Supporting Information

Unique Effect of Cholesterol on Modifying the Aggregation Behavior of Surfactant Assemblies: Investigation of Photophysical and Dynamical properties of 2,2′-Bipyridine-3,3′-diol, $BP(OH)_2$ in Micelles and Surfactant-Cholesterol Forming Vesicles

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Useful Equations to Calculate the Analytical parameters for Rotational Motion:

The experimentally measured τ_{slow} and τ_{fast} are related to τ_D, D_W, τ_e and τ_M by the equations proposed by Quitevis et al.

$$\frac{1}{\tau_{slow}} = \frac{1}{\tau_D} + \frac{1}{\tau_M} \qquad (1)$$

$$\frac{1}{\tau_{fast}} = \frac{1}{\tau_e} + \frac{1}{\tau_{slow}} \qquad (2)$$

For the calculation of τ_M, we have used Stokes-Einstein-Debye equation:

$$\tau_M = \frac{4\pi\eta r_h^3}{3kT} \qquad (3)$$

where η, r_h, k and T represent viscosity of the bulk medium, hydrodynamic radius, Boltzmann constant and absolute temperature, respectively.

The lateral diffusion coefficient D_L is obtained by using the following equation:

$$D_L = \frac{r_h^2}{6\tau_D} \qquad (4)$$

Besides dynamical parameters, the order parameter (S) is calculated using equation 5 to get an idea about the location of probe molecules and restriction imposed on it by surrounding environment.

$$S^2 = a_{slow} \qquad (5)$$

where S^2 is square of the order parameter. The magnitude of S denotes the spatial restriction. In case of unrestricted motion, one can assume its value is '0', whereas in completely restricted motion it becomes '1'

The cone angle, θ_0 and wobbling diffusion coefficient, D_W has been estimated using the following equation 6 and 7.

$$\theta_0 = cos^{-1}\left[\frac{1}{2}\left((1+8S)^{1/2} - 1\right)\right] \qquad (6)$$

$$D_W = \frac{7\theta^2}{24\tau_e} \qquad (7)$$

We have used the following Stokes-Einstein-Debye equation to calculate the microviscosity of the vesicle bilayer:

$$< \tau_r >= \frac{\eta_{mic} V}{kT} \qquad (8)$$

Where V, $< \tau_r >$ and T represent the volume of probe molecule, average rotational time and absolute temperature, respectively. The volume of $BP(OH)_2$ was taken as 157 $Å^3$.

But some approximations are applied for the calculation of microviscosity using Stokes-Einstein-Debye equation. First, experimentally obtained $<\tau_r>$ has two contributions: (i) owing to rotation of the probe in the aggregate and (ii) rotation of the aggregate itself.

If we consider the average reorientation time due to the rotation of the probe molecule as $<\tau_{rP}>$ and rotation of the vesicle aggregate as τ_M, then these parameters can be related to average rotational time, $< \tau_r >$ by following equation:

$$\frac{1}{< \tau_r >} = \frac{1}{< \tau_{rp} >} + \frac{1}{\tau_M} \qquad (9)$$

The contribution of τ_M depends upon the size of the aggregates. If the size of aggregate is small and rotation of the probe is comparable to its time scale, then the contribution of τ_M is important. In our system, the size of the aggregates is large and $\tau_M >> \tau_r$. So the equation 2 can be reduced to

$$\frac{1}{< \tau_r >} = \frac{1}{< \tau_{rp} >} \qquad (10)$$

i.e, $$< \tau_r >=< \tau_{rp} > \qquad (11)$$

Therefore, we have directly used the average rotational time ($< \tau_r >$) to calculate the microviscosity of the vesicle bilayer.

