<u>**Electronic Supplementary Information:**</u>

Solvation dynamics and rotational relaxation of Coumarin 153 in mixed micelles of

Triton X-100 and cationic gemini surfactants: Effect of composition and spacer chain

length of gemini surfactants

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**Table S1**: FT-IR and ^{1}H NMR data for the synthesized gemini surfactants.

| Gemini surfactants	FT-IR ν^{a}/cm^{-1}	^{1}H-NMR
12-3-12	2924 (CH$_3$) 1466 (CH2),	**(400 MHz, CDCl$_3$) δ:** 0.85 (t, J = 6.9 Hz, 6H, CH$_3$), 1.35 − 1.19 (m, 36H, CH$_2$), 1.80 − 1.69 (m, 4H, CH$_2$), 2.72 − 2.58 (m, 2H, CH$_2$), 3.39 (s, 12H, CH$_3$), 3.56 − 3.45 (m, 4H, CH$_2$), 3.85 − 3.72 (m, 4H, CH$_2$).
12-6-12	2924 (CH$_3$) 1466 (CH2),	**(400 MHz, CDCl$_3$) δ:**0.84 (t, J = 6.8 Hz, 6H, CH$_3$), 1.34 − 1.18 (m, 36H, CH$_2$), 1.57 − 1.45 (m, 4H, CH$_2$), 1.73 - 1.62 (m, 4H, CH$_2$), 2.00 − 1.89 (m, 4H, CH$_2$), 3.36 (s, 12H, CH$_3$), 3.50 − 3.43 (m, 4H, CH$_2$), 3.72 − 3.60 (m, 4H, CH$_2$).
12-8-12	2924 (CH$_3$) 1466 (CH2),	**(400 MHz, CDCl$_3$) δ:**0.80 (t, J = 6.8 Hz, 6H, CH$_3$), 1.37 − 1.16 (m, 44H, CH$_2$), 1.69 − 1.58 (m, 4H, CH$_2$), 1.85 − 1.69 (m, 4H, CH$_2$), 3.28 (s, 12H, CH$_3$), 3.47 − 3.37 (m, 4H, CH$_2$), 3.61 − 3.48 (m, 4H, CH$_2$).
12-12-12	2924 (CH$_3$) 1466 (CH2),	**(400 MHz, CDCl$_3$) δ:**0.82 (t, J = 6.8 Hz, 6H, CH$_3$), 1.36 − 1.17 (m, 52H, CH$_2$), 1.74 − 1.59 (m, 8H, CH$_2$), 3.32 (s, 12H, CH$_3$), 3.51 − 3.44 (m, 4H, CH$_2$), 3.58 − 3.51 (m, 4H, CH$_2$).

[a] = frequency

Table S2 UV-visible absorption peak maxima (λ_{max}^{ab}) and fluorescence peak maxima[a] (λ_{max}^{fl}) of C-153 in mixed systems, TX-100+12-s-12 (s = 8 and 12), Cmc and E$_T$(30) values of mixed systems, TX-100+12-s-12 (s = 8 and 12)

$X_{12\text{-}8\text{-}12}$	cmc (mM)	λ_{max}^{ab} (nm)	λ_{max}^{fl} (nm)	$E_T(30)$ (kcal mol^{-1})	$X_{12\text{-}12\text{-}12}$	cmc (mM)	λ_{max}^{ab} (nm)	λ_{max}^{fl} (nm)	$E_T(30)$ (kcal mol^{-1})
0.0	0.41	429	530	47.9	0.0	0.41(0.33)	429	530	47.9
0.2	0.42	432	538	51.9	0.2	0.41(0.34)	432	538	51.9
0.4	0.42	435	540	53.1	0.4	0.43(0.36)	435	540	53.1
0.6	0.43	438	541	53.9	0.6	0.45(0.38)	438	541	53.9
0.8	0.45	438	542	55.1	0.8	0.50(0.40)	438	542	55.1
1.0	0.81	438	542	55.1	1.0	0.63(0.46)	438	542	55.1
Water	-	433	552	63.1	Water	-	433	552	63.1

