

**Supplementary Information for**

**Modulated Photophysics and Rotational-Relaxation Dynamics of Coumarin 153 in**

**Nonionic Micelles: The Role of Headgroup Size and Tail Length of the Surfactants**

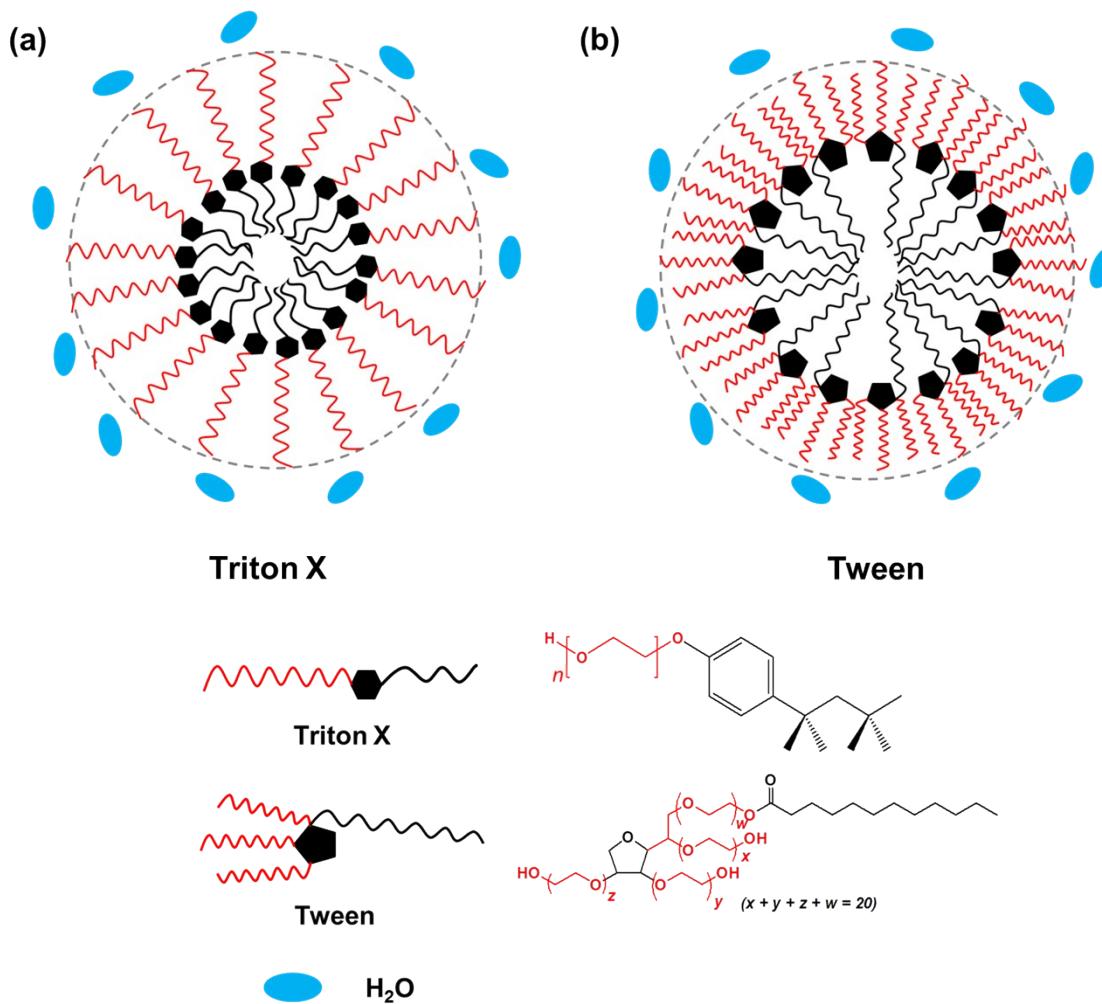
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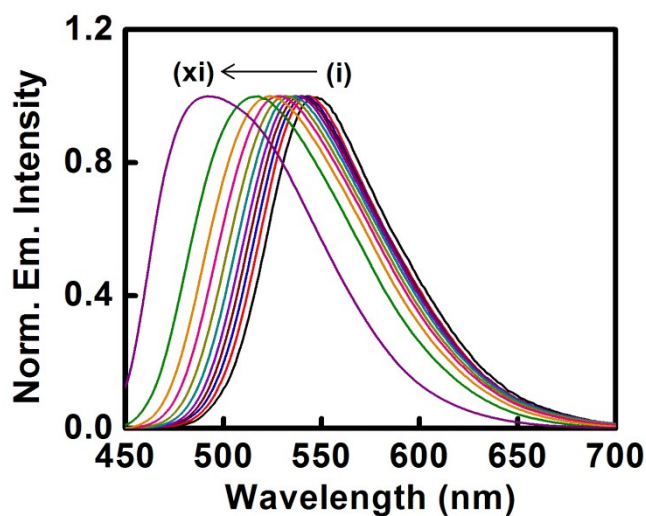
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**Scheme S1: Simplified schematic structure of (a) Triton X and (b) Tween micellar units. The description of the structures of the surfactant monomers are given in the lower panel. The ellipsoid represents a paradigm for water molecule.**