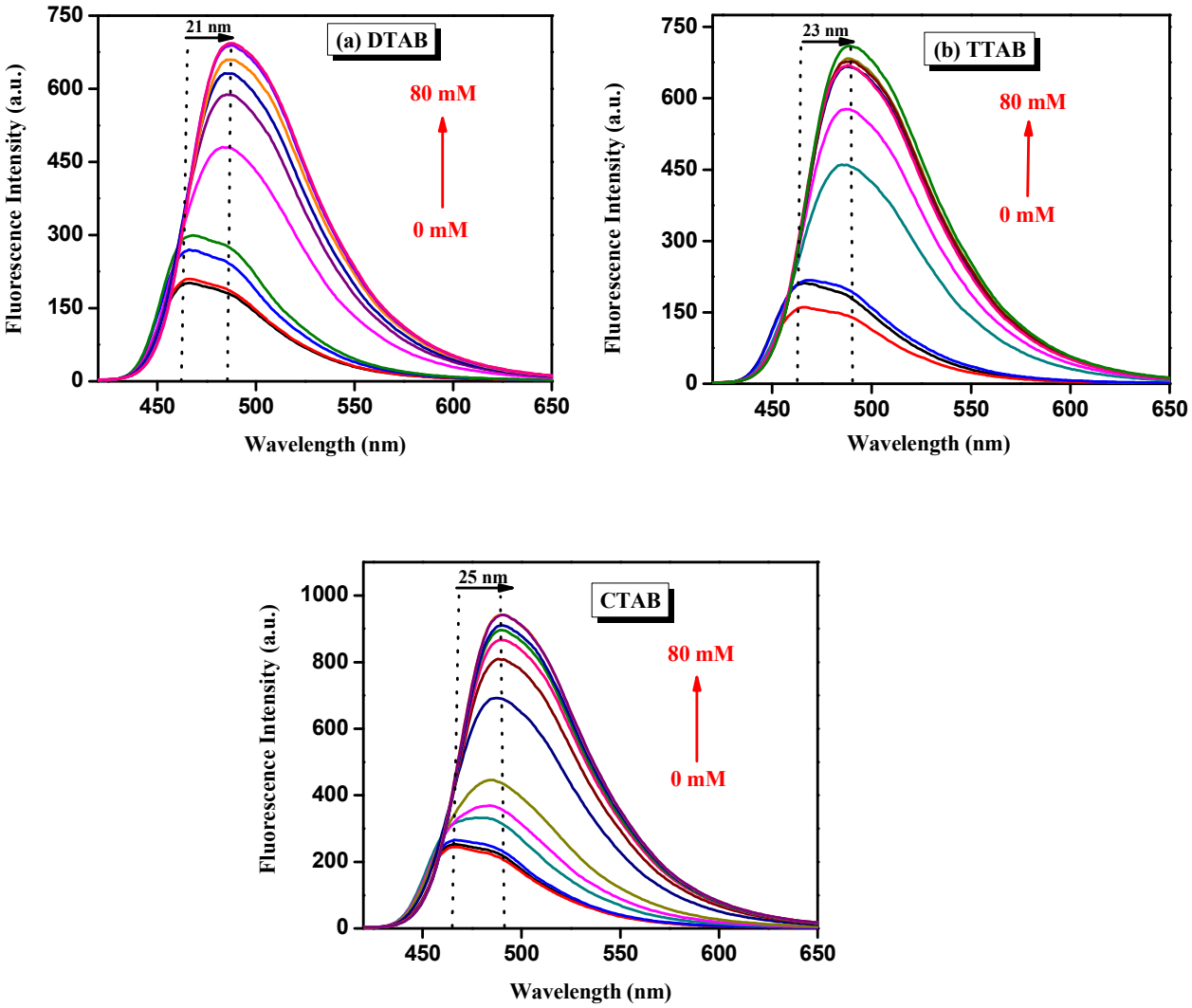

Figure S1: Steady-state fluorescence spectra ($\lambda_{ex} = 336\,nm$) of $BP(OH)_2$ in aqueous solution with increasing concentration of (a)DTAB, (b) TTAB and (c) CTAB.

