Supplementary Information for

Exploring cationic polyelectrolyte-micelle interaction via excited-state proton transfer. Signatures of probe transfer

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Fitting of TRANES: The time-resolved area normalized emission spectrum (TRANES) of HPTS consists of two bands, protonated and deprotonated. With the help of this following bi-lognormal function, the emission spectra have been fitted.

$$I(v) = I_0^1 \exp\left\{-\ln(2)\left[\frac{\ln\left(1 + \frac{2b_1\left(\lambda - \lambda_p^1\right)}{\Delta_1}\right)}{b_1}\right]^2\right\} + I_0^2 \exp\left\{-\ln(2)\left[\frac{\ln\left(1 + \frac{2b_2\left(\lambda - \lambda_p^2\right)}{\Delta_2}\right)}{b_2}\right]^2\right\} \quad (S1)$$

When both $\dfrac{2b_1\left(\lambda - \lambda_p^1\right)}{\Delta_1} \leq -1$ and $\dfrac{2b_2\left(\lambda - \lambda_p^2\right)}{\Delta_2} \leq -1$

Else, $I(\lambda) = 0$

Here, I_0, λ_p, Δ, b represent the maximum peak intensity, wavelength maximum, asymmetry factor and width parameter of each of the bands, respectively. The label (1,2) in the subscript or superscript denotes the protonated and deprotonated bands' parameters, respectively.

The ratio of emission intensities, R, can be calculated as

$$R = \frac{I_0^1}{I_0^2}$$
(S2)
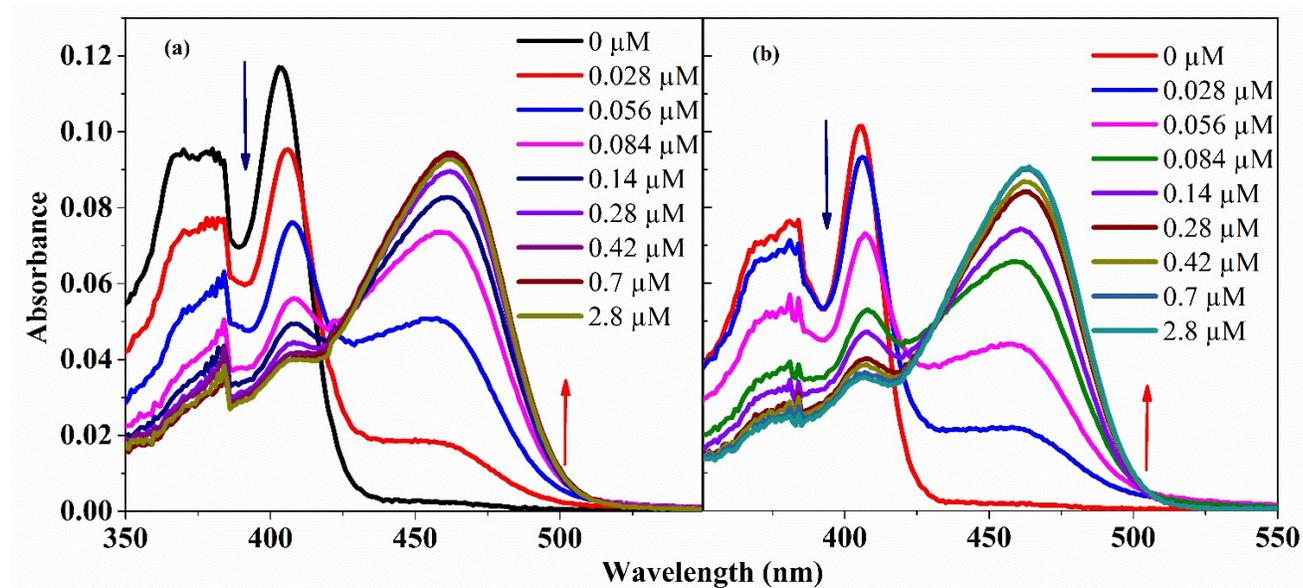
Figure S1. Absorption spectra of HPTS in (a) water and (b) SB12 (10 mM) micellar medium with increasing PDADMAC concentrations. PDADMAC addition changes the pH of the medium (see Table S1).

Table S1. The measured pH at different PDADMAC concentrations in aqueous and SB12 (10 mM) micellar medium.