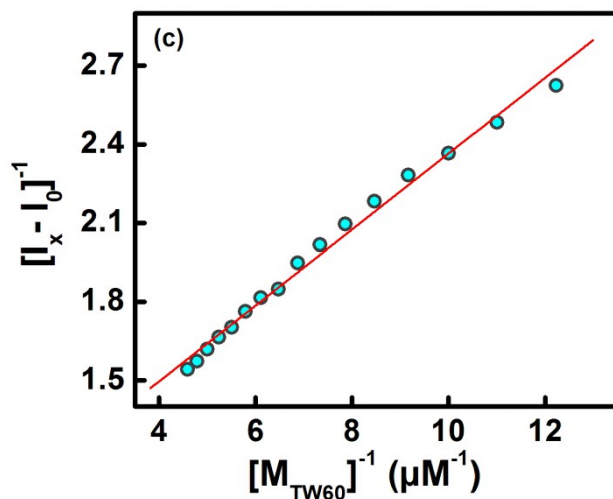
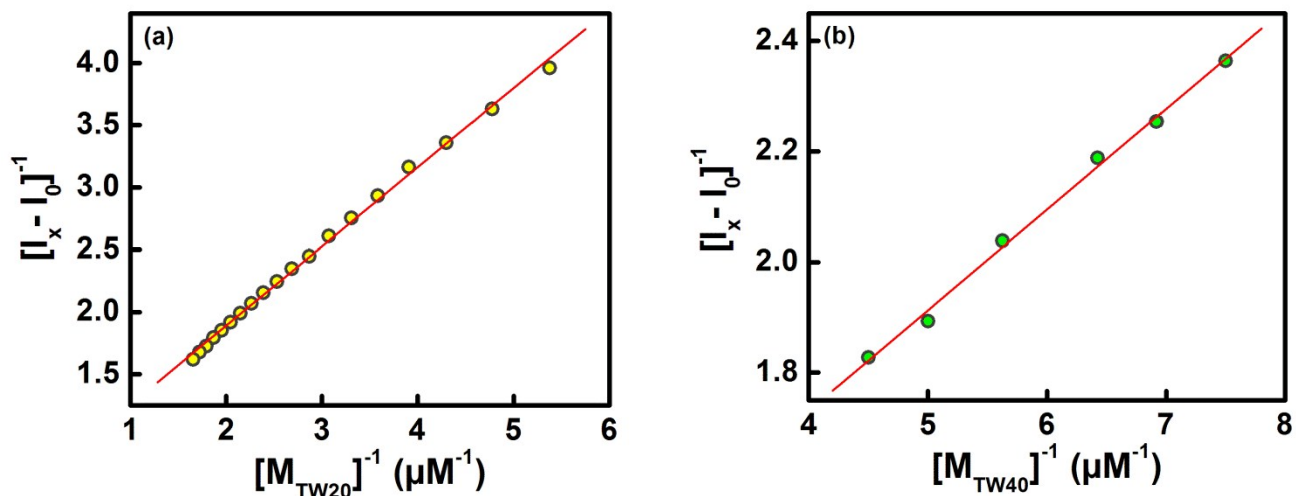
The Triton X family of surfactants contains a *p-tert*-octylphenyl (OP) hydrophobic moiety with a poly(ethylene oxide) (PEO) constituting the hydrophilic part. The Triton X series of surfactant employed in the present study are: Triton X-165 (OP + 16 PEO), Triton X-100 (OP + 9.5 PEO), and Triton X-114 (OP + 7.5 PEO).

