Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information

Self-assembly of modified Rhodamine-6G with tri-block copolymer: Unusual vesicles formation, pH sensing and dye release properties

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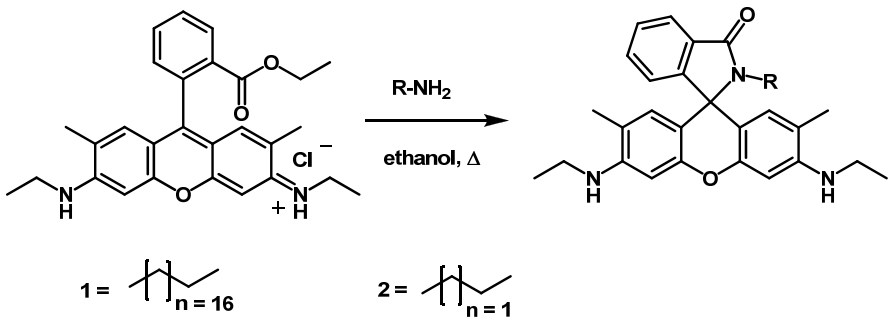
Experimental



Scheme S1: Synthesis of rhodamine-6G derivatives.

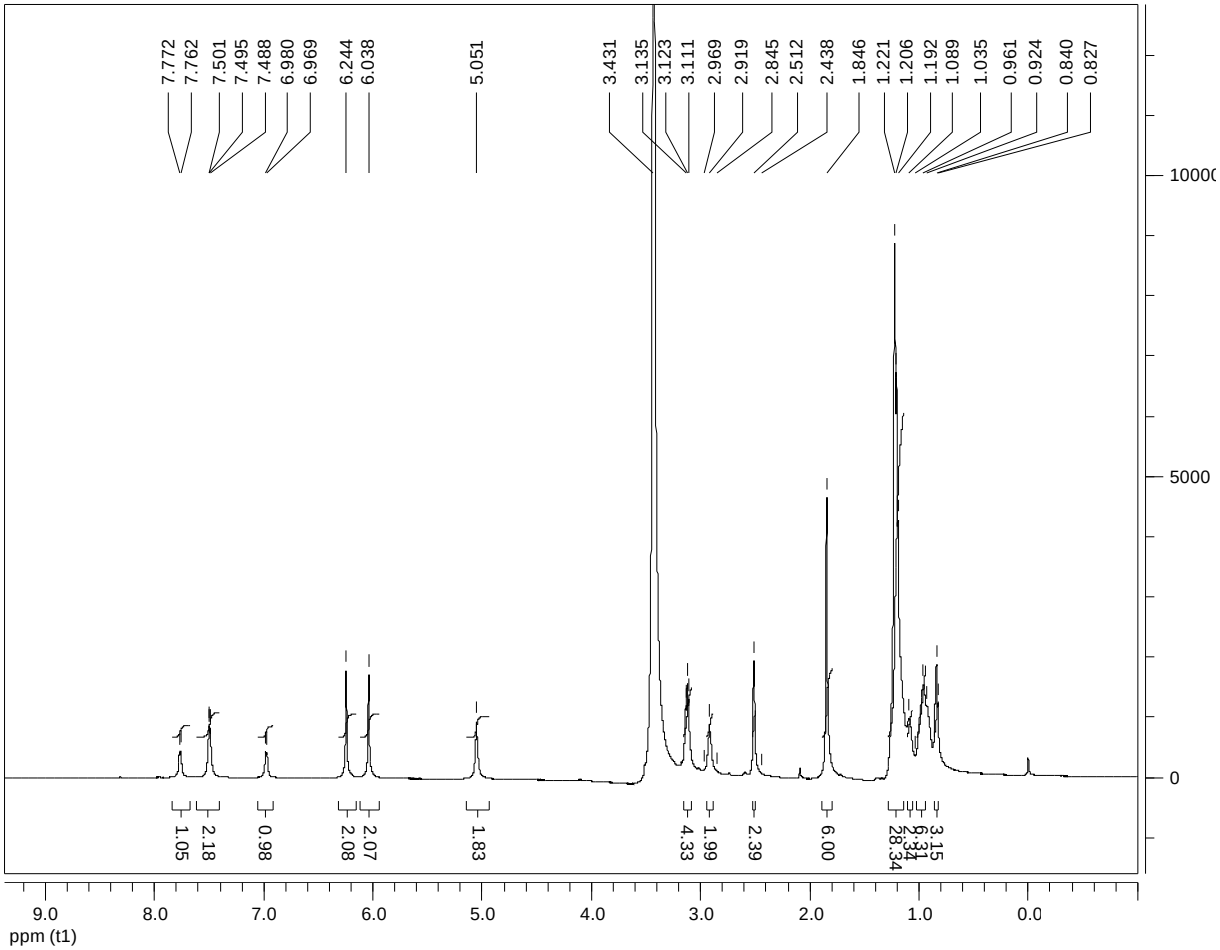


Figure S2: ^{1}H NMR spectrum of octadecyl rhodamine-6G (**R**) in d_6-DMSO.