[a]λ_{ex} = 375 nm. Cmc values in parenthesis are taken from the ref 47.
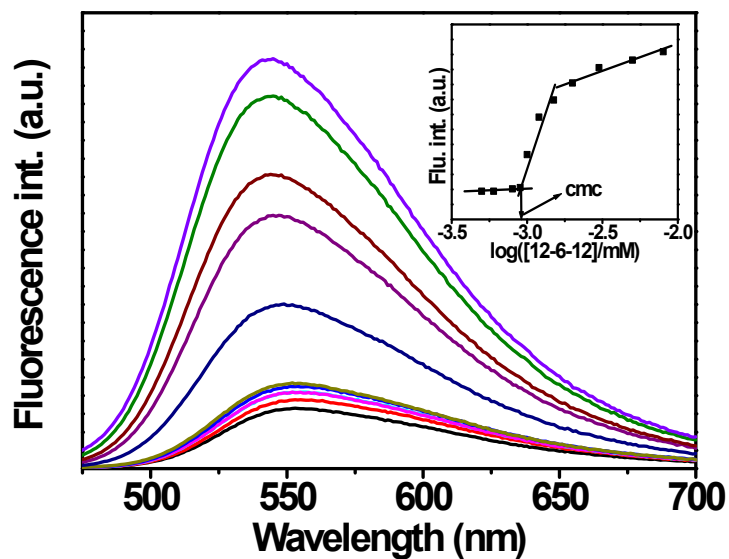
Figure S1 Fluorescence spectra of C-153 with increasing concentration (from bottom to top) of 12-6-12. Inset shows the plot of fluorescence intensity with concentration of 12-6-12, (λ_{exc} = 375 nm).
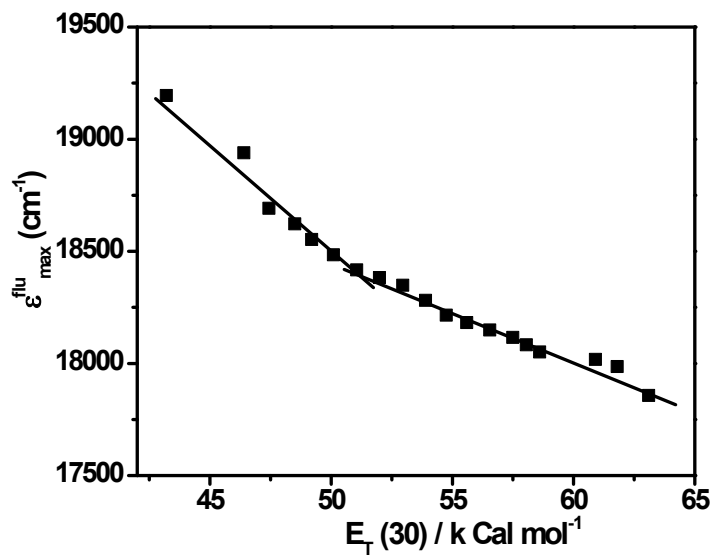
Figure S2 Plot of fluorescence energy at peak maxima (ε_{max}^{fl}) of C-153 versus $E_T(30)$ of different percentage of dioxane-water mixture. λ_{ex} = 375 nm.