Tween family of surfactants contains 20 poly(ethylene oxide) hydrophilic headgroups with varying alkyl chain lengths. The Tween series of surfactants employed in the present study are: Tween 20 (12 carbon chain length), Tween 40 (16 carbon chain length), and Tween 60 (18 carbon chain length).

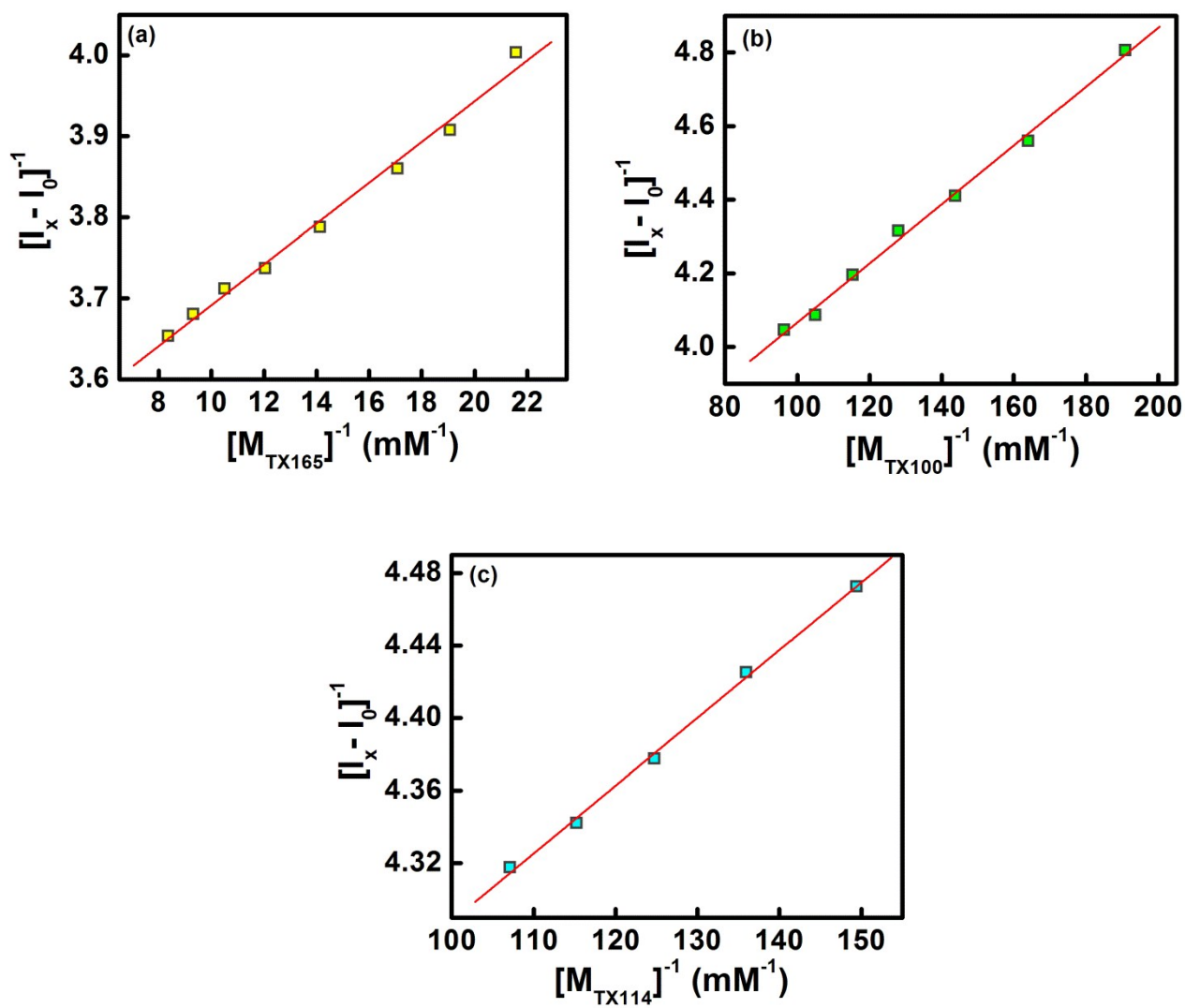


**Figure S1:** Normalized emission profile of C153 in varying composition of water/1,4-dioxane reference solvent mixture of varying polarity. Curves (i) → (xi) correspond to % water (by vol.) = 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0.

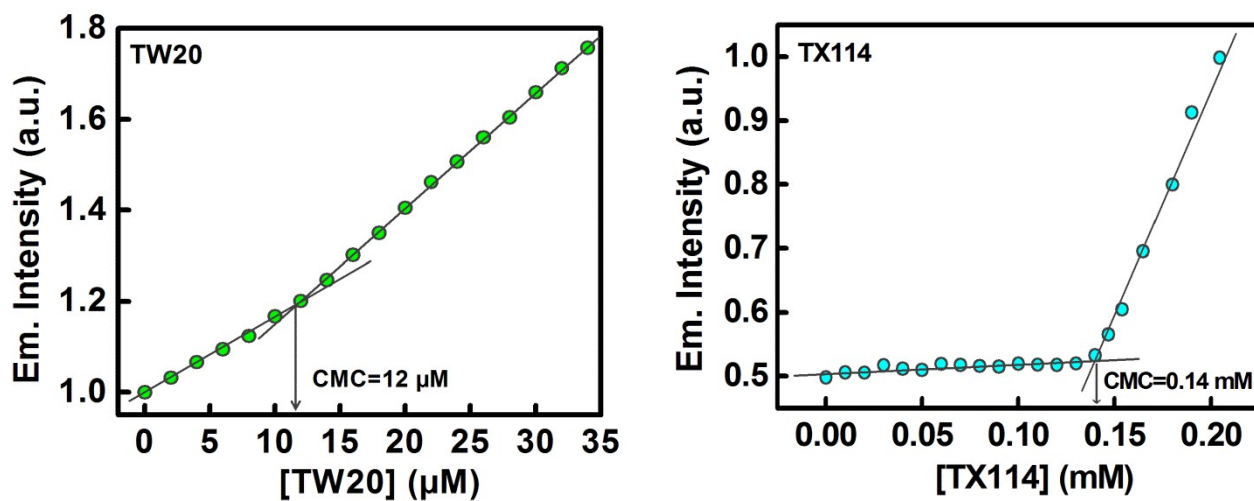
The aim of the data presented in Figure 4 of the text (Section 3.2) is to find an estimate of the local polarity of the C153 binding site within the micellar systems. For this purpose the spectroscopic properties of C153 in varying composition of water/1,4-dioxane having varying polarity (on  $E_T(30)$  scale) is directly compared with those obtained within the micellar aggregates. The method described in Figure 4 is a standard protocol reported in the literature.<sup>S1-S6</sup> Here, the data are plotted as  $\lambda_{em}$  vs.  $E_T(30)$  and a standard equation is generated from the linear fit in the form:  $\lambda_{em} = 421 + 2.1 \times E_T(30)$ . The micropolarity of C153 in the vicinity of the binding site within the micelles is then estimated by interpolating the  $\lambda_{em}$  on the above equation. The goodness of the presently analyzed linear fit is assessed from a reasonably acceptable correlation coefficient of  $r^2 = 0.99$ .