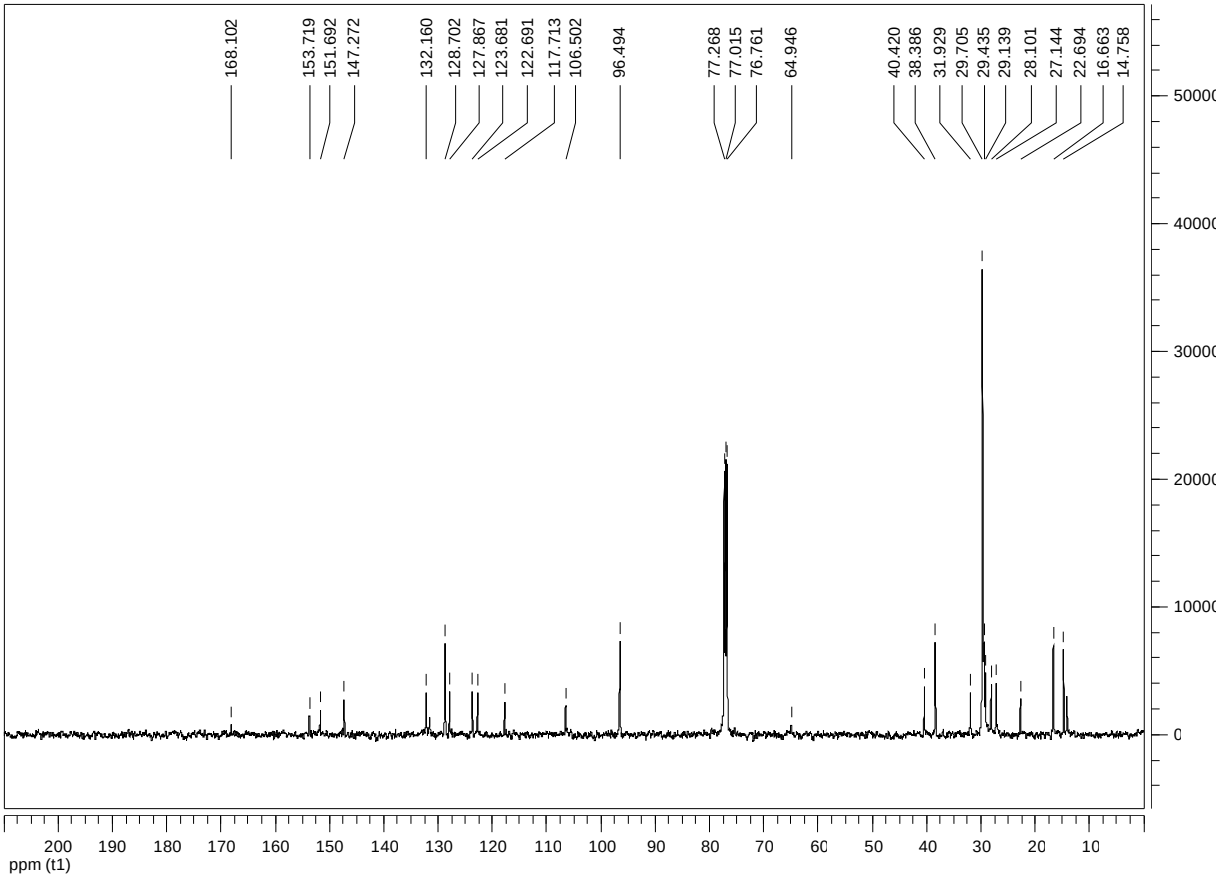


Figure S3: ^{13}C NMR spectrum of octadecyl rhodamine-6G (**R**) in $CDCl_3$.