[PDADMAC] (μM)	pH	
	Water	SB12
0	5.69	5.02
0.028	5.67	4.90

0.056	5.65	4.85
0.084	5.62	4.82
0.14	5.61	4.80
0.28	5.50	4.75
0.42	5.35	4.70
0.70	5.10	4.65
2.8	4.99	4.59
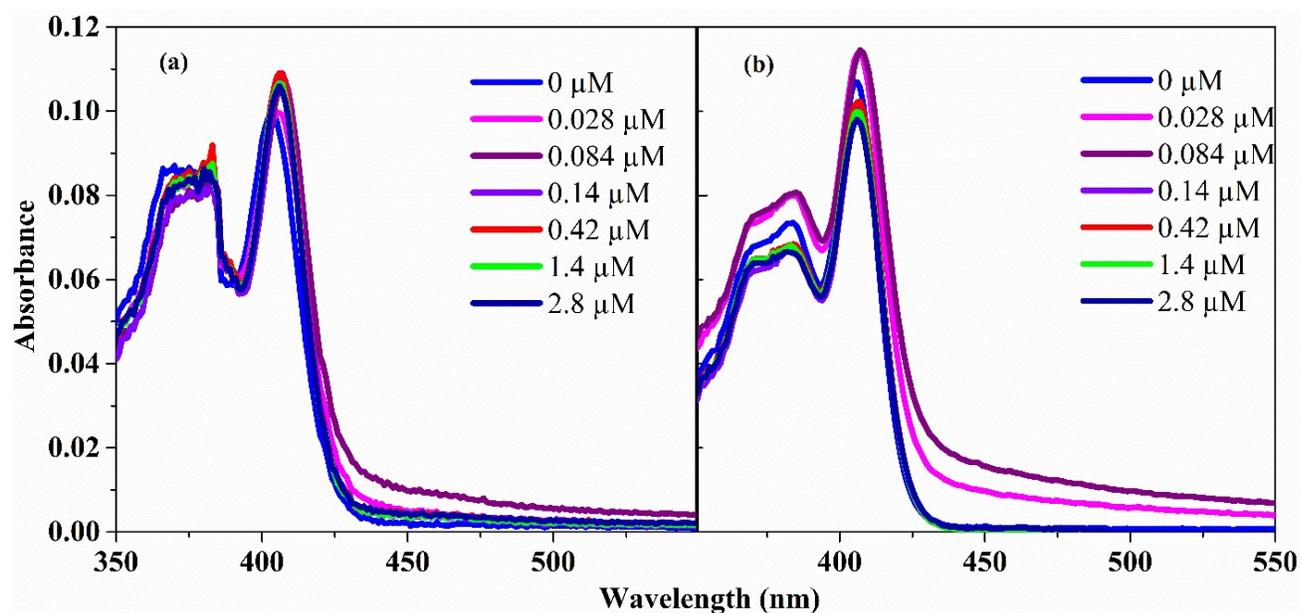
Figure S2. Absorption spectra of HPTS in (a) water and (b) SB12 (10 mM) micellar medium with increasing PDADMAC concentrations. The pH of both systems was adjusted to 2.5 by adding HCl to suppress the ground-state proton transfer.
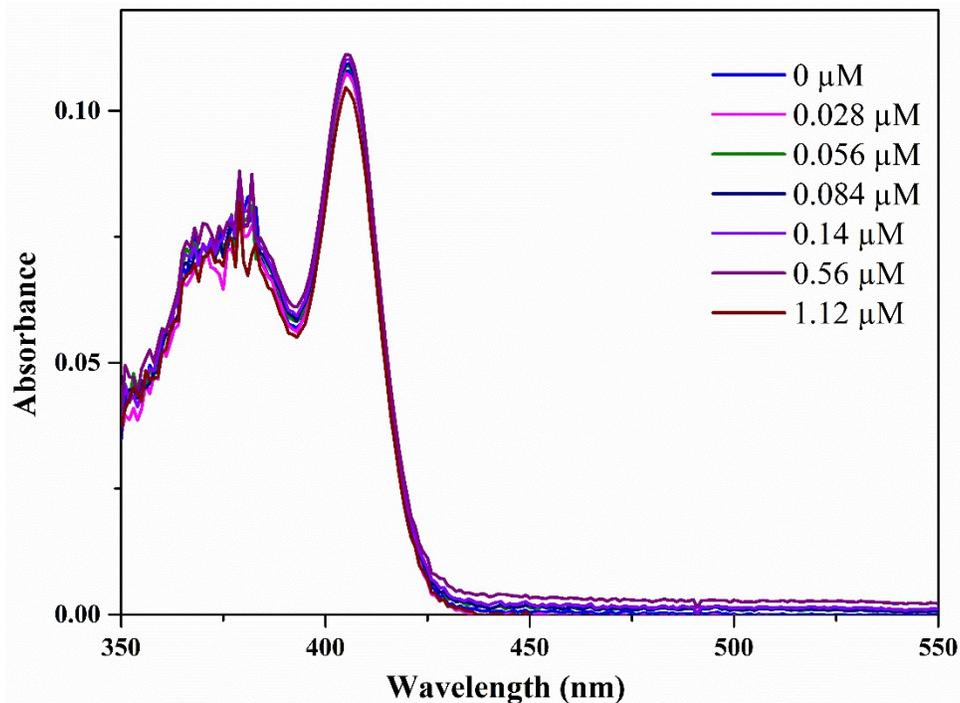
Figure S3. Absorption spectra of HPTS in 30 mM DTAB micellar media with increasing PDADMAC concentration. The pH of the medium was ~5.6.
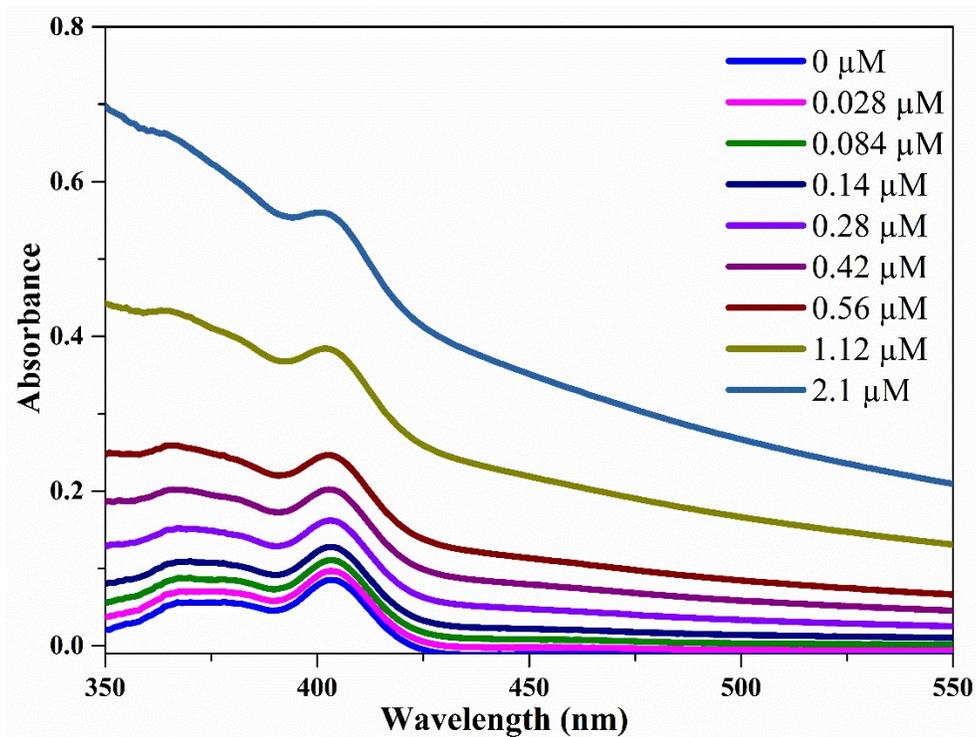
