Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

SUPPORTING INFORMATION

Effect of Micellar and Sol-Gel Media on the Spectral and Kinetic Properties of Tetracycline and its Complexes with Mg^{2+}.

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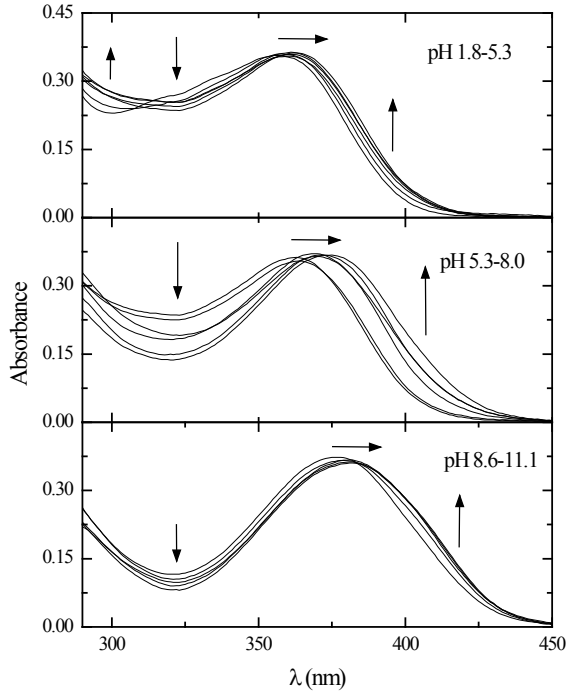

Figure S1. Absorption spectra of TC (2.6 x 10^{-5} M) in aqueous solution buffered at different pHs in the presence of *p*DoTABr at 0.0300 M.

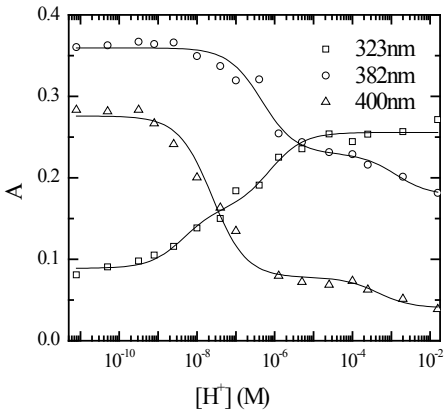

Figure S2. pH dependence of the absorption spectral intensities of TC in aqueous solution in the presence of pDoTABr at 0.0300 M. The full lines represent the best fittings obtained by taking into account acid-base equilibria.

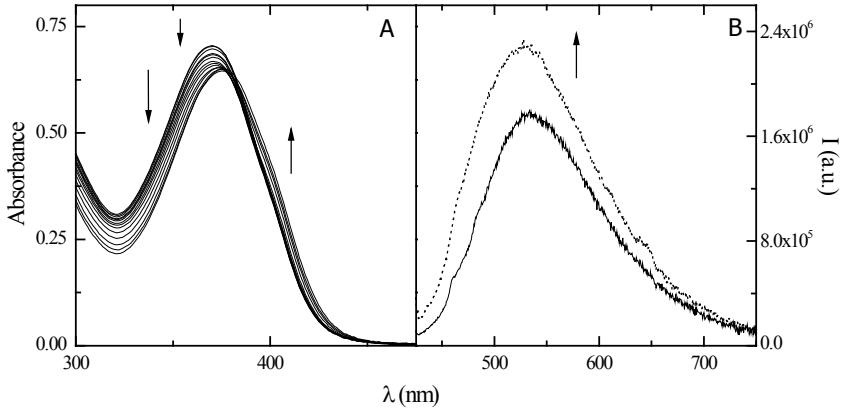

Figure S3. (A) Absorption spectra of TC (5.4 x 10^{-5} M) in aqueous solution at pH 9 alone and in the presence of increasing amount of *p*DoTABr up to 1.7 x 10^{-3} M. (B) Fluorescence spectra of TC (8.0 x 10^{-6} M) in aqueous solution at pH 9 alone and in the presence of *p*DoTABr 3 x 10^{-2} M.