Note1: 1,6-diphenyl-1,3,5-hexatriene (DPH) has been used as a probe molecule to estimate the microviscosity (η_m) for pure and mixed surfactant systems at 298.15 K using following Debye-Stokes-Einstein relation (Equation S1)[71, 72]:

$$\eta_m = k\, T\tau_R\, / \, \upsilon_h \tag{S1}$$

where k is Boltzman constant, T is temperature in Kelvin scale, τ_R is rotational correlation time of DPH and υ_h is hydrodynamic volume of DPH. The υ_h value is taken as 313 Å^3.[72] The rotational correlation time, τ_R is obtained from Perrin's equation (Equation S2)[15] :

$$\tau_R = \tau_f \, / \, \left[\left(r_o / r \right) - 1 \right] \tag{S2}$$

where τ_f and r are florescence lifetime and steady-state fluorescence anisotropy of DPH, respectively and r_o is the steady-state fluorescence anisotropy of DPH in a highly viscous solvent and is taken to be 0.362.[73]

Table S3a Fluorescence anisotropy (r)[a], excited singlet state lifetime (τ_f)[b], rotational correlation time (τ_R) of DPH, microviscosities (η_m) of micelles of pure and mixed surfactant systems of TX-100 + 12-3-12 and TX-100 + 12-6-12. Total concentration of surfactants = 10 mM

$X_{12\text{-}3\text{-}12}$	r	τ_f (ns)	χ^2	τ_R (ns)	η_m (mPa s)	$X_{12\text{-}6\text{-}12}$	r	τ_f (ns)	χ^2	τ_R (ns)	η_m (mPa s)
0.0	0.128	7.52	1.0	4.11	54.05	0.0	0.128	7.52	1.0	4.11	54.05
0.2	0.115	6.90	1.0	3.21	42.25	0.2	0.112	6.75	1.1	3.02	39.76
0.4	0.110	6.28	1.1	2.74	36.02	0.4	0.098	6.11	1.0	2.27	29.84
0.6	0.098	5.82	1.0	2.16	28.38	0.6	0.095	5.57	1.0	1.98	26.04
0.8	0.097	5.63	1.1	2.06	27.09	0.8	0.089	5.34	1.0	1.74	22.87
1.0	0.094	5.38	1.0	1.88	24.70	1.0	0.075	5.21	1.1	1.36	17.90

[a]Fluorescence anisotropy at 430 nm. λ_{ex} = 375 nm. [a][DPH] = 5 μM. A solution of DPH was prepared in tetrahydrofuran. [b]λ_{ex} = 375 nm, λ_{em} = 430 nm.

Table S3b Fluorescence anisotropy $(r)^a$, excited singlet state lifetime $(\tau_f)^b$, rotational correlation time (τ_R) of DPH, microviscosities (η_m) of micelles of pure and mixed surfactant systems of TX-100+12-8-12 and TX-100+12-12-12. Total concentration of surfactants = 10 mM

$X_{12\text{-}8\text{-}12}$	r	τ_f (ns)	χ^2	τ_R (ns)	η_m (mPa s)	$X_{12\text{-}12\text{-}12}$	r	τ_f (ns)	χ^2	τ_R (ns)	η_m (mPa s)
0.0	0.128	7.52	1.0	4.11	54.05	0.0	0.128	7.52	1.0	4.11	54.05
0.2	0.102	6.72	1.1	2.64	34.68	0.2	0.091	6.40	1.0	2.15	28.27
0.4	0.094	6.18	1.0	2.17	28.51	0.4	0.083	6.03	1.0	1.79	23.59
0.6	0.091	5.37	1.0	1.80	23.68	0.6	0.076	5.89	1.0	1.56	20.57
0.8	0.087	5.50	1.1	1.74	22.85	0.8	0.065	5.88	1.1	1.29	16.91
1.0	0.068	5.50	1.0	1.27	16.70	1.0	0.056	5.82	1.0	1.07	14.10

[a]Fluorescence anisotropy at 430 nm. λ_{ex} = 375 nm. [a][DPH] = 5 μM. A solution of DPH was prepared in tetrahydrofuran. [b]λ_{ex} = 375 nm, λ_{em} = 430 nm.

Table S4a Rotational Relaxation Parameters for C-153 in the Mixed Micelles of TX-100+12-s-12, 2Br$^-$ with s = 3 and 6.