Figure S4. Absorption spectra of HPTS in 20 mM SDS micellar media with increasing PDADMAC concentration. The pH of the medium is ~5.6.
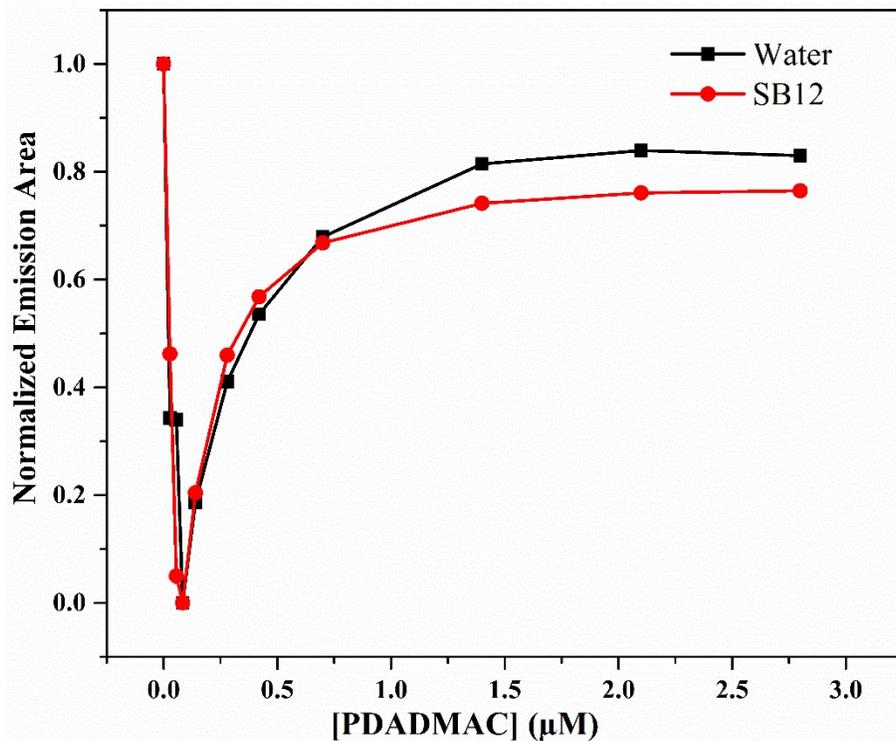
Figure S5. Variation of normalized emission curve area representing the relative quantum yield of the HPTS in water and SB12 media with increasing PDADMAC concentration.
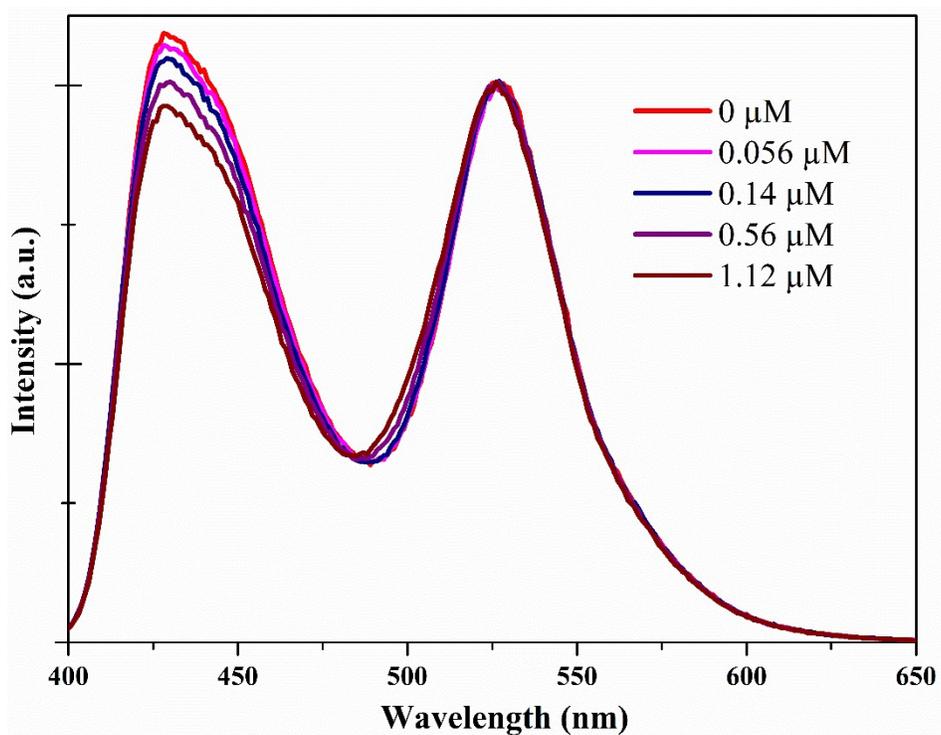
Figure S6. Emission spectra of HPTS in DTAB (30 mM) micellar medium with increasing PDADMAC concentration. The pH of the medium was 5.6.
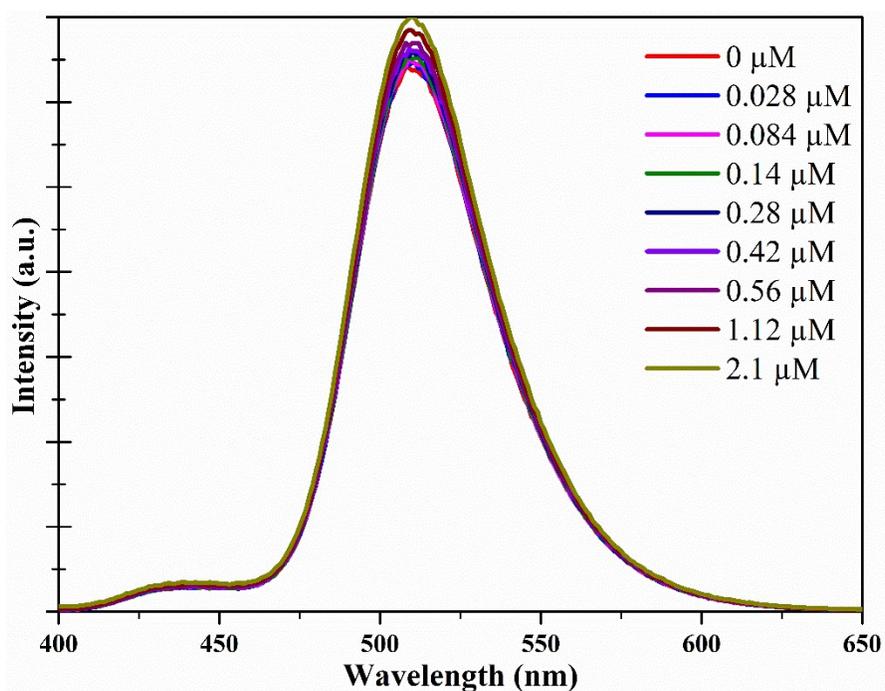
Figure S7. Emission spectra of HPTS in SDS micellar system with increasing PDADMAC concentration. The pH of the medium was ~5.6.
