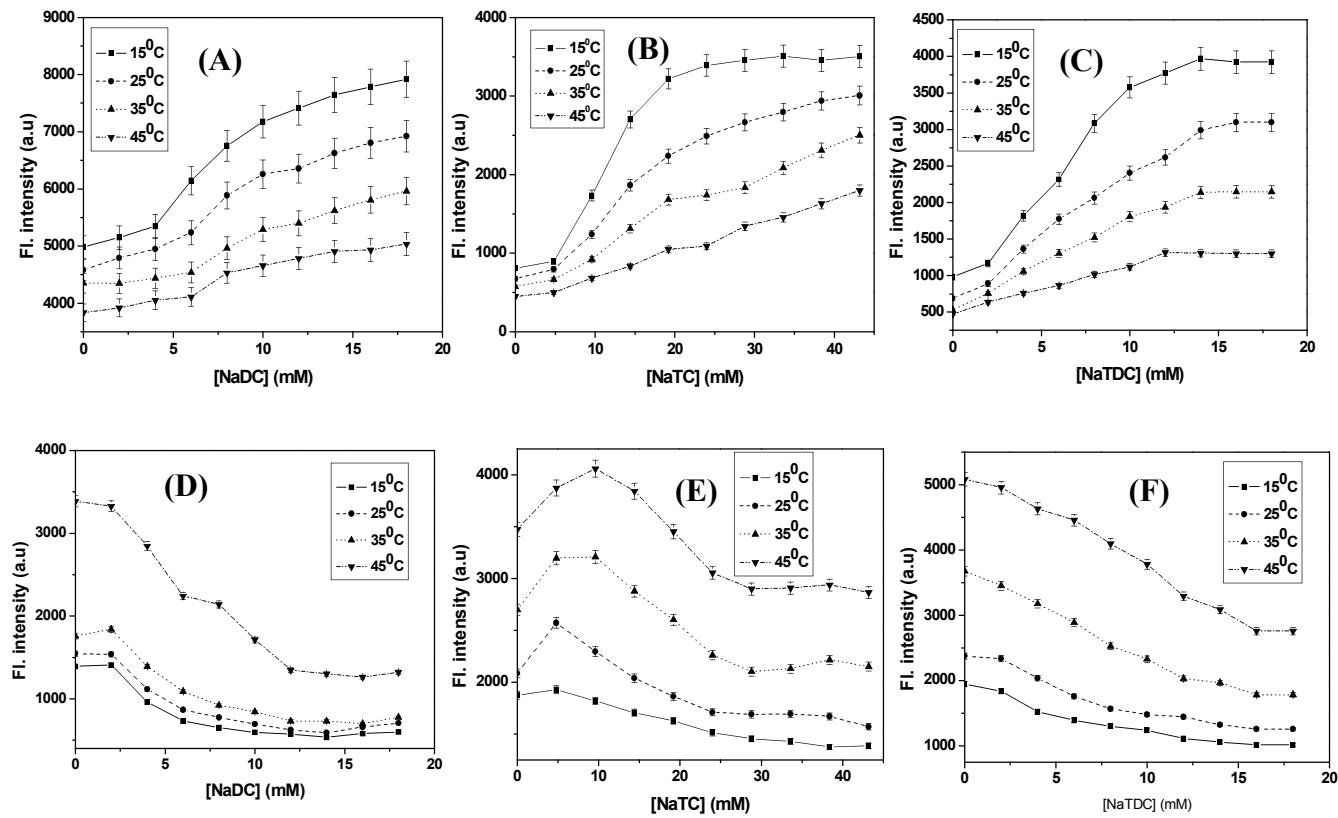


Figure S8 Correspondence of fluorescence intensity of FT emission ($\lambda_{\text{ex}} 369 \text{ nm}$, $\lambda_{\text{em}} 540 \text{ nm}$) in (A) NaDC, (B) NaTC and (C) NaTDC micelles and (FA)_{GS} emission ($\lambda_{\text{ex}} 418 \text{ nm}$, $\lambda_{\text{em}} 490 \text{ nm}$) in (D) NaDC, (E) NaTC and (F) NaTDC micelles with different concentrations of bile salts at various temperatures.