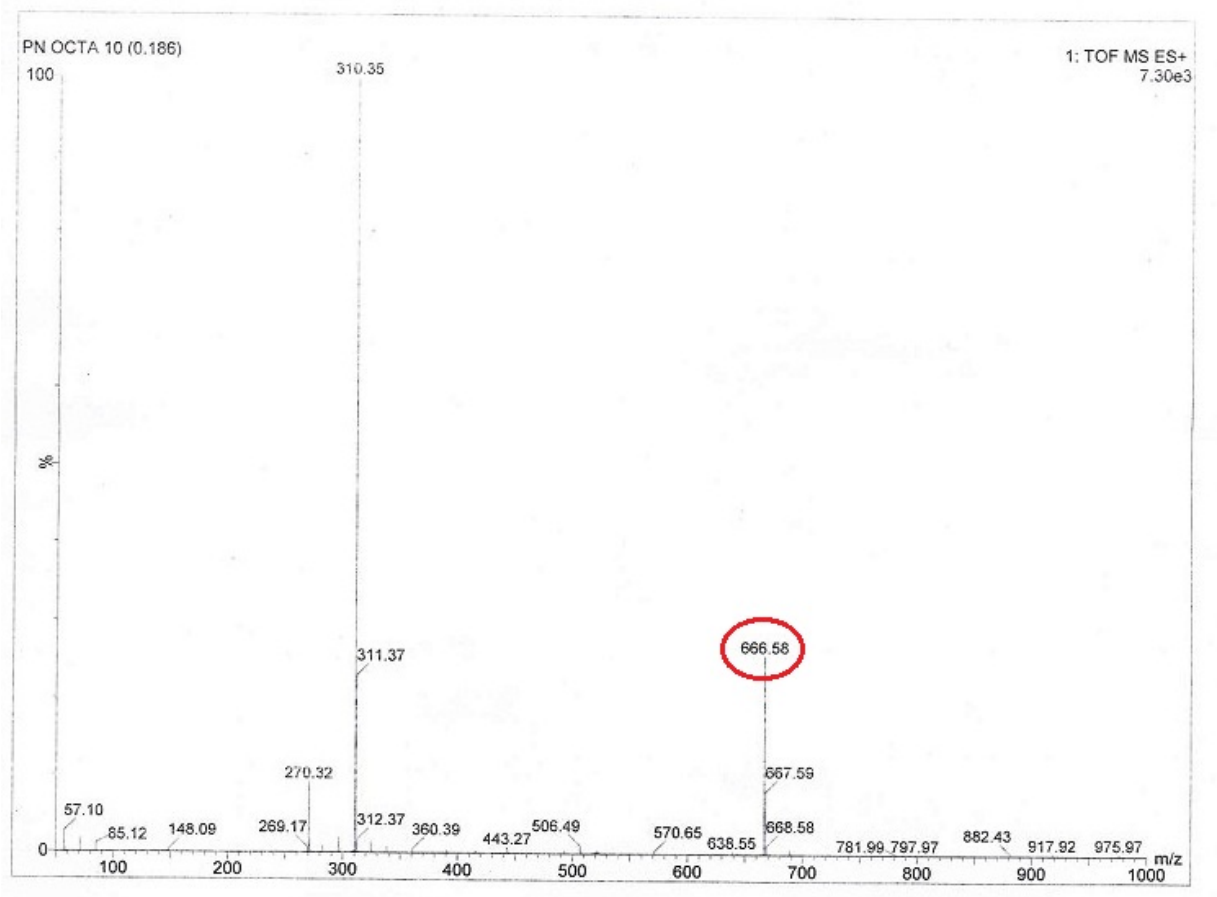


Figure S4: Mass spectrum of octadecyl rhodamine-6G (**R**).