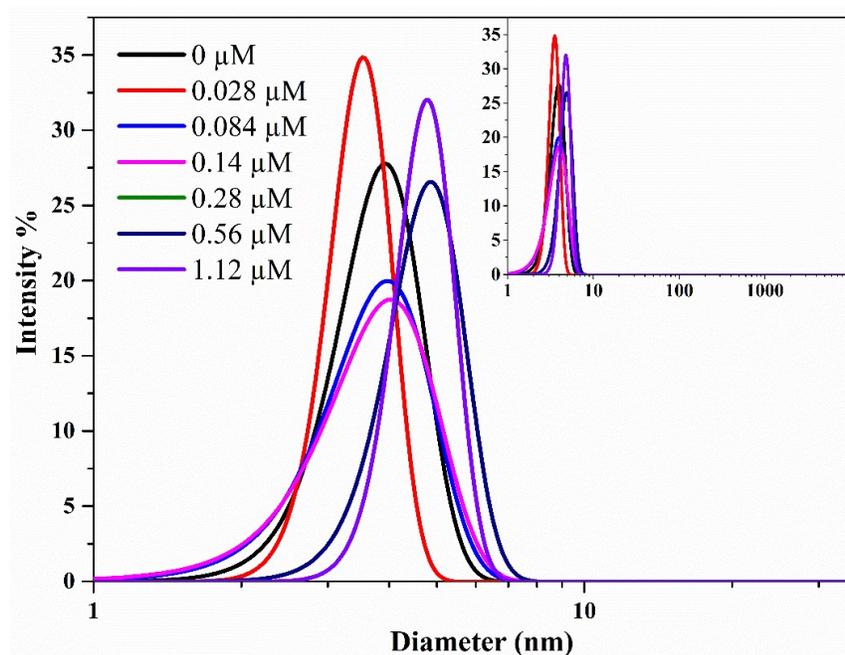
Figure S8. Hydrodynamic diameter variation of DTAB-PDADMAC complex with increasing PDADMAC concentration obtained from dynamic light scattering measurements. The inset shows the same data at full scale.
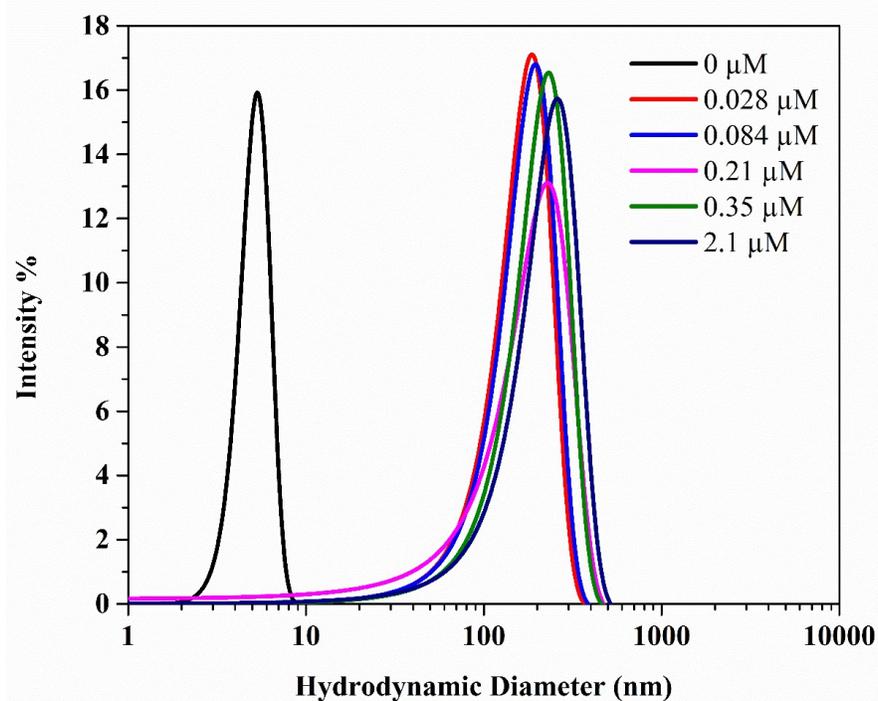
Figure S9. Hydrodynamic diameter variation of SDS-PDADMAC complex with increasing PDADMAC concentration obtained from dynamic light scattering measurements. The pH of the medium is ~ 5.6.
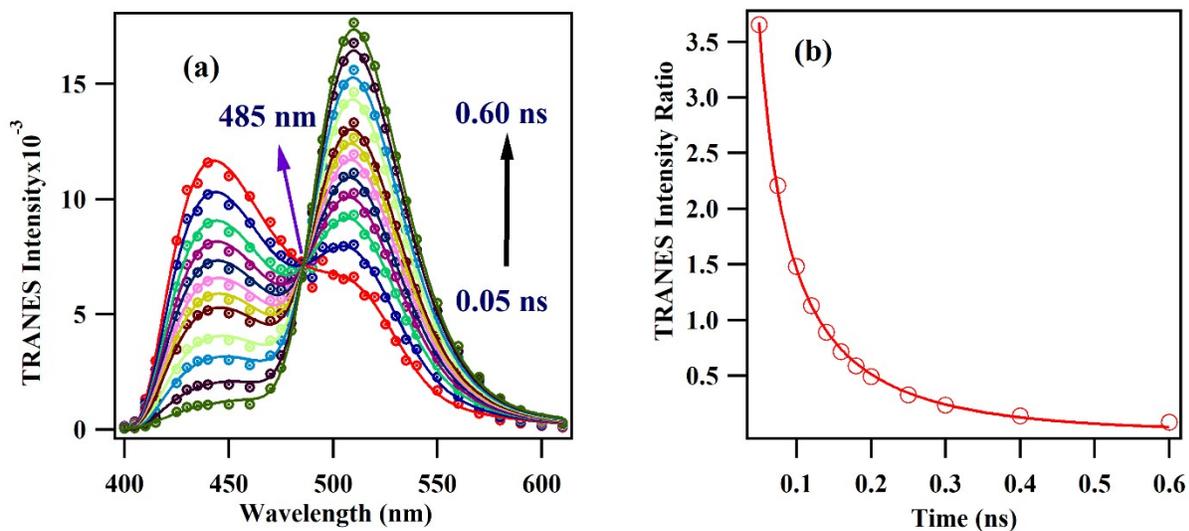