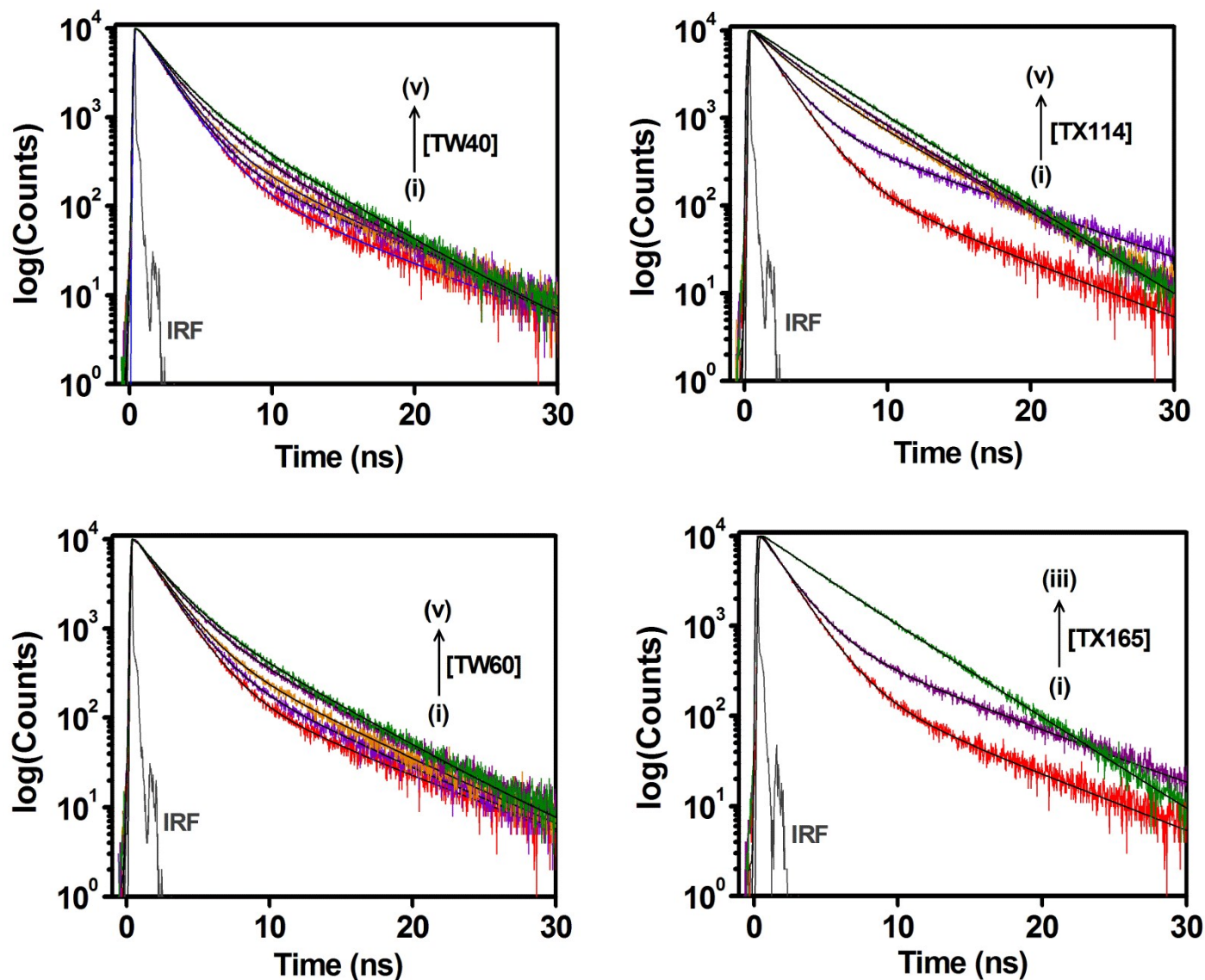
**Figure S2:** Double reciprocal plot of  $1/[I_x - I_0]$  vs.  $1/[M_{\text{Surfactant}}]$  for the determination of probe-micelle binding constant for interaction of C153 with (a) TW20, (b) TW40, and (c) TW60.