$X_{12\text{-}3\text{-}12}$	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$<\tau_r>$ (ns)	$X_{12\text{-}6\text{-}12}$	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$<\tau_r>$ (ns)
0.0	0.27	0.67	0.73	6.23	4.73	0.0	0.27	0.67	0.73	6.23	4.73
0.2	0.46	0.48	0.54	8.21	4.65	0.2	0.39	0.50	0.61	5.92	3.81
0.4	0.50	0.49	0.50	8.23	4.36	0.4	0.40	0.57	0.60	5.75	3.68
0.6	0.50	0.46	0.50	7.69	4.01	0.6	0.40	0.37	0.60	5.18	3.26
0.8	0.52	0.43	0.48	5.85	3.03	0.8	0.43	0.48	0.57	3.87	2.41
1.0	0.81	0.65	0.19	5.74	1.63	1.0	0.54	0.41	0.46	2.31	1.28

Table S4b Rotational Relaxation Parameters for C-153 in the Mixed Micelles of TX-100+12-s-12, 2Br$^-$ with s = 8 and 12.

$X_{12\text{-}8\text{-}12}$	a_{1r}	τ_{1r} (ns)	α_{2r}	τ_{2r} (ns)	$<\tau_r>$ (ns)	$X_{12\text{-}12\text{-}12}$	α_{1r}	τ_{1r} (ns)	α_{2r}	τ_{2r} (ns)	$<\tau_r>$ (ns)
0.0	0.27	0.67	0.73	6.23	4.73	0.0	0.27	0.67	0.73	6.23	4.73
0.2	0.81	0.85	0.19	8.35	2.28	0.2	0.76	0.66	0.24	4.79	1.65
0.4	0.78	0.64	0.22	5.40	1.69	0.4	0.65	0.57	0.35	3.29	1.52
0.6	0.55	0.55	0.45	2.65	1.50	0.6	0.73	0.56	0.27	3.15	1.26
0.8	0.44	0.36	0.56	2.05	1.31	0.8	0.75	0.54	0.25	3.39	1.25
1.0	0.50	0.35	0.50	2.19	1.27	1.0	0.49	0.28	0.51	2.14	1.23

Note 2: To explore the bimodal behaviour of rotational motions, the two-step and wobbling-in-the cone model have been used.[10,21,41] Various rotational motions are (1) the lateral diffusion of the probe molecule along the spherical surface of the micelle, (2) the wobbling

motion of the probe in the micelle, and (3) the rotational motion of the micelle as a whole containing the probe molecule. The two-step model describes (1) and (3) motions. According to this model the slow rotational relaxation is because of the lateral diffusion of the probe molecule and the rotational motion of the micelle as a whole. The slow rotational relaxation time (τ_{2r}) is related to the time for lateral diffusion of the probe molecule (τ_D) and the time for rotational motion of the micelle as a whole (τ_m) as follows (Equation S3):

$$\frac{1}{\tau_{2r}} = \frac{1}{\tau_D} + \frac{1}{\tau_m} \tag{S3}$$

τ_m can be calculated using Debye-Stokes-Einstein (DSE) equation assuming the rotation of the spherical micelle in a solvent which is water in the present case with sticking boundary conditions as follows[72]:

$$\tau_m = \frac{4\pi\eta r_h^3}{3kT} \tag{S4}$$

where η is the shear viscosity of water, r_h is the hydrodynamic radius of the micelle, k is the Boltzmann constant and T is the temperature in Kelvin scale.

The time constant for the wobbling motion (τ_{wob}) of the probe molecule can be calculated by using the following equation S5:

$$\frac{1}{\tau_{1r}} = \frac{1}{\tau_{wob}} + \frac{1}{\tau_{2r}} \tag{S5}$$

where τ_{1r} and τ_{2r} are the observed fast and slow rotational components.