Figure S10. TRANES of HPTS in water at different times and the variation of TRANES intensity ratio of protonated to deprotonated (ROH/RO) emission band with time. The pH of the medium is 2.5.
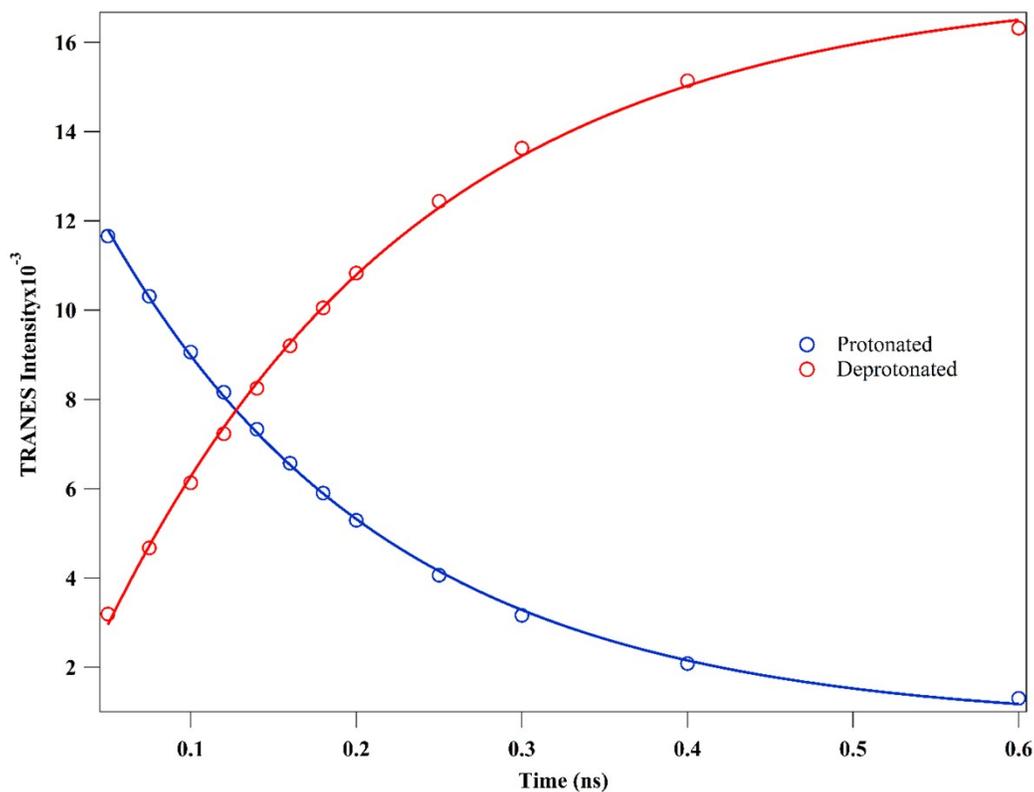
Figure S11. Decay of TRANES intensities of the protonated and deprotonated moieties of HPTS in water.
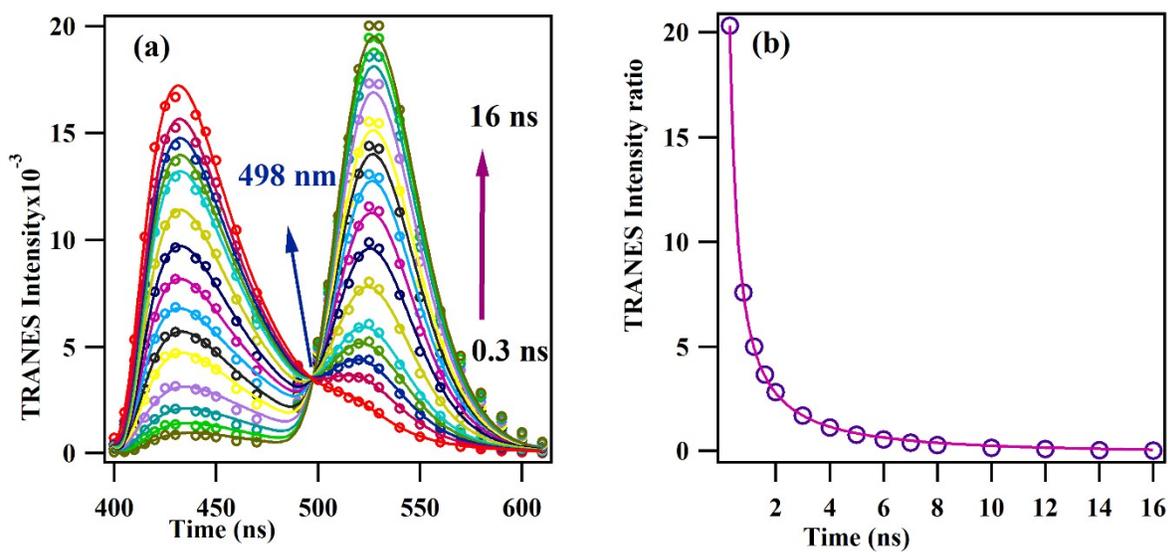
Figure S12. (a)TRANES of HPTS in SB12 micellar media at different times and (b) the variation of TRANES intensity ratio of protonated to deprotonated (ROH/RO) emission band with time. The pH of the medium is 2.5.
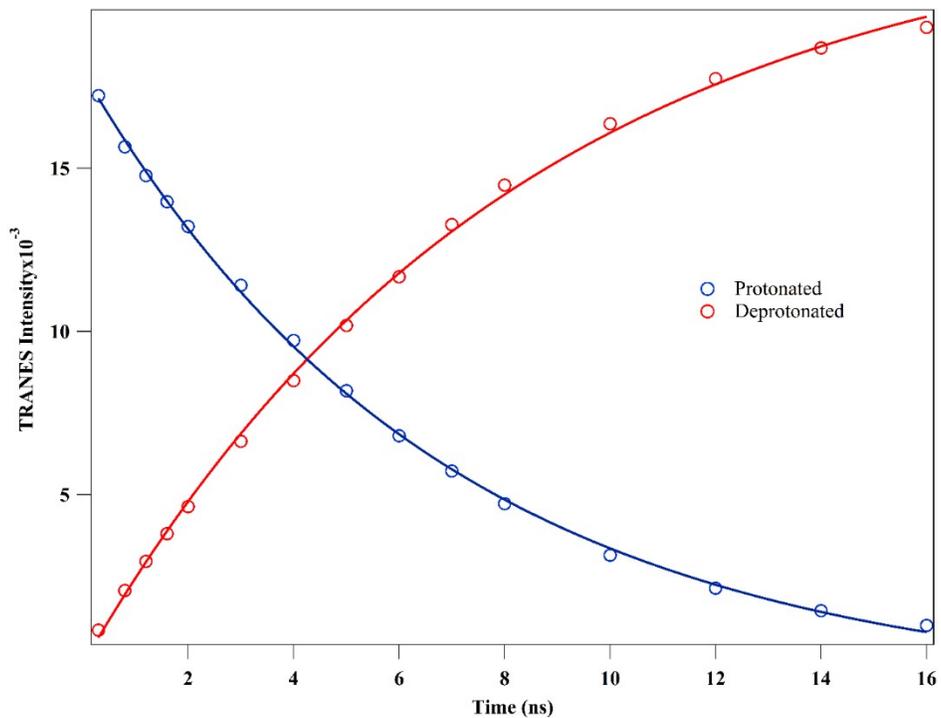
Figure S13. Time evolution of TRANES intensities of the protonated and deprotonated moieties of HPTS in SB12 micelle.
