Supporting Materials

Fluorescence Resonance Energy Transfer in Polydiacetylene Liposomes

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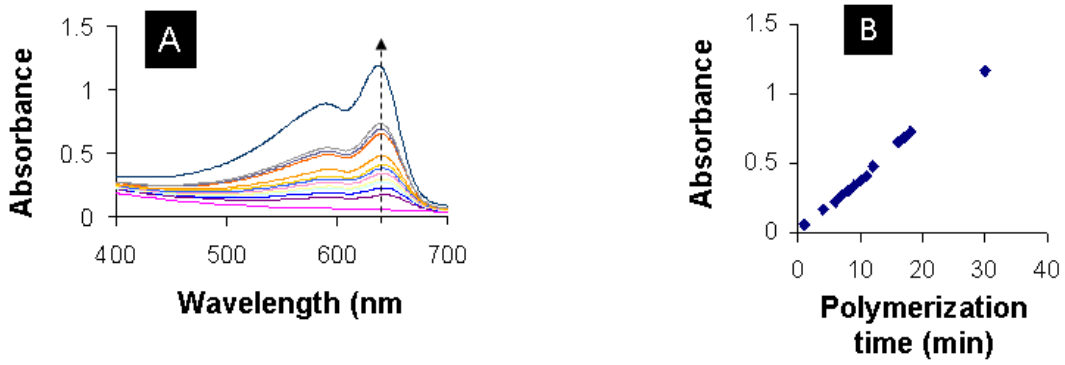

Figure 1S. (A) UV-Vis spectra of a PDA liposome solution polymerized for different time (from 1 to 30 minutes) in air atmosphere. Corresponding curve between absorbance (at 630 nm)-versus-polymerization time is shown in (B).

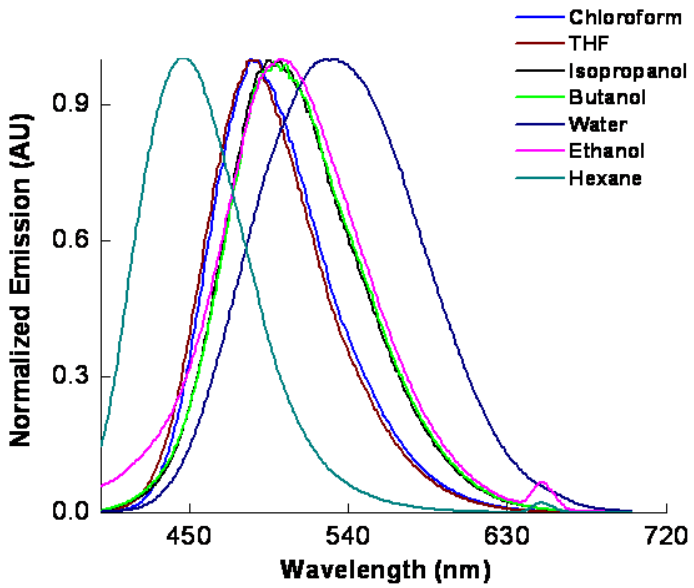

Figure 2S. Emission of ***5a*** in solvents of different polarities. Note that the dansyl emission red-shifted with increase in the solvent polarity.

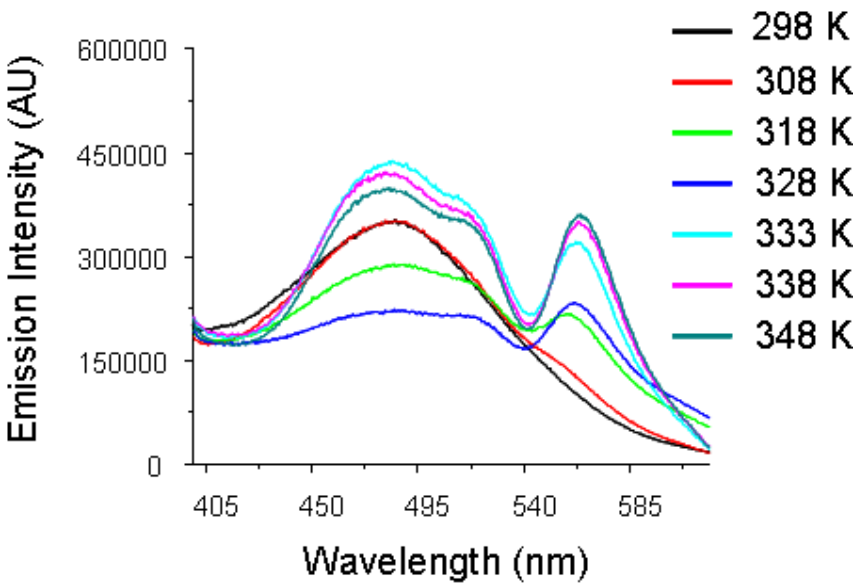

Figure 3S. The emission spectra of dansyl-tagged PDA at different temperature with R_{1b}=1000 (subscript ***1b*** represents donor is ***1b***).