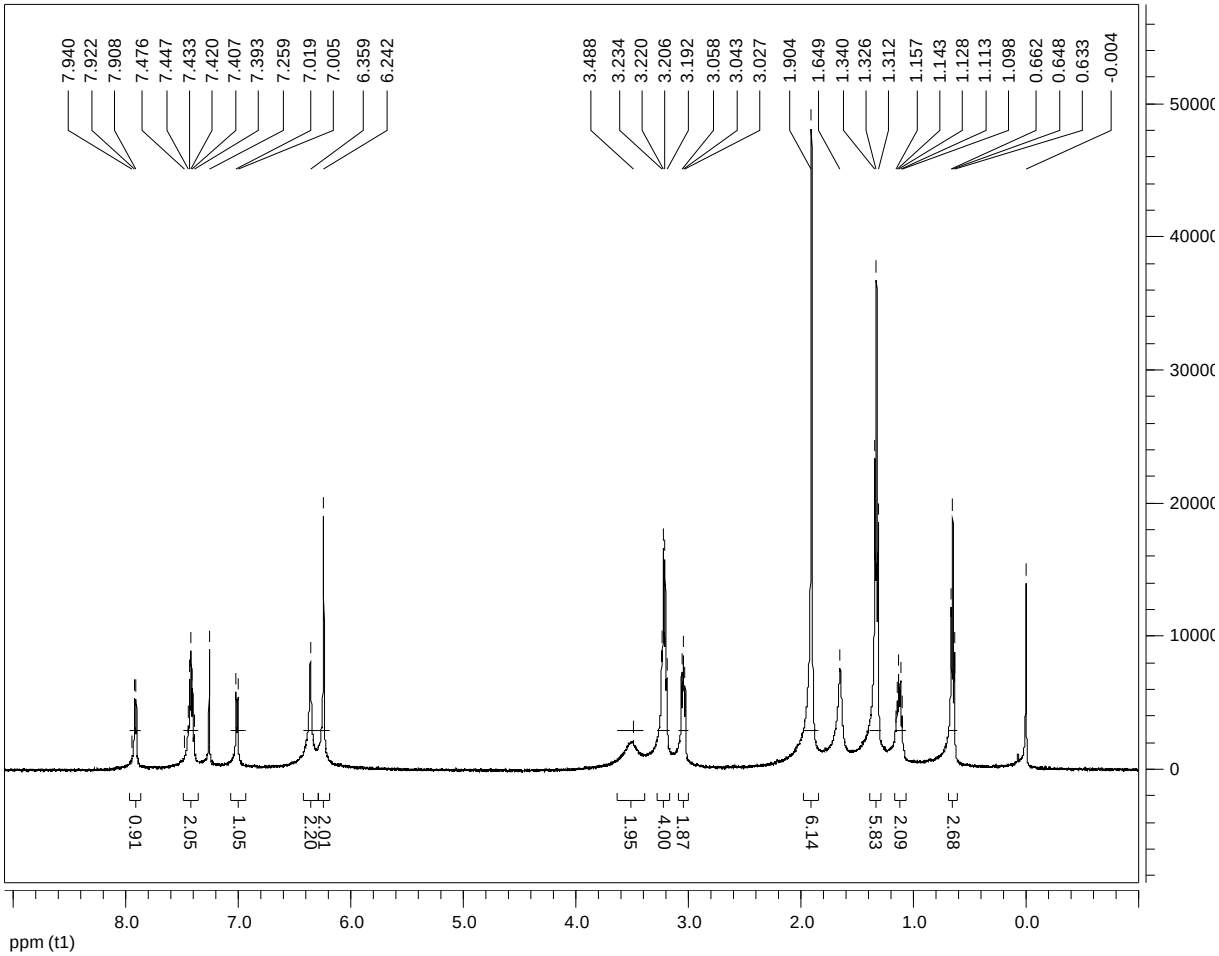


Figure S5: ^{1}H NMR spectrum of propyl rhodamine-6G (**R$_1$**) in $CDCl_3$.