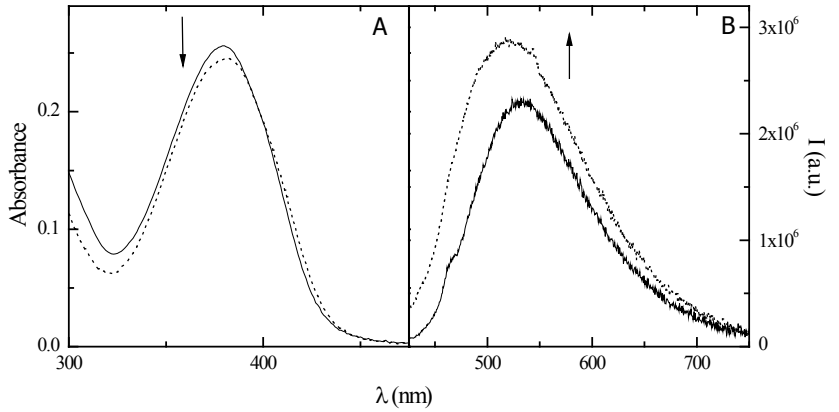

Figure S4. (A) Absorption spectra of TC (2.2 x 10^{-5} M) in aqueous solution at pH 11 alone and in the presence of *p*DoTABr 3 x 10^{-2} M. (B) Fluorescence spectra of TC (9.0 x 10^{-6} M) in aqueous solution at pH 11 alone and in the presence of *p*DoTABr 3 x 10^{-2} M.

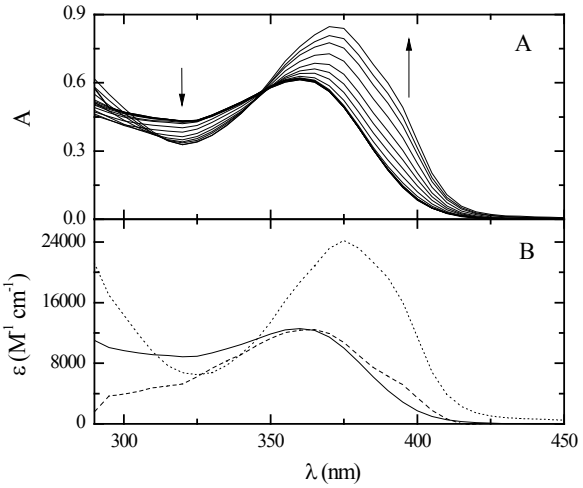

Figure S5. (A) Absorption spectra of TC (4.9 x 10^{-5} M) in micellar environment at pH 5 ([*p*DoTABr] = 5 x 10^{-3} M) alone and in the presence of increasing amount of Mg^{2+} up to a concentration of 0.380 M. (B) Quantitative absorption spectra of TC (full line) and of its 1:1 (dashed line) and 1:2 (dotted line) complexes with Mg^{2+} in micellar environment at pH 5 ([*p*DoTABr] = 5 x 10^{-3} M).

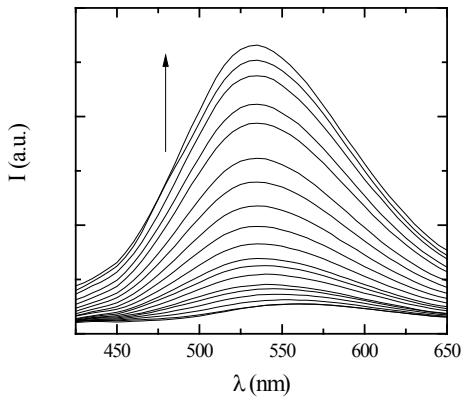

Figure S6. Fluorescence spectra of TC (9.7 x 10^{-6} M) in micellar environment at pH 5 ([*p*DoTABr] = 5 x 10^{-3} M) alone and in the presence of increasing amount of Mg^{2+} up to a concentration of 0.30 M.