**Figure S3:** Double reciprocal plot of  $1/[I_x - I_0]$  vs.  $1/[M_{\text{Surfactant}}]$  for the determination of probe-micelle binding constant for interaction of C153 with (a) TX165, (b) TX100, and (c) TX114.



**Figure S4:** Representative examples of plot of variation of emission intensity of C153 with increasing surfactant concentrations (left: TW20 and right: TX114) for determination of CMC of the respective surfactants.



**Figure S5:** Representative examples of fluorescence decay transients of C153 in various micellar environments as specified in the figure legend. Left panel: curves (i)  $\rightarrow$  (v) represent 0, 4, 6, 10, 20  $\mu$ M TW40 (top), and 0, 4, 10, 15, 20  $\mu$ M TW60 (bottom). Right panel: Curves (i)  $\rightarrow$  (v) represent 0, 0.06, 0.13, 0.25, 0.5 mM TX114 (top), and curves (i)  $\rightarrow$  (iii) represent 0, 0.5, 2.5 mM TX165 (bottom). IRF: instrument response function. The black solid lines are the fitted curves.

**Table S1: (a) Time-resolved fluorescence decay parameters of C153 in various micellar environments of the Tween series**

<b>System</b>	<b><math>\tau_1^a</math> (ns)</b>	<b><math>\tau_2^a</math> (ns)</b>	<b><math>\alpha_1</math> (%)</b>	<b><math>\alpha_2</math> (%)</b>
<b>[TW20]</b>				
<b>(<math>\mu\text{M}</math>)</b>				
0	1.66	6.93	91	9
2	1.68	6.63	84	16
6	1.71	5.43	78	22
8	1.72	5.28	76	24
12	1.75	5.10	72	28
16	1.74	4.81	65	35
20	1.76	4.69	61	39
22	1.79	4.69	57	43
30	1.79	4.51	52	48
38	1.87	4.46	45	55
<b>[TW40]</b>				
<b>(<math>\mu\text{M}</math>)</b>				
2	1.68	6.91	83	17
4	1.71	6.27	81	19
6	1.72	6.01	79	21
10	1.75	5.39	74	26
15	1.78	5.21	69	31
20	1.79	4.96	63	37
25	1.79	4.79	58	42
35	1.83	4.65	51	49
40	1.84	4.50	44	56
<b>[TW60]</b>				
<b>(<math>\mu\text{M}</math>)</b>				
2	1.69	6.13	82	18
4	1.71	5.94	79	21
6	1.72	5.77	76	24
10	1.72	5.17	71	29
15	1.78	5.25	64	36
20	1.81	5.09	61	39
25	1.82	4.97	57	43
30	1.83	4.88	53	47
40	1.87	4.69	46	53

<sup>a</sup>± 4%.



**Table S1: (b) Time-resolved fluorescence decay parameters of C153 in various micellar environments of the Triton X series**

<b>System</b>	$\tau_1^a$ <b>(ns)</b>	$\tau_2^a$ <b>(ns)</b>	$\alpha_1$ <b>(%)</b>	$\alpha_2$ <b>(%)</b>
<b>[TX165]</b>				
<b>(mM)</b>				
0	1.66	6.93	91	9
0.5	1.68	7.33	91	9
1	1.68	7.08	91	9
2.5	2.19	4.26	87	13
<b>[TX100]</b>				
<b>(mM)</b>				
0.13	1.66	6.84	93	7
0.25	1.81	5.11	74	26
0.38	1.92	4.38	31	69
0.5	2.21	4.34	16	84
<b>[TX114]</b>				
<b>(mM)</b>				
0.063	1.70	7.66	89	11
0.13	1.98	4.31	69	31
0.19	2.00	4.76	55	45
0.25	2.04	4.5	42	58
0.38	2.11	4.35	21	79
0.5	2.27	4.27	13	87

<sup>a</sup>± 4%.