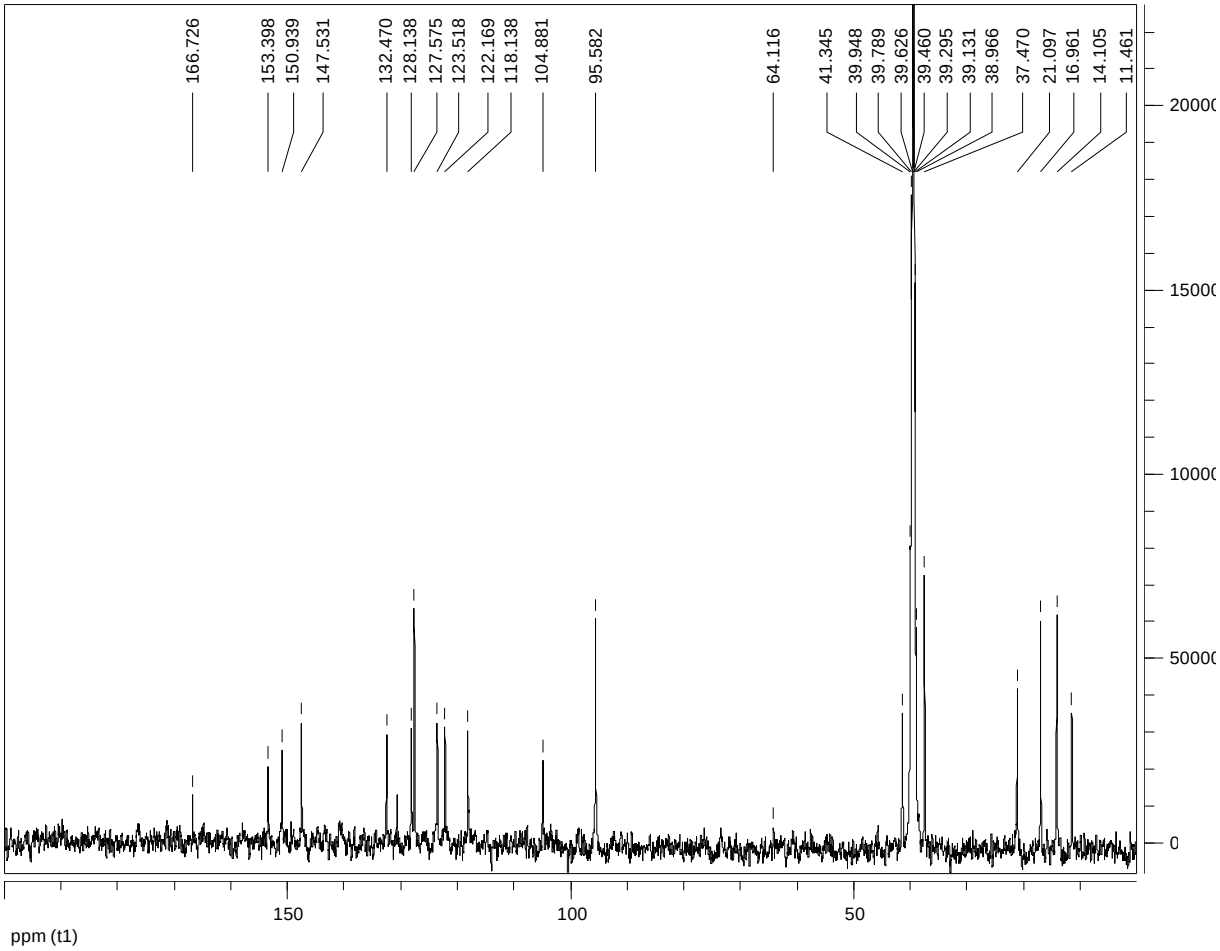


Figure S6: ^{13}C NMR spectrum of propyl rhodamine-6G (**R$_1$**) in DMSO-d$_6$.

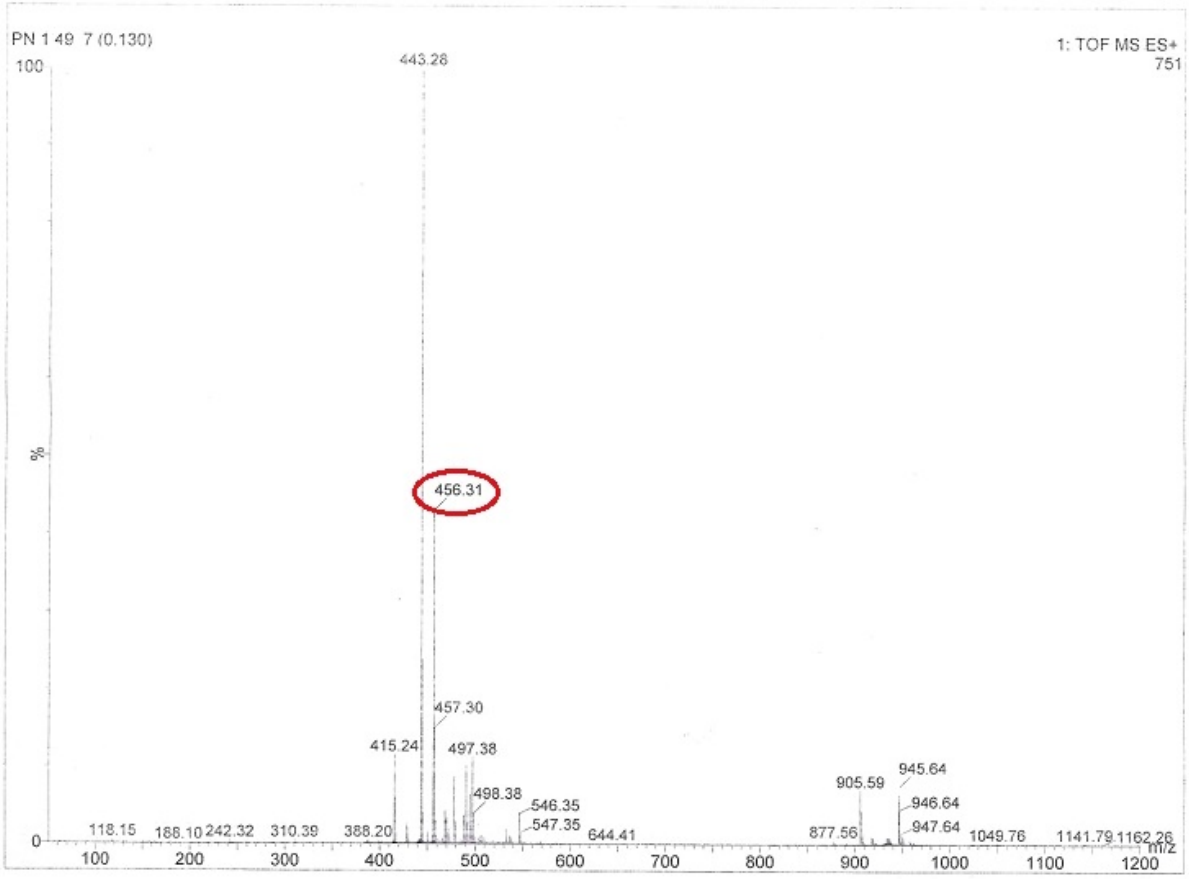


Figure S7: Mass spectrum of propyl rhodamine-6G (**R_1**).