Figure S9

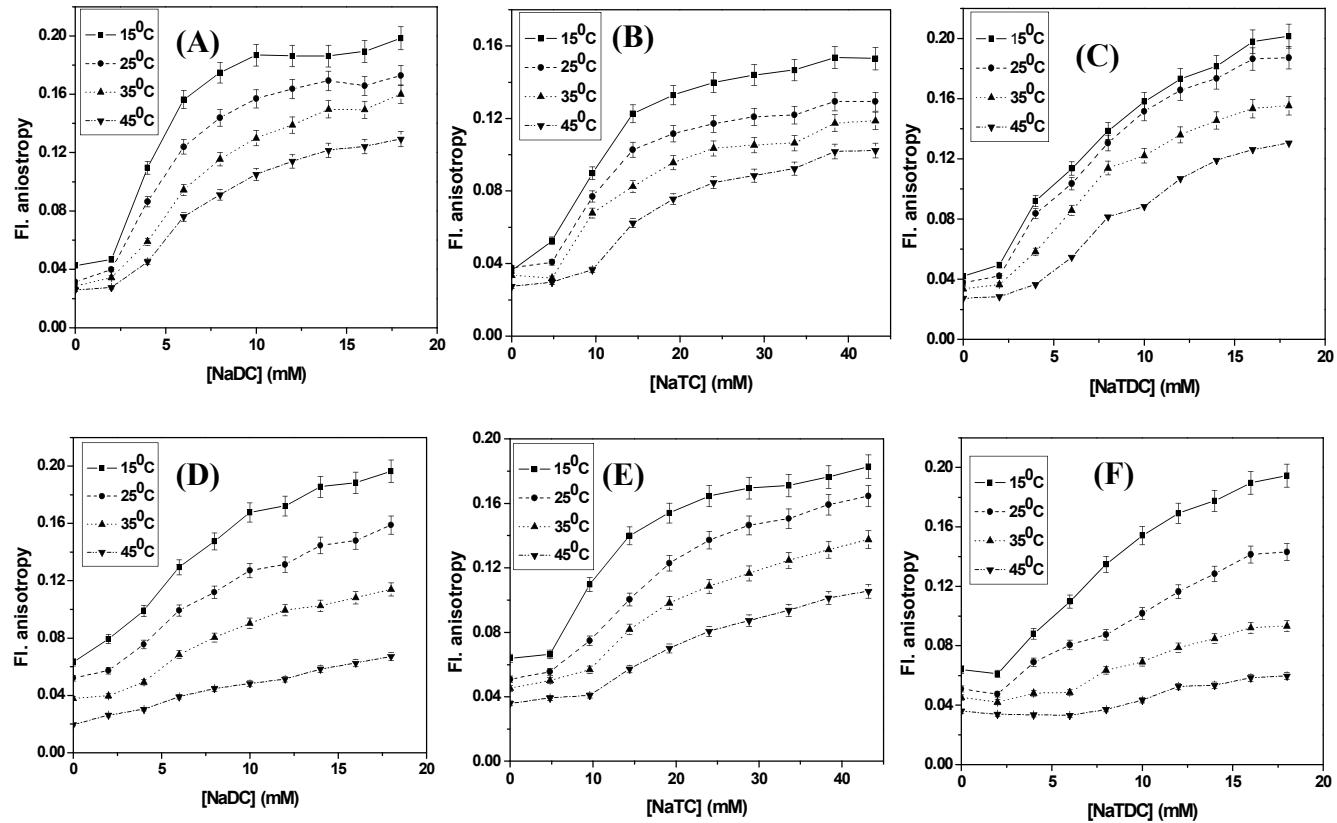


Figure S9 Correspondence of steady state fluorescence anisotropy of FT emission (λ_{ex} 369 nm, λ_{em} 540 nm) in (A) NaDC, (B) NaTC and (C) NaTDC micelles and (FA)_{GS} emission (λ_{ex} 418 nm, λ_{em} 490 nm) in (D) NaDC, (E) NaTC and (F) NaTDC micelles with different concentrations of bile salts at various temperatures.