**Table S2: Time-resolved fluorescence decay parameters of C153 in various compositions of water/1,4-dioxane reference solvent mixture of varying polarity (as indicated on  $E_T(30)$  scale)**

<b>% Water/1,4-Dioxane</b>	<b><math>E_T(30)</math></b>	<b><math>\tau_1^a</math></b>	<b><math>\tau_2^a</math></b>	<b><math>\alpha_1</math></b>	<b><math>\alpha_2</math></b>	<b><math>\langle\tau_f\rangle</math></b>
<b>(v/v)</b>	<b>(kcal mol<sup>-1</sup>)</b>	<b>(ns)</b>	<b>(ns)</b>	<b>(%)</b>	<b>(%)</b>	<b>(ns)</b>
100/0	63.1	1.65	4.55	87	13	2.03
80/20	58.6	1.55	2.55	3	97	2.52
70/30	57.1	1.42	2.81	1	99	2.79
50/50	53.6	1.76	3.46	1	99	3.44
40/60	52.3	1.96	3.84	1	99	3.82
20/80	49		4.63		100	4.63
0/100	36		5.47		100	5.47

<sup>a</sup>± 4%.

**Table S3: (a) Different photophysical parameters of C153 in various nonionic micellar environments of the Tween series**

<b>[TW20] (mM)</b>	<b><math>\langle\tau_f\rangle</math> (ns)</b>	<b><math>\Phi_f</math></b>	<b><math>10^{-7}k_r</math> (s<sup>-1</sup>)</b>	<b><math>10^{-8}k_{nr}</math> (s<sup>-1</sup>)</b>
0	2.30	0.079	3.43	3.99
2	2.47	0.082	3.31	3.71
4	2.57	0.085	3.29	3.55
8	2.58	0.091	3.53	3.52
12	2.70	0.098	3.63	3.34
16	2.80	0.106	3.78	3.19
20	2.91	0.116	3.99	3.04
22	3.06	0.129	4.22	2.85
30	3.10	0.136	4.39	2.78
38	3.29	0.156	4.74	2.56
<b>[TW40] (mM)</b>				
2	2.55	0.083	3.24	3.59
4	2.56	0.087	3.38	3.56
6	2.63	0.091	3.44	3.45
10	2.69	0.098	3.64	3.36
15	2.83	0.106	3.74	3.16
20	2.96	0.119	4.02	2.98
25	3.05	0.127	4.16	2.86
35	3.21	0.14	4.36	2.68
40	3.32	0.16	4.81	2.53
<b>[TW60] (mM)</b>				
4	2.61	0.087	3.32	3.49
6	2.70	0.091	3.35	3.37
10	2.73	0.099	3.65	3.29
15	3.03	0.113	3.72	2.92
20	3.08	0.122	3.96	2.85
25	3.18	0.134	4.21	2.72
30	3.25	0.142	4.38	2.64
40	3.37	0.159	4.72	2.49

**Table S3: (b) Different photophysical parameters of C153 in various nonionic micellar environments of the Triton X series**

<b>[TX165]</b> <b>(mM)</b>	<b><math>\langle\tau_f\rangle</math></b> <b>(ns)</b>	<b><math>\Phi_f</math></b>	<b><math>10^{-7}k_r</math></b> <b>(s<sup>-1</sup>)</b>	<b><math>10^{-8}k_{nr}</math></b> <b>(s<sup>-1</sup>)</b>
0	2.14	0.079	3.68	4.31
0.50	2.19	0.084	3.86	4.19
1.0	2.19	0.086	3.92	4.17
2.5	2.45	0.396	16.2	2.46
<b>[TX100]</b>				
<b>(mM)</b>				
0.13	2.03	0.082	4.04	4.52
0.25	2.65	0.11	4.15	3.36
0.38	3.61	0.374	10.4	1.73
0.50	4.01	0.451	11.2	1.37
<b>[TX114]</b>				
<b>(mM)</b>				
0.063	2.30	0.080	3.48	4.00
0.13	2.70	0.099	3.66	3.33
0.19	3.25	0.126	3.87	2.68
0.25	3.46	0.111	3.21	2.56
0.38	3.88	0.172	4.43	2.13
0.50	4.02	0.234	5.82	1.91

**References:**

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