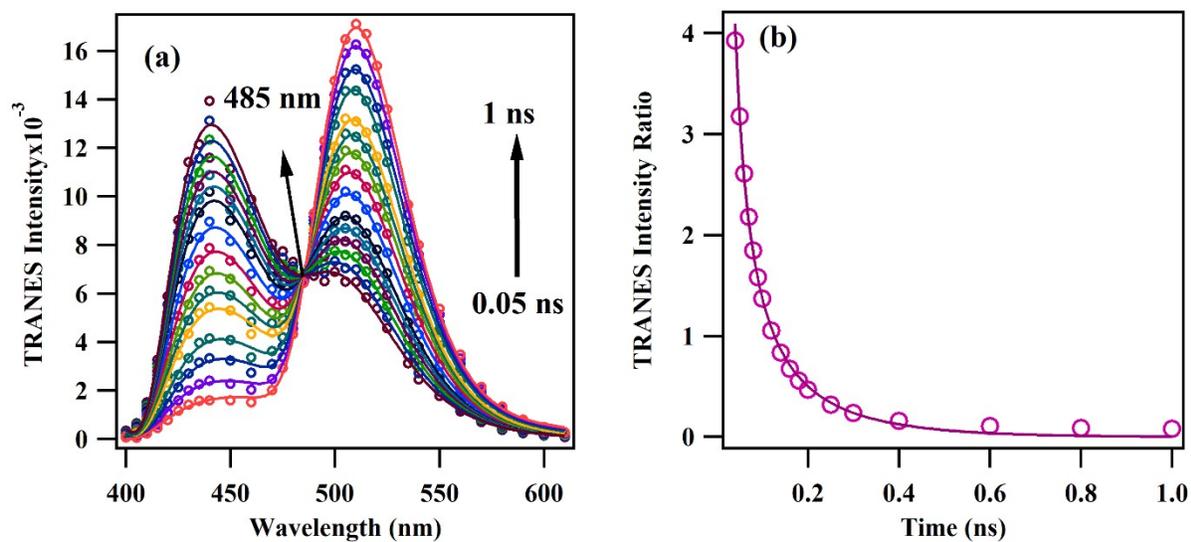
Figure S14. (a)TRANES of HPTS in water in the presence of 0.028 µM PDADMAC at various times and (b) The variation of the TRANES intensity ratio of protonated/deprotonated band of HPTS with times. The pH of the medium is 2.5.
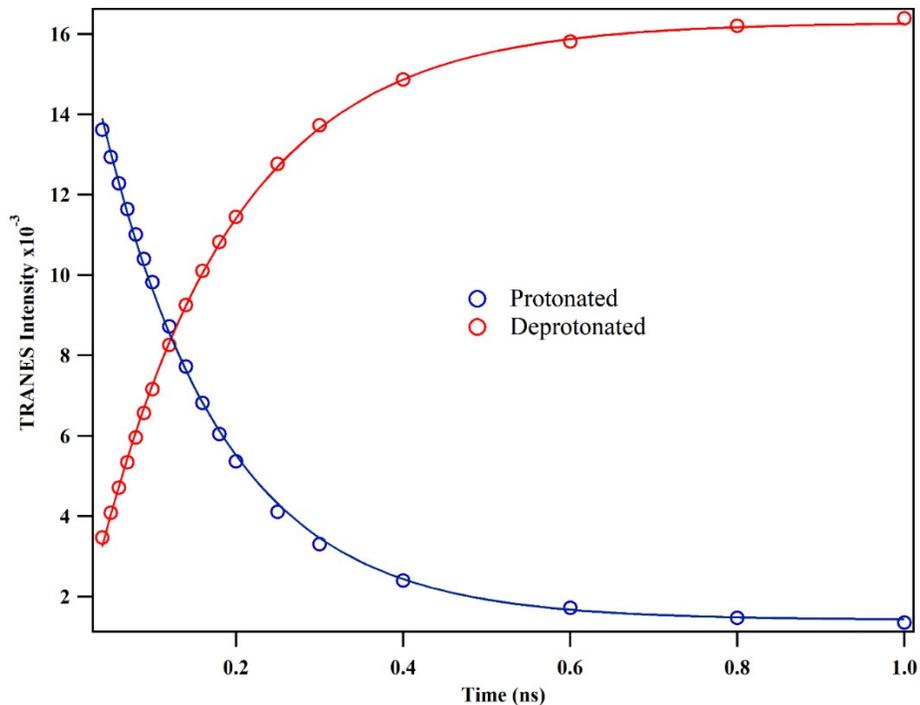
Figure S15. Time evolution of TRANES intensities of the protonated and deprotonated moieties of HPTS in an aqueous 0.028 μM PDADMAC medium.
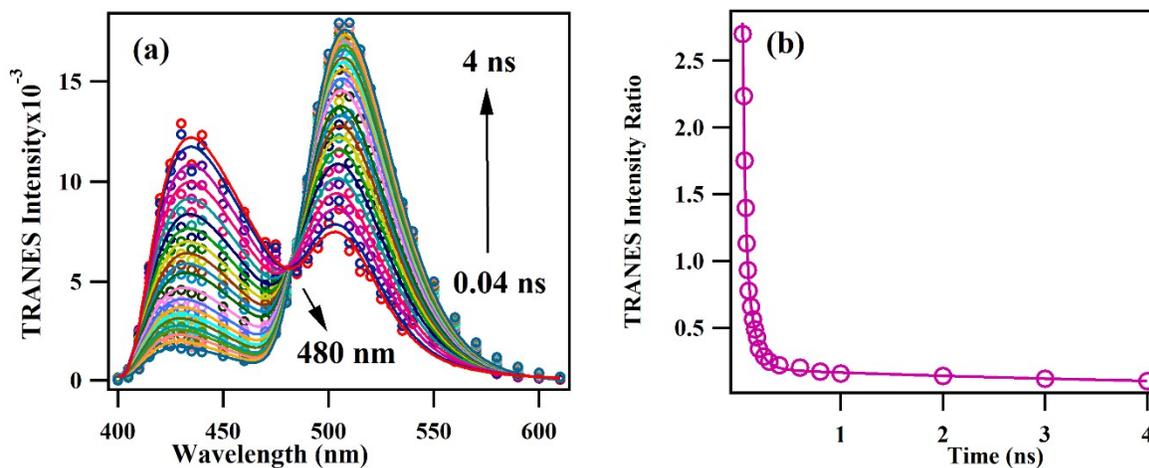
Figure S16. (a)TRANES of HPTS in water in the presence of 2.1 μM PDADMAC at various times and (b) The variation of TRANES intensity ratio of protonated/deprotonated band of HPTS with times. The pH of the medium is 2.5.