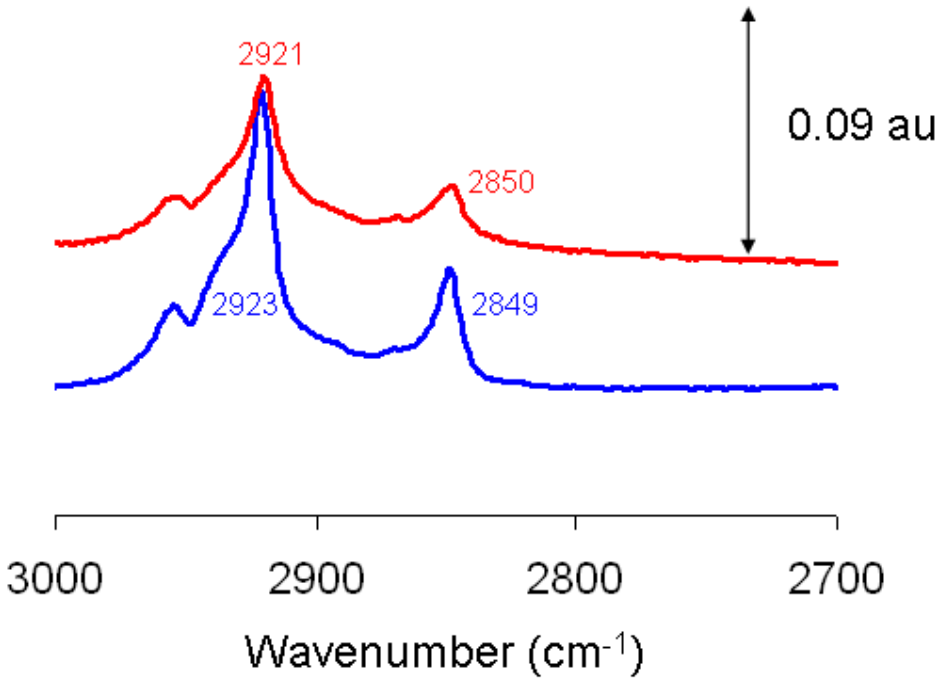

Figure 4S. FTIR spectra of blue-phase (blue curve) and red-phase (red curve) dansyl containing PDA liposomes ($R_{ad,1a}$ = 10000) and total monomer concentration is 1 mM.

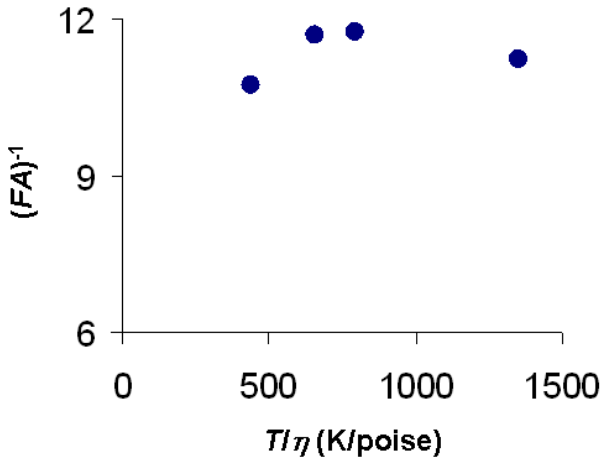

Figure 5S. Perrin plot of 1,2-Dimyristoyl-*sn*-Glycero-3-Phosphocholine (DMPC, 1 mM) and dansyl-tagged diacetylene (***1a***, 1 mM) at different temperatures. Note that the concentration of ***1a*** is much smaller (1000 times) than that of DMPC, so the photopolymerization of the liposomes is less likely to occur. Viscosity data of DMPC liposome was taken from B. R. Lentz, *Y.* Barenholz, and T. E. Thompson Biochemistry **1976,** *15,* 4521-4528.