Figure S10

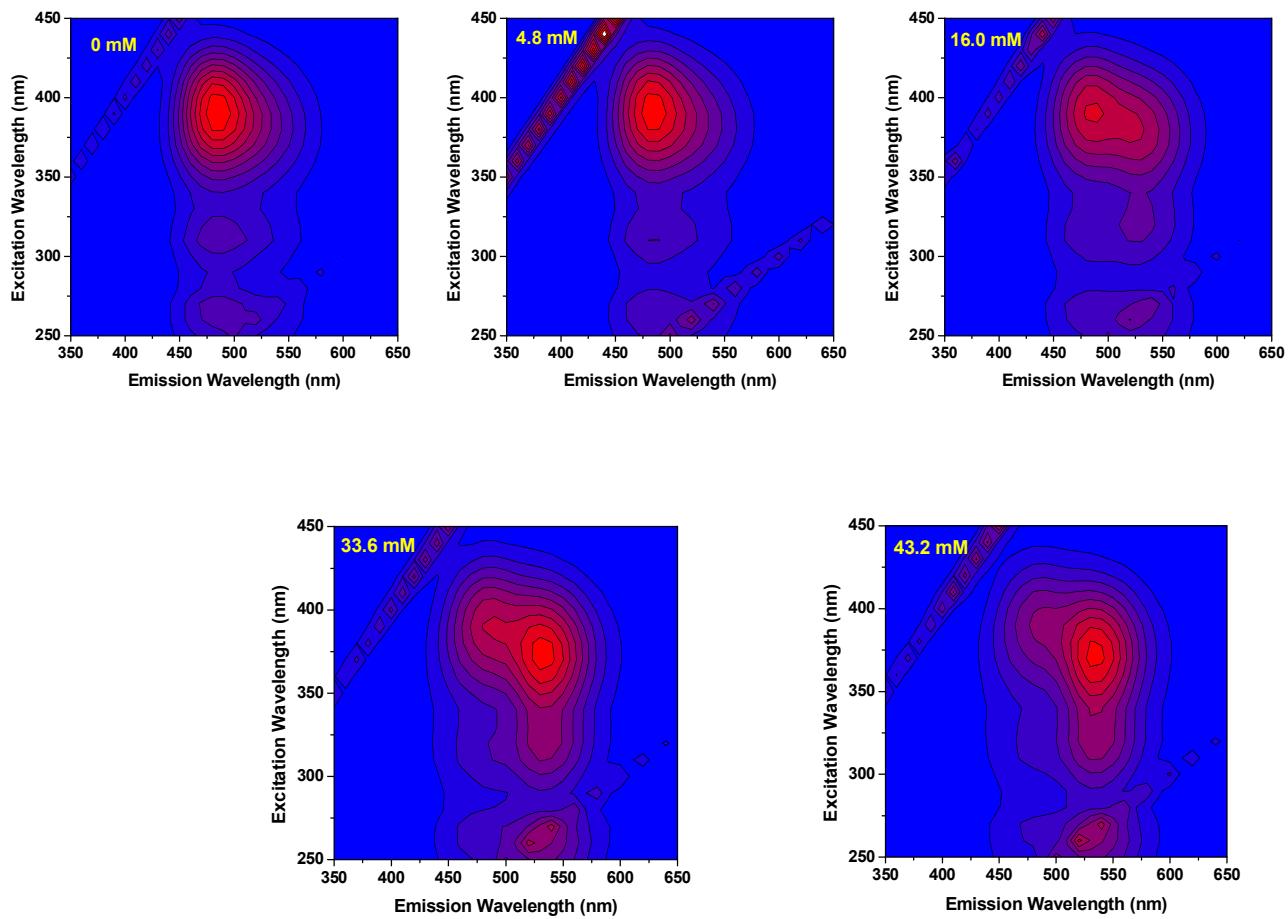


Figure S10. Excitation Emission Matrix Fluorescence (EEMF) of fisetin in buffer medium and different concentrations of NaCl at 45 °C

Table S1. Emission wavelength dependent fluorescence lifetimes of fisetin in NaC micelles ([NaC] = 43.2 mM), excitation of 370 nm LED

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)
480	0.7 (84)	3.0 (16)
490	0.7 (74)	3.3 (26)
500	0.8 (74)	2.9 (26)
510	1.0 (66)	3.2 (34)
520	1.1 (60)	3.3 (40)
530	1.2 (54)	3.3 (46)
540	1.0 (45)	3.3 (54)
550	1.2 (54)	3.4 (46)