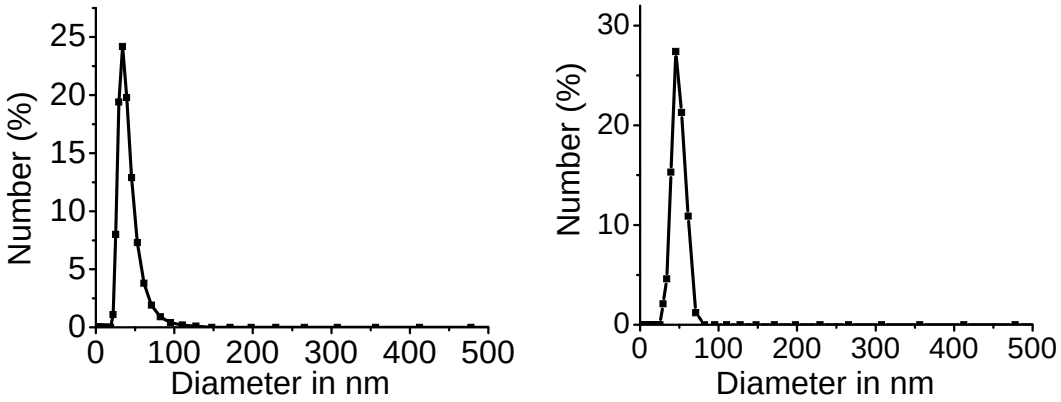


Figure S8: DLS result of PDMA-b-PMMA-b-PDMA polymer in water-ethanol solvent system at a pH = 5 & 7.

Table S9: Average hydrodynamic diameter of vesicles at different pH.

Entry	At pH 6	At pH 7	At pH 8
Av. hydrodynamic diameter (nm)	92	85	55

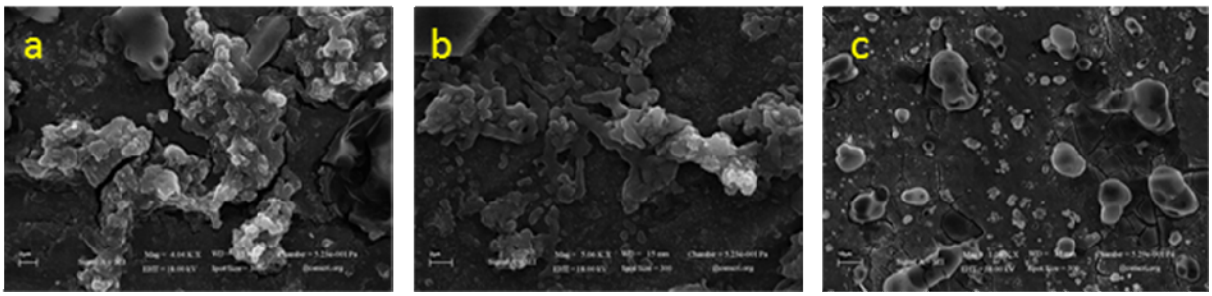


Figure S10: SEM picture of vesicles upon exposure to different pH over a period of 24 h; Figure a: pH 3, b: pH 4 and c: pH 5.

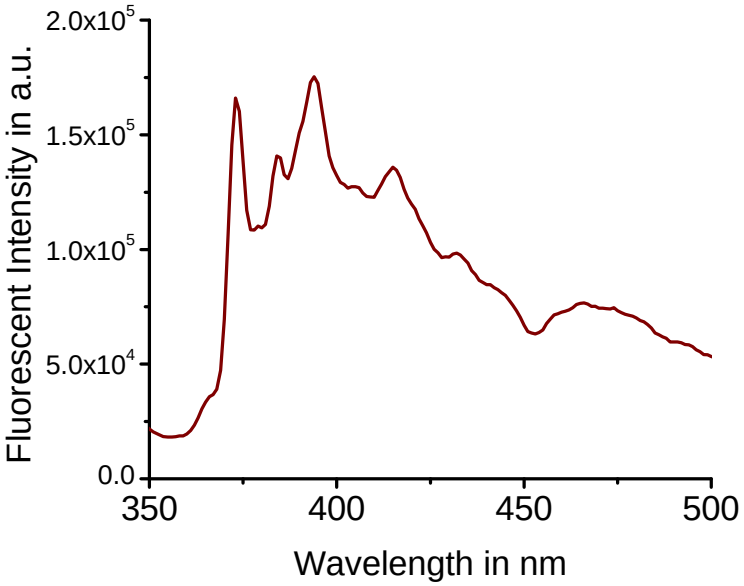


Figure S11: Emission spectra of pyrene (2.0 x 10^{-6} M) in the vesicle after dialysis.