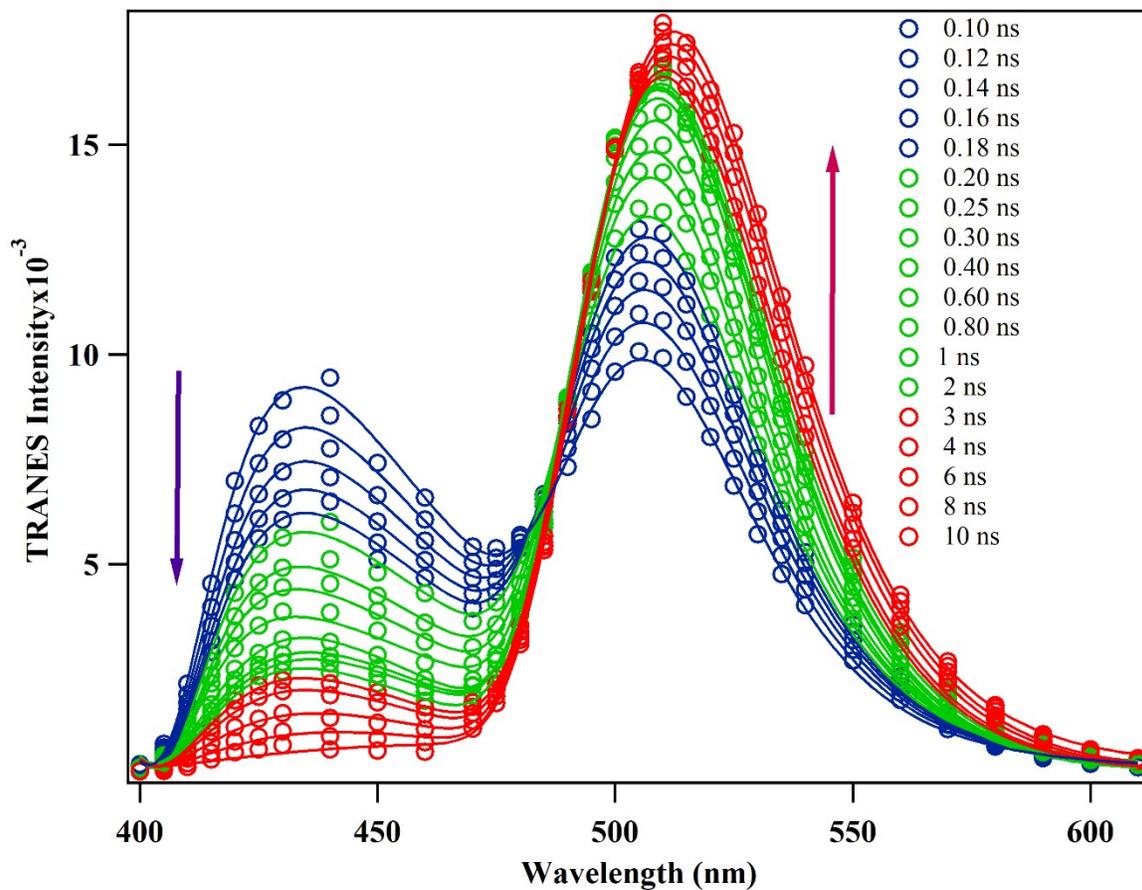
Figure S17. TRANES profile of HPTS in micellar SB12- 0.084 µM PDADMAC.
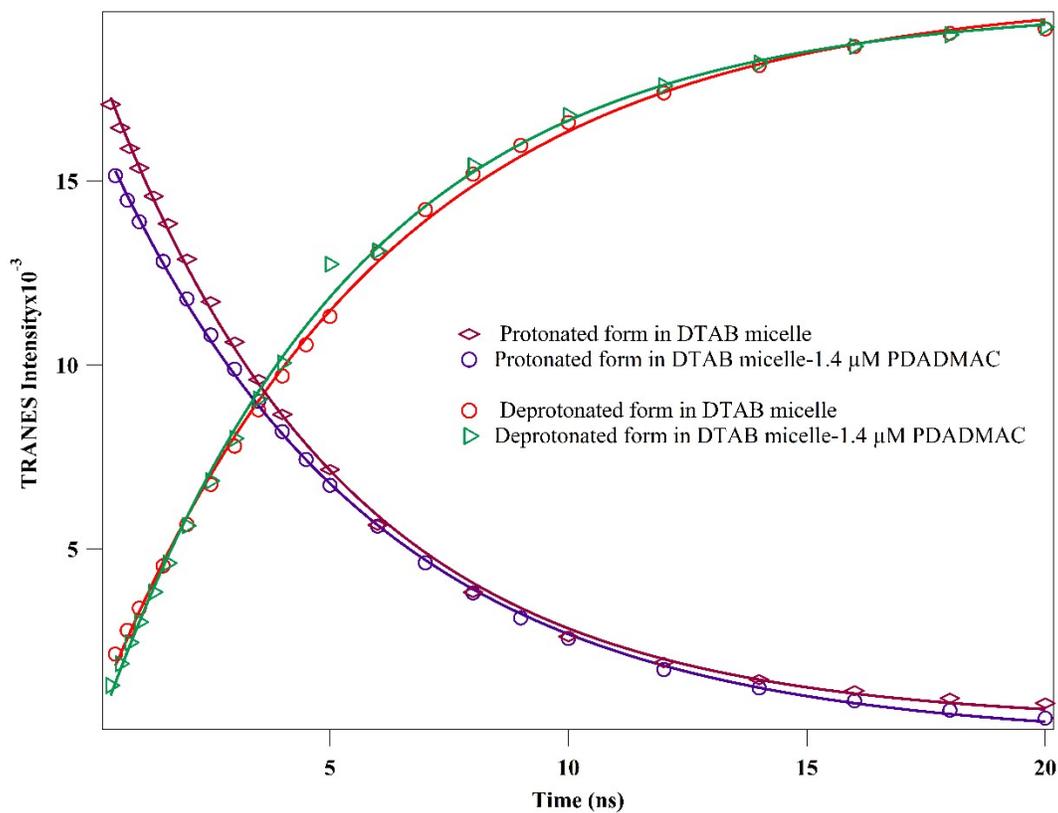
Figure S18. Comparison of the time evolution of TRANES intensities of the protonated and deprotonated moieties of HPTS in micellar DTAB medium in the absence and presence of 1.4 µM PDADMAC.
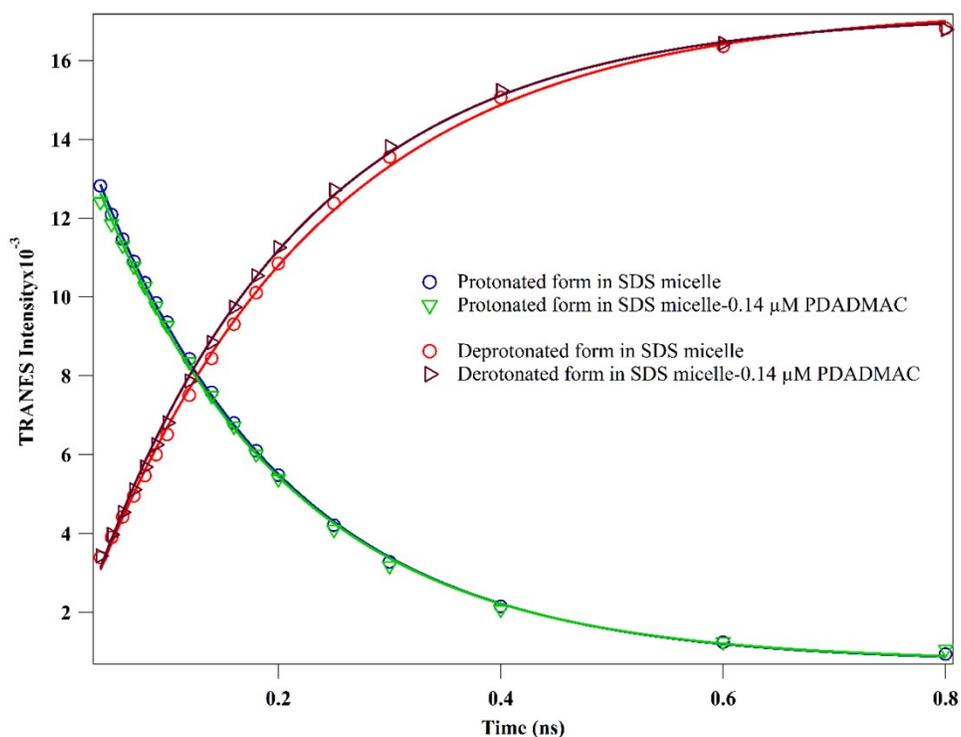
Figure S19 Comparison of the time evolution of TRANES intensities of the protonated and deprotonated moieties of HPTS in micellar SDS in the absence and presence of 0.14 μM PDADMAC.