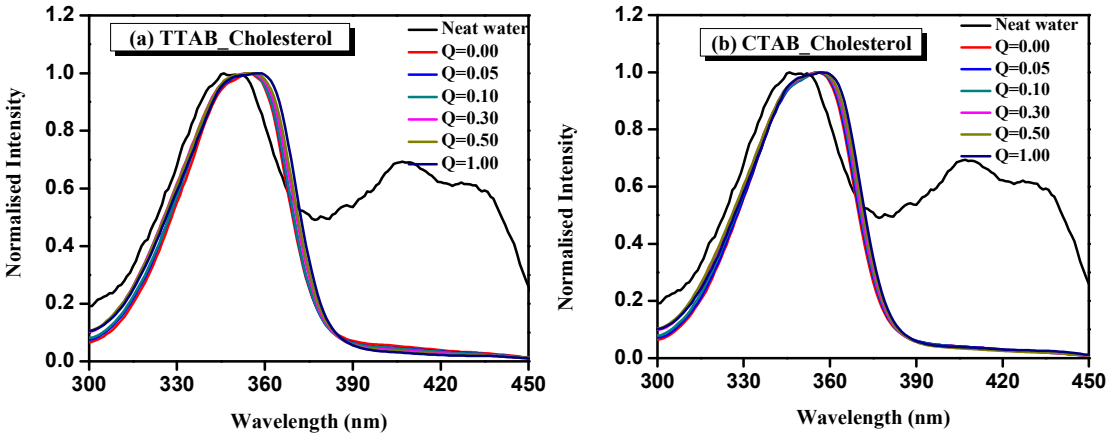

Figure S2: Fluorescence excitation spectrum of $BP(OH)_2$ in water and 30 mM surfactant solution with increasing concentration of cholesterol.

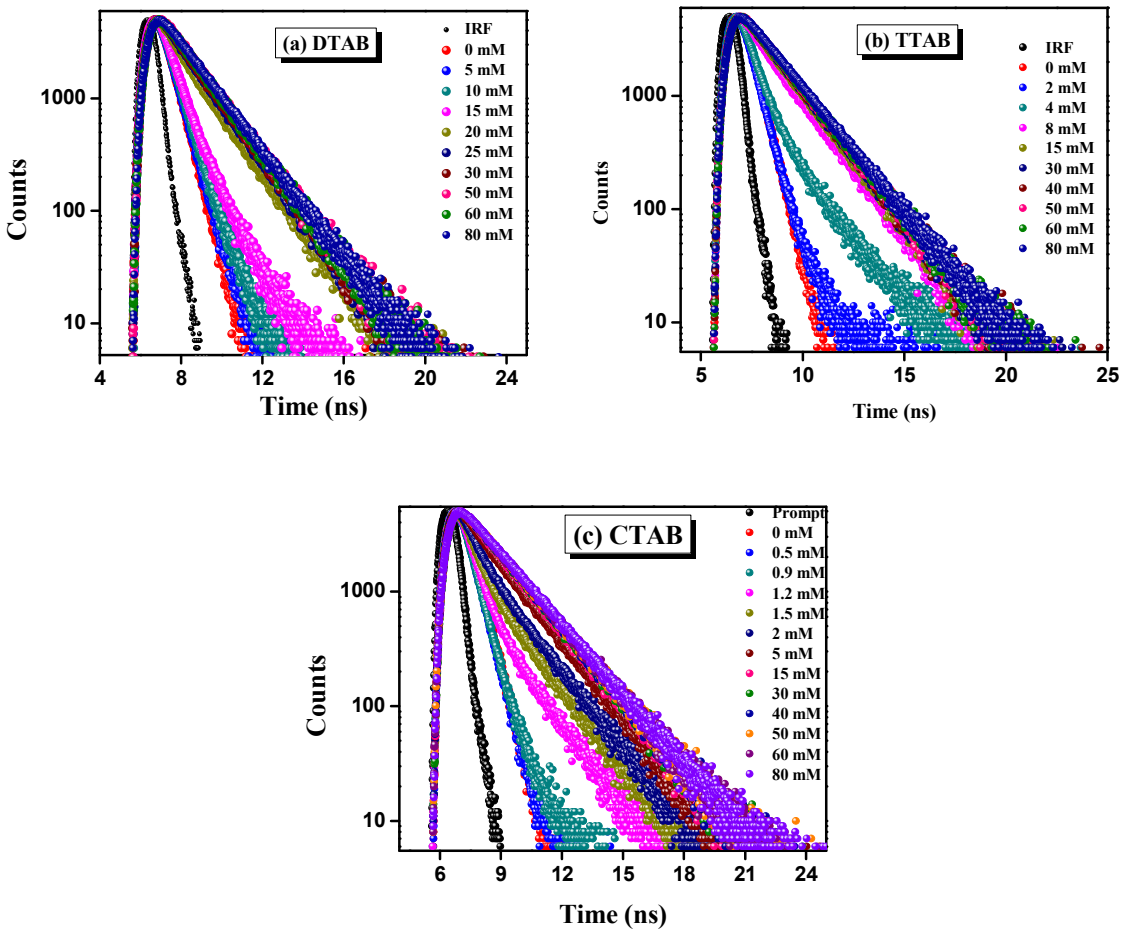

Figure S3: Time-resolved emission decays of $BP(OH)_2$ in aqueous solutions of (a) DTAB, (b) TTAB, and (c) CTAB with increasing concentrations (λ_{ex} = 336 nm).