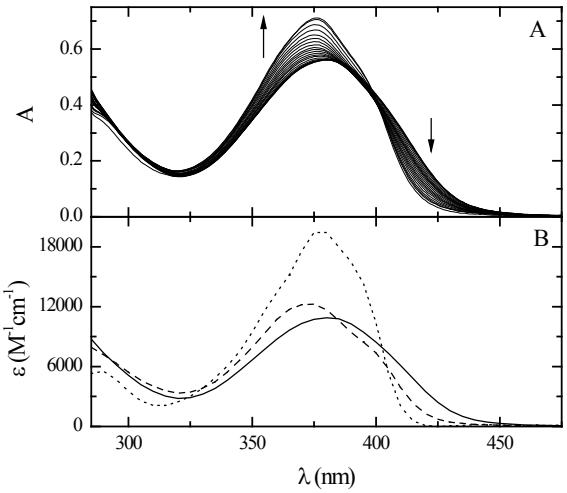

Figure S7. (A) Absorption spectra of TC (5.1 x 10^{-5} M) in micellar environment at pH 11 ([*p*DoTABr] = 3 x 10^{-2} M) alone and in the presence of increasing amount of Mg^{2+} up to a concentration of 0.023 M. (B) Quantitative absorption spectra of TC (full line) and of its 1:1 (dashed line) and 1:2 (dotted line) complexes with Mg^{2+} in micellar environment at pH 11 ([*p*DoTABr] = 3 x 10^{-2} M).

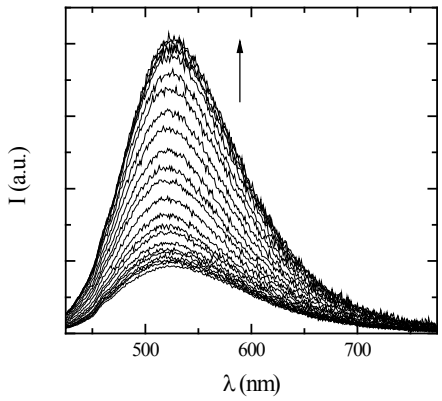

Figure S8. Fluorescence spectra of TC (1.3 x 10^{-5} M) in micellar environment at pH 11 ([*p*DoTABr] = 3 x 10^{-2} M) alone and in the presence of increasing amount of Mg^{2+} up to a concentration of 0.023 M.

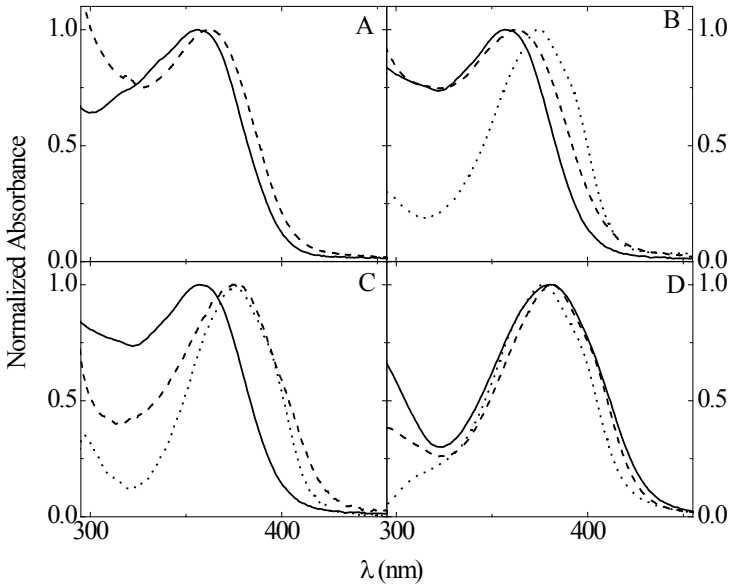

Figure S9. Normalized absorption spectra of TC (~ 5 x 10^{-5} M) in aqueous solution (full line) and in Gel(+/-) ([*p*DoAO] = 0.067 M) alone (dashed line) at pH 2 (A). Normalized absorption spectra of TC (~ 5 x 10^{-5} M) in aqueous solution (full line) and in Gel(+/-) ([*p*DoAO] = 0.067 M) alone (dashed line) and in the presence of Mg^{2+} (dotted line) in concentration 0.17 M at pH 5 (B), and in concentration 0.0067 M at pH 9 (C) and 11 (D).