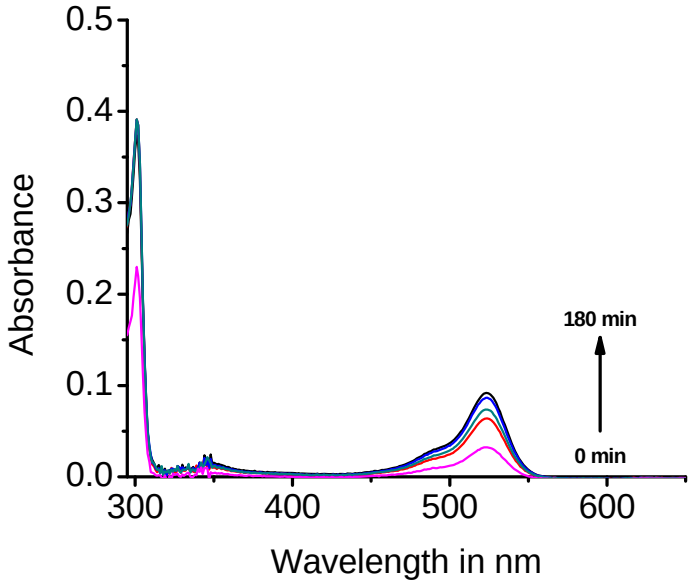


Figure S12: UV-Vis response of octadecyl rhodamine-6G (8.0 x 10^{-5} M) in aqueous media (ethanol-water, 1:4, v/v) at a pH 6.

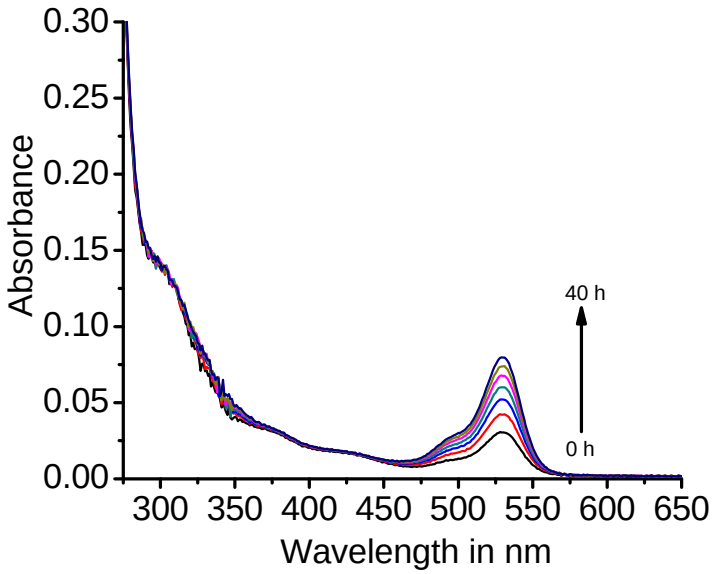


Figure S13: UV-Vis response of vesicle in aqueous media (ethanol-water, 1:4, v/v) at a pH 6.

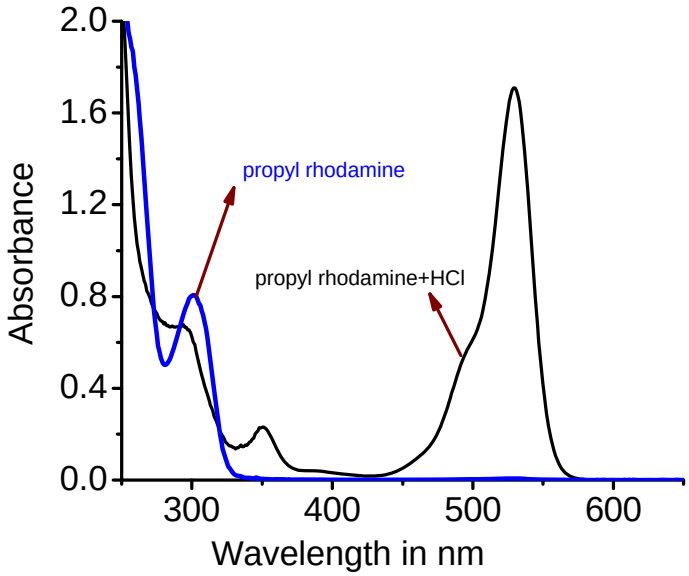


Figure S14: UV-Vis spectra of propyl rhodamine-6G (5.0×10^{-4} M) in ethanol upon addition of 10 equiv of HCl (in water).

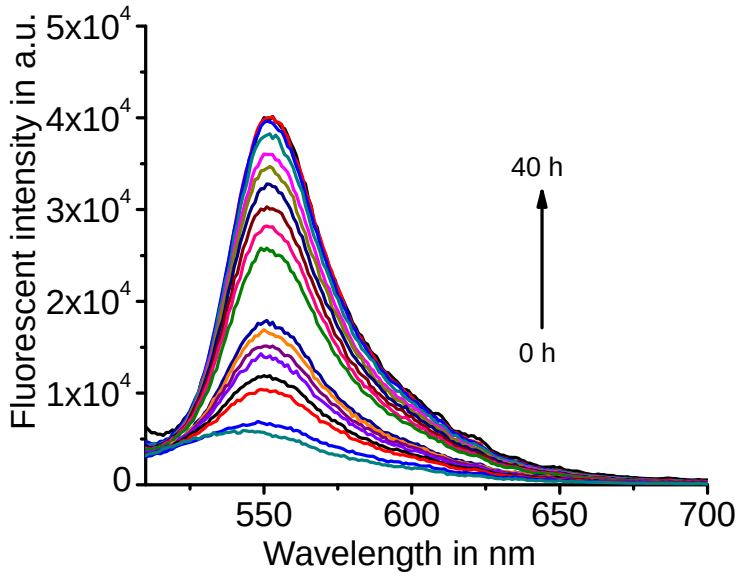


Figure S15: Emission spectra of the vesicle solution in aqueous media (ethanol-water, 1:4, v/v) at a pH 6 for a period 40 h.

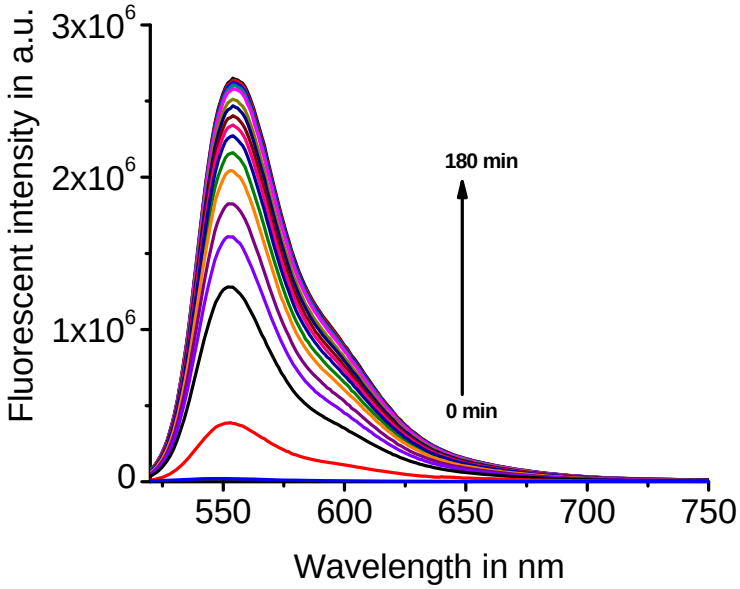


Figure S16: Emission response of the octadecyl rhodamine-6G (8.0×10^{-5} M) in aqueous media (ethanol-water, 1:4, v/v) at a pH 6 for a period 3 h.

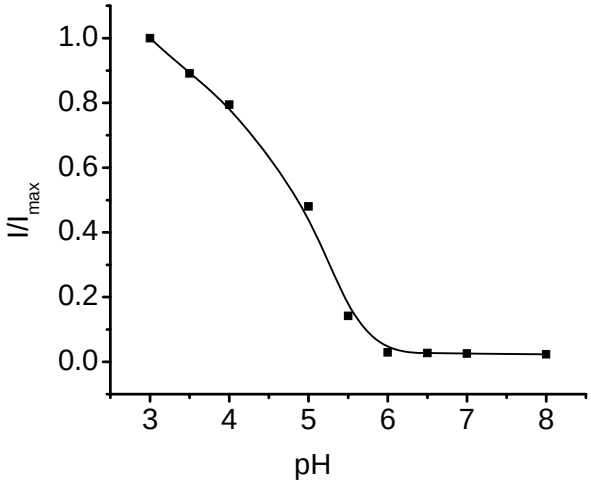


Figure S17: Plot of I/I_{max} of propyl rhodamine-6G in different pH

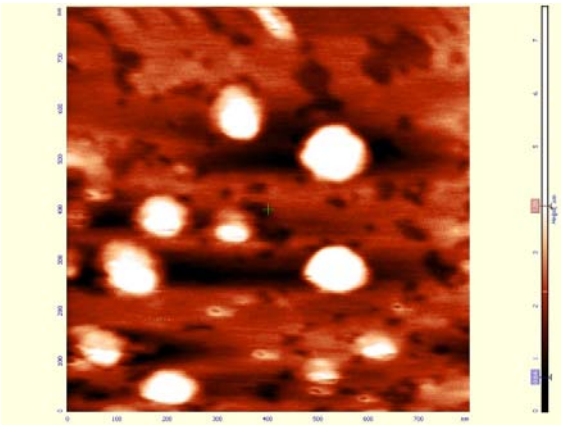