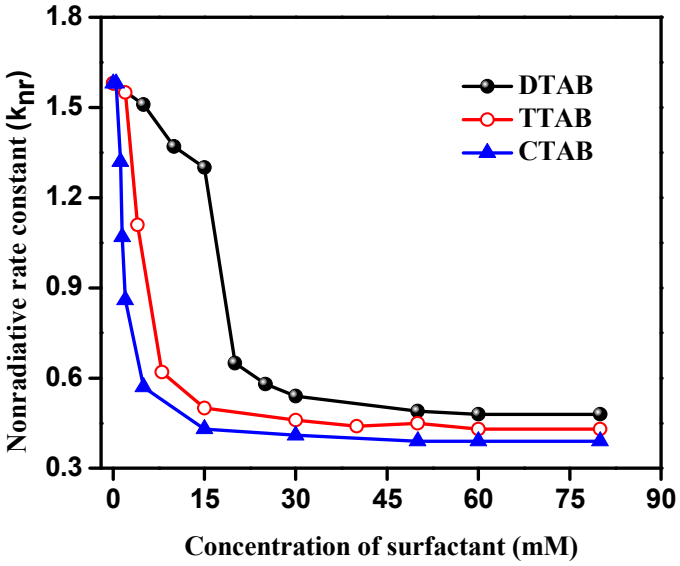

Figure S4: Variation of nonradiative rate constant of $BP(OH)_2$ with concentration of surfactant, DTAB, TTAB and CTAB.

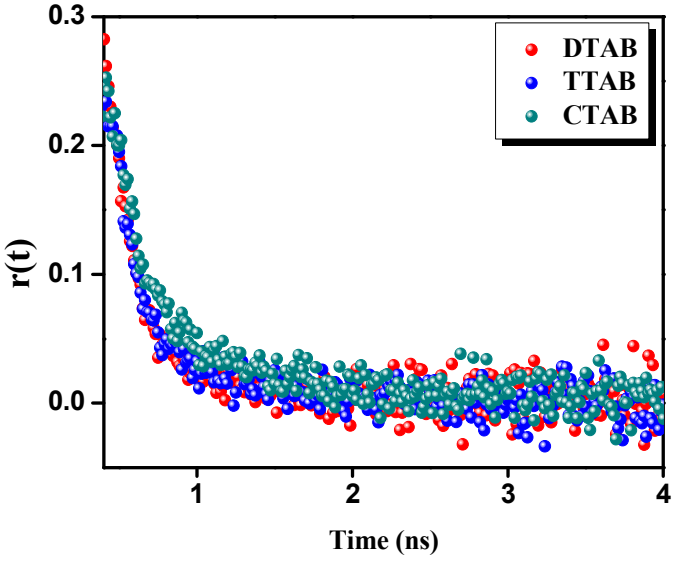

Figure S5: Anisotropy decays of $BP(OH)_2$ in water and 50 mM DTAB, TTAB and CTAB solution (λ_{ex}=375 nm).

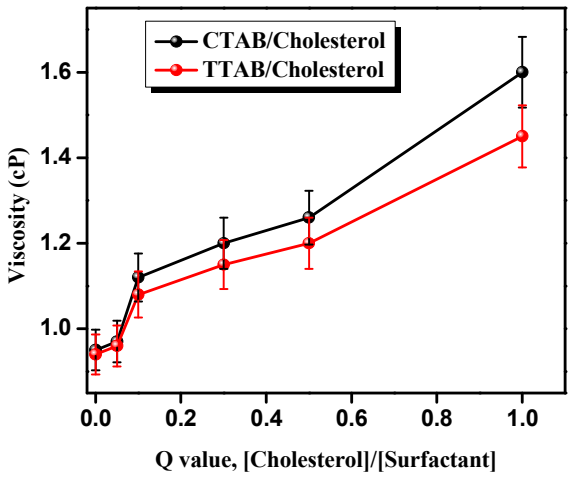

Figure S6: Variation of bulk viscosity of 30 mM CTAB (black line) and TTAB solution (red line) with increasing concentration of cholesterol.