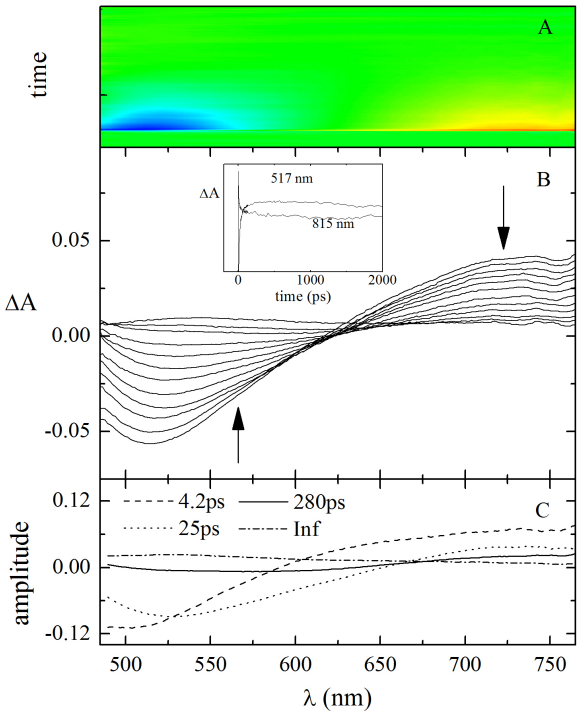

Figure S10. Pump-probe absorption spectroscopy of TC in micellar environment at pH 9 (λ_{exc} = 400 nm; [*p*DoTABr] = 5 x 10^{-3} M): A) contour plot of the experimental data; B) time resolved absorption spectra recorded 0.8 (a), 1.3 (b), 2.0 (c), 3.1 (d), 5.0 (e), 7.2 (f), 10 (g), 17 (h), 26 (i), 53 (j), 95 (k) and 370 (l) ps after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) amplitudes of the decay components obtained by SVD and Global Analysis.

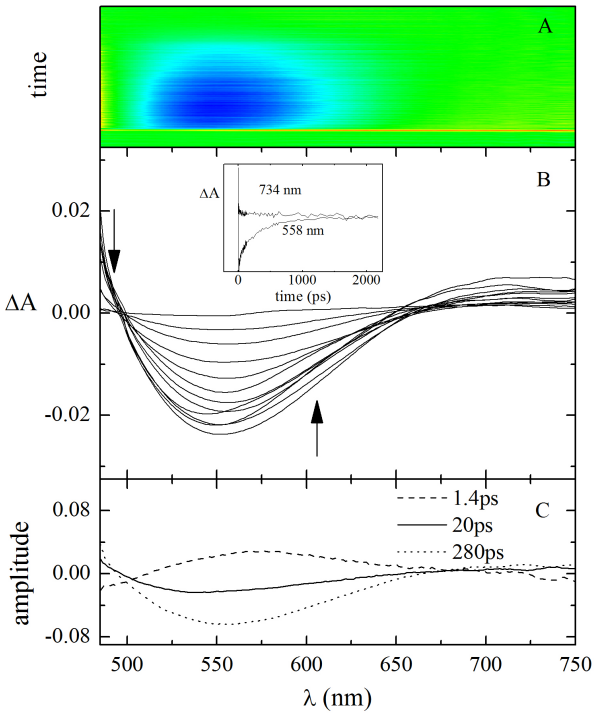

Figure S11. Pump-probe absorption spectroscopy of TC in micellar environment at pH 9 (λ_{exc} = 400 nm; [*p*DoTABr] = 5 x 10^{-3} M) in the presence of Mg^{2+}: A) contour plot of the experimental data; B) time resolved absorption spectra recorded 0.6 (a), 1.4 (b), 3.7 (c), 9.3 (d), 18 (e), 32 (f), 50 (g), 100 (h), 190 (i), 350 (j), 570 (k) and 1100 (l) ps after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) amplitudes of the decay components obtained by SVD and Global Analysis.