Table S2. Time evolution of the protonated and deprotonated moieties of HPTS residing in the respective systems

System	[PDADMAC] (μM)	Protonated		Deprotonated	
		τ_1 (ps) (β_1)	τ_2 (ps) (β_2)	τ_1 (ps) (β_1)	τ_2 (ps) (β_2)
Water	0	170 (1)		190 (-1)	
	0.028	145 (1)		160 (-1)	
	2.1	90 (0.88)	1410 (0.12)	100 (-0.89)	1320 (-0.11)
SB12 micelle	0	7060		7610	

		(1)		(-1)	
	0.056#	140 (1)		120 (1)	
	0.056¥	6890 (1)		7750 (1)	
	0.084	120 (0.93)	2360 (0.07)	170 (-1)	
	2.1	100 (0.75)	2000 (0.25)	130 (-0.85)	2200 (-0.15)
SDS micelle	0	170 (1)		190 (-1)	
	0.14	170 (1)		200 (1)	
DTAB micelle	0	5070 (1)		5320 (-1)	
	1.4	5990 (1)		5640 (-1)	

\# Components are obtained by fitting the initial region of the intensity for that particular concentration.

¥ Components are obtained by fitting the end region of the intensity for that particular concentration.
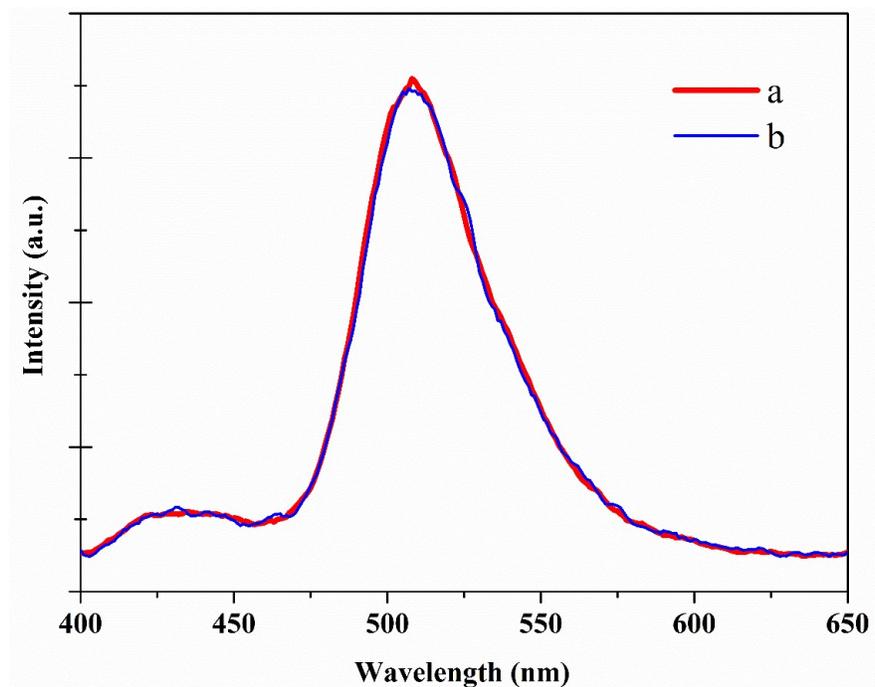
Figure S20. Emission spectra of HPTS in (a) 0.084 μM PDADMAC solution and (b) after the addition of 10 mM SB12. The reverse addition (first PDADMAC and then SB12) does not lead to any change.
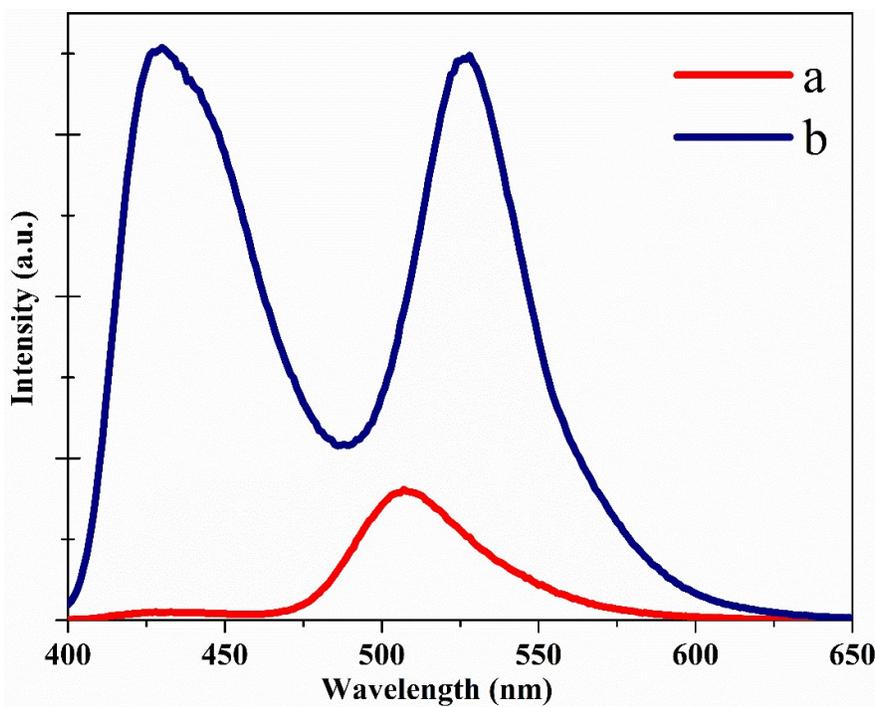
Figure S21. Emission spectra of HPTS in (a) 0.084 μM PDADMAC solution and (b) after the addition of 30 mM DTAB. The reverse addition (first PDADMAC and then DTAB) dramatically changes the emission spectrum.
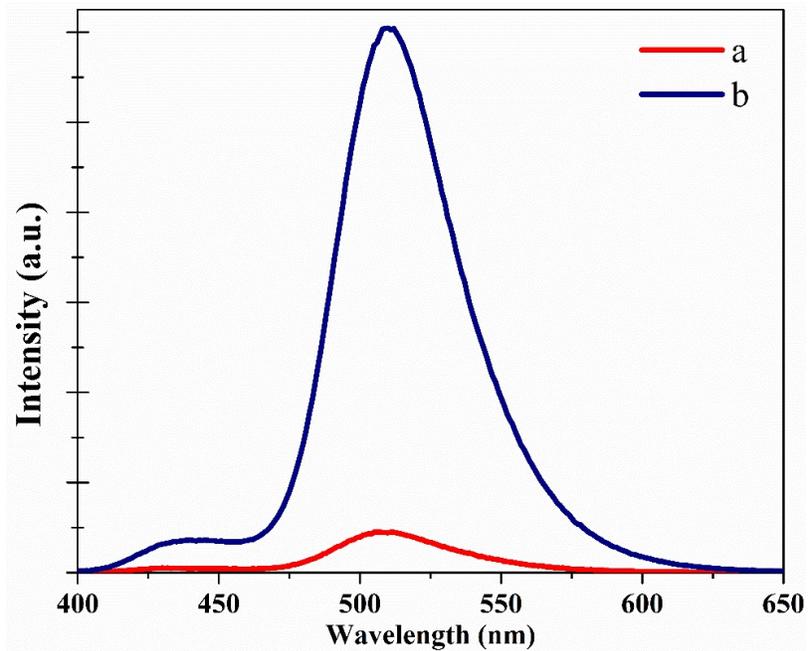
Figure S22. Emission spectra of HPTS in (a) 0.084 µM PDADMAC solution and (b) after the addition of 20 mM SDS. The reverse addition (first PDADMAC and then SDS) leads to a remarkable change in the emission spectrum.