A. Fluorescence Anisotropy (r) of dansyl-tagged to liposomes. r was determined using Perrin equation:[1]

$$(r_0/r) = 1 + (\tau/\phi) \qquad \text{Eq. 1S}$$

where τ is life time of dansyl, ϕ is the rotational correlation time, and r_0 is the fluorescence limiting anisotropy. r_0 is a measure of anisotropy in the absence of rotational diffusion, and it is 0.325 for dansyl.[2] ϕ can be calculated using modified Debye-Stokes-Einstein equation[1]:

$$\phi = \eta M (v_s + s)/RT \qquad \text{Eq. 2S}$$

where η is the viscosity of the solvent in which fluorophore resides; M is the molecular weight of the rotating fluorophore; R is gas constant and T is the solution temperature (in K). For dansyl in bilayers, we have estimated ϕ at 298 K and 328 K. M = 250 g/mole, η is 7.25 cP and 3.03 cP at 298 K and 328K respectively,[3] $v_s \sim 1.00$ and $s = 0.1$. The viscosity of the bilayers are assumed to equivalent of nonanoic acid ($C_8H_{39}COOH$) whose chemical structure is similar to hydrophobic portion of our bilayers (above yne-ene polymer backbone) (see Figure 6S). We estimate $\phi = 0.73$ ns and 0.27 ns for dansyl at 298 K and 328K respectively. Inserting these values in Equation 1S gives r of 0.018 and 0.0056 at 298 K and 328 K respectively. We have corrected the steady-state anisotropy values at 328 K due to contribution from FRET using Eq. 3S.[4] Assuming FRET contribution to r at 298 K is negligible (that E~0 at 298) and experimental value of $E = 0.3$, we obtain corrected $r = 0.0014$ at 328 K.

$$E = 1- (r_o/r_{DA} - 1) (r_o/r_D - 1)^{-1} \qquad \text{Eq. 3S}$$

where r_o is the limiting anisotropy, r_D and r_{DA} is emission anisotropy in the absence and presence of acceptor respectively. The assumption that E~0 at 298 K is reasonable considering J is extremely small and Qy dansyl is also much smaller at 298 K compared to 328 K.

B. Estimation of rotation correlation time liposomes. We have also estimated the rotation correlation time of our liposomes. Assuming the liposomes are monodisperse with an average diameter of 100 nm and cross-section area of diacetylene acid of 27 $Å^2$, we estimate 3.24 million diacetylene monomers in the bilayers in every liposome. Thus, M for liposome is 347 x 10^6 gm/mol and $\eta = 1$ cP and ϕ = 0.14 and 0.12 ms at 298 K and 328 K respectively. These rotation correlation time values are much longer than emission life-time of dansyl, and for all practical purposes the liposomes behave like stationary surfaces.

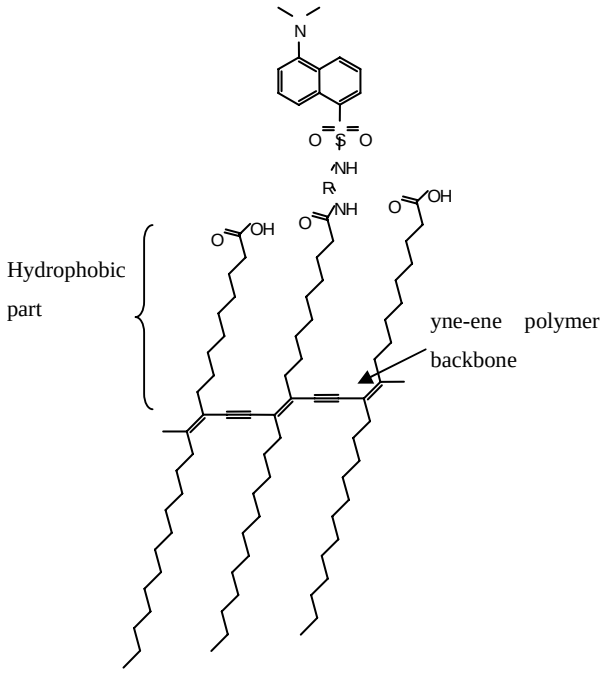

Figure 6S. Schematic presentation of PDA and dansyl fluorophores attached to PDA bilayer.

Reference

1. Lakowing, J.R.; Principle of fluorescence of spectroscopy, chapter 5, 1983, Plenum Press, NY,
2. Hu, Y.; Horie, K.; Ushiki, H. Macromolecules **1992**, *25*, 6040; (6) Munson, C.A.; Page, Philip. M.; Bright, K.V. *Macromolecules* **2005**, *38*, 1341-1348.
3. Nonreddini, H.; Teoh, B.C.; Clements, L.D. *J. Am. Oil. Chem. Soc.* **1992**, *69*, 1189-1191.
4. Matko, J; Jenei, A; Matyus, L; Damjanovich, S; Ameloot, M. *Journal of Photochemistry and Photobiology. B, Biology* **1993**, *19*, 69-73.