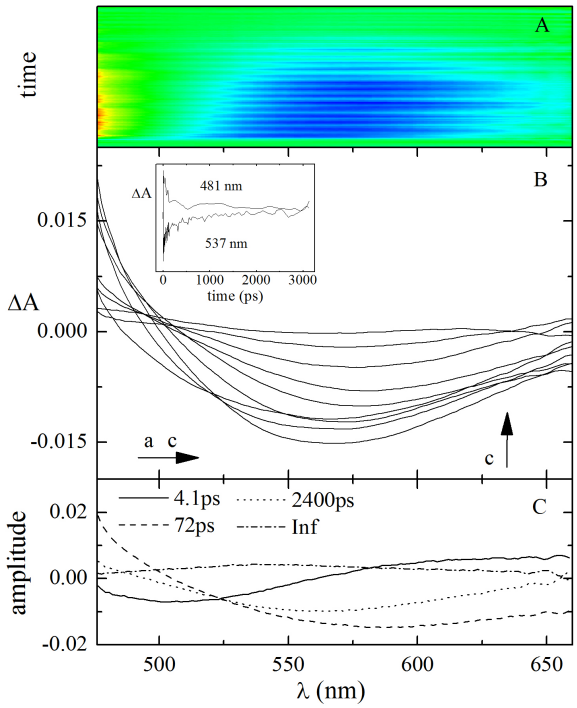

Figure S12. Pump-probe absorption spectroscopy of TC in Gel(+/-) at pH 5 (λ_{exc} = 400 nm; [*p*DoAO] = 0.067 M): A) contour plot of the experimental data; B) time resolved absorption spectra recorded 0.1 (a), 0.9 (b), 2.8 (c), 9.5 (d), 28 (e), 68 (f), 120 (g), 610 (h) and 1600 (i) ps after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) amplitudes of the decay components obtained by SVD and Global Analysis.

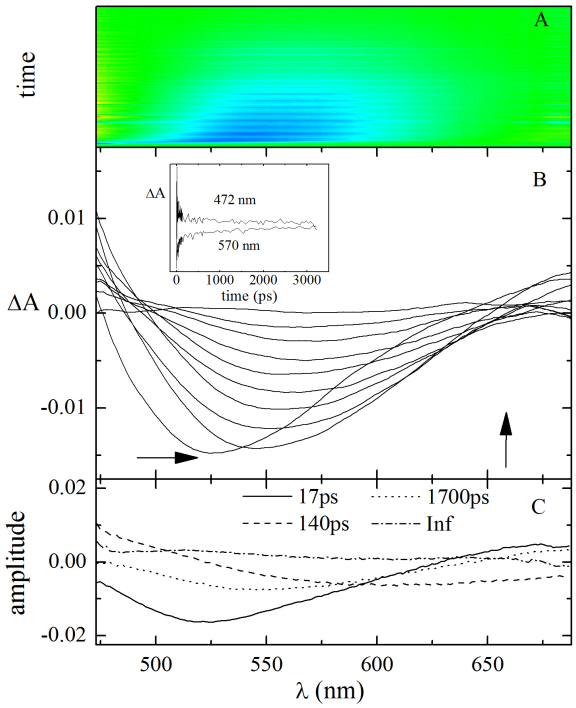

Figure S13. Pump-probe absorption spectroscopy of TC in Gel(+/-) at pH 9 (λ_{exc} = 400 nm; [*p*DoAO] = 0.067 M): A) contour plot of the experimental data; B) time resolved absorption spectra recorded 0.3 (a), 1.9 (b), 4.3 (c), 8.2 (d), 17 (e), 32 (f), 59 (g), 200 (h), 940 (i) and 2600 (j) ps after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) amplitudes of the decay components obtained by SVD and Global Analysis.