Table S1: Quantum Yield (Φ), Fluorescence Lifetime (τ_f), Radiative (k_r) and Non radiative (k_{nr}) rate constant of $BP(OH)_2$ with increasing Concentration of Surfactant (DTAB, TTAB, and CTAB) in Aqueous Solution:

Surfactant	Conc. (mM)	Quantum Yield (Φ)	$\tau_1(a_1)$ (ns)	$\tau_2(a_2)$ (ns)	$< \tau^*_{av} >$ (ns)	k_r $(10^9\ s^{-1})$	k_{nr} $(10^9\ s^{-1})$
DTAB	0	0.08	0.58 (1.00)		0.58	0.14	1.58
	5	0.08	0.54 (0.80)	0.87 (0.20)	0.61	0.13	1.51
	10	0.08	0.58 (0.80)	1.02 (0.20)	0.67	0.12	1.37
	15	0.09	0.59 (0.85)	1.33 (0.15)	0.70	0.13	1.30
	20	0.13	0.59 (0.35)	1.73 (0.65)	1.33	0.09	0.65
	25	0.15	0.59 (0.26)	1.76 (0.74)	1.46	0.10	0.58
	30	0.15	0.66 (0.18)	1.78 (0.82)	1.58	0.09	0.54
	50	0.15		1.81 (1.00)	1.81	0.08	0.47
	60	0.16		1.80 (1.00)	1.80	0.09	0.48
	80	0.16		1.82 (1.00)	1.82	0.09	0.48
TTAB	0	0.08	0.58 (1.00)		0.58	0.14	1.58
	2	0.08	0.57 (0.98)	1.47 (0.02)	0.59	0.14	1.55
	4	0.08	0.56 (0.88)	1.82 (0.12)	0.71	0.11	1.11
	8	0.14	0.57 (0.34)	1.85 (0.66)	1.41	0.09	0.62
	15	0.15	0.57 (0.15)	1.87 (0.85)	1.68	0.09	0.50
	30	0.16		1.90 (1.00)	1.90	0.08	0.45
	40	0.16		1.92 (1.00)	1.92	0.08	0.44
	50	0.16		1.91 (1.00)	1.91	0.08	0.45
	60	0.17		1.94 (1.00)	1.94	0.09	0.43
	80	0.18		1.96 (1.00)	1.96	0.09	0.43
CTAB	0	0.08	0.58 (1.00)		0.58	0.14	1.58
	0.5	0.08	0.58 (1.00)		0.58	0.14	1.58
	1.2	0.09	0.54 (0.88)	1.82 (0.12)	0.69	0.13	1.32
	1.5	0.10	0.54 (0.78)	1.90 (0.22)	0.84	0.12	1.07
	2	0.12	0.55 (0.65)	1.90 (0.35)	1.02	0.12	0.86
	5	0.15	0.55 (0.33)	1.96 (0.67)	1.49	0.10	0.57
	15	0.18	0.59 (0.09)	2.07 (0.91)	1.94	0.09	0.43
	30	0.18		2.08 (1.00)	2.08	0.09	0.41
	50	0.18		2.09 (1.00)	2.09	0.09	0.39
	60	0.18		2.11 (1.00)	2.11	0.09	0.39
	80	0.18		2.12 (1.00)	2.12	0.09	0.39

* Experimental error ~5%

Table S2: Dynamic Parameters of Fluorescence Anisotropy of $BP(OH)_2$ in Aqueous 50 mM Surfactant solutions at ($\lambda_{ex} = 375\ nm$)

Surfactant Solutions	a_{slow}	τ_{slow} (ns)	a_{fast}	τ_{fast} (ns)	$< \tau_r^* >$ (ns)
DTAB	0.06	1.12	0.94	0.16	0.22
TTAB	0.10	1.20	0.90	0.18	0.28
CTAB	0.15	1.36	0.85	0.24	0.41

* Experimental error ~6%