To obtain information about the motional restriction of the probe within the micelles, the generalized order parameter, S, has been calculated by using $S^2 = a_{2r}$, where a_{2r} is the amplitude of the slower component. Values of order parameter, S exist between 0 and 1.[10,21,41] 0 value of S, indicates unrestricted motion of the probe molecule and 1 for completely

restricted motion. Cone angle (θ_o) and wobbling diffusion coefficient (D_W) have also been calculated using equations S6 and S7, respectively:

$$\theta_0 = \cos^{-1}\left[\frac{1}{2}\left((1+8S)^{1/2}-1\right)\right] \tag{S6}$$

$$D_w = \frac{7\theta^2}{24\tau_D} \tag{S7}$$
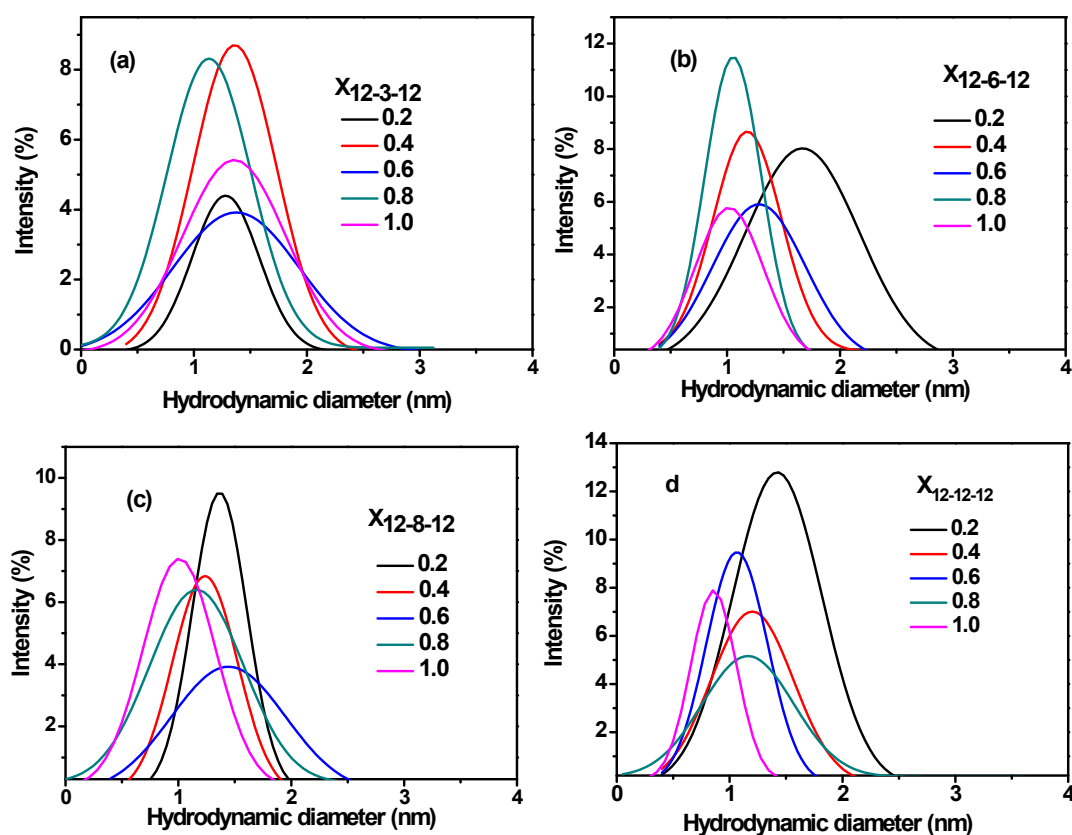
where θ is cone angle in radians.

Figure S3 The size distribution graph for the micelles of TX-100 + 12-s-12 obtained from DLS measurement (a) s = 3, (b) s = 6, (c) s = 8, and (d) s = 12.