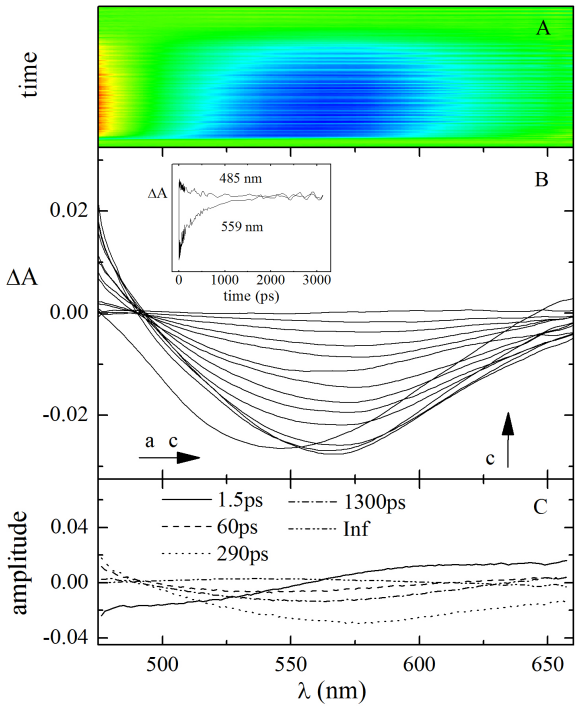

Figure S14. Pump-probe absorption spectroscopy of TC in Gel(+/-) at pH 5 (λ_{exc} = 400 nm; [*p*DoAO] = 0.067 M) in the presence of Mg^{2+}: A) contour plot of the experimental data; B) time resolved absorption spectra recorded 0.4 (a), 1.5 (b), 2.7 (c), 13 (d), 54 (e), 110 (f), 130 (g), 190 (h), 310 (i), 430 (j), 570 (k), 930 (l), 1400 (m) and 1800 (n) ps after the laser pulse. Insets: decay kinetics recorded at meaningful wavelengths and C) amplitudes of the decay components obtained by SVD and Global Analysis.

Table S1. Association constants (K_{ass}) obtained by absorption and fluorescence titrations and interaction sites of the complexes between TC and Mg^{2+} cations in aqueous solutions at pH 5 and in *p*DoTABr micelles ([*p*DoTABr] = 5 x 10^{-3} M)[a].

pH	System	complex	$logK_{ass}$	
			solution	micelle
5	TC-Mg^{2+}	1:1	1.36±0.01	0.71±0.04
		1:2	-2.59÷0	0.57±0.04

[a] Data in solution retrieved from ref. 34. Values in micellar medium refer to this work.

Table S2. Spectral and kinetic properties of the excited states of TC complexes (1:1 and 1:2) with Mg^{2+} ([TC]/[Mg^{2+}] are given in brackets) in *p*DoAO sol-gel at different pHs (λ_{exc}=400 nm).

pH	system	τ(ps)	λ(nm)	assignment
5	TC-Mg^{2+} (1:35)	69	535(-)	S_1 (1:1A) gel
		420	560(-)	S_1 (1:2A,BCD) H_2O
	TC-Mg^{2+} (1:65)	57	535(-)	S_1 (1:1A) gel
		390	560(-)	S_1 (1:2A,BCD) H_2O
9	TC-Mg^{2+} (1:20)	30	525(-), 730(+)	S_1 (TC) H_2O
		380	555(-)	S_1 (1:1BCD/1:2A,BCD) H_2O
		1900	560 (-), 690(+)	S_1 (1:1BCD/1:2A,BCD) gel
		Inf	510(+), 660(+)^{sh}	T_1
	TC-Mg^{2+} (1:100)	31	515(-), 660(+)	S_1 (TC) H_2O
		380	555(-)	S_1 (1:1BCD/1:2A,BCD) H_2O
		1900	555(-), 675(+)	S_1 (1:1BCD/1:2A,BCD) gel
		Inf	510(+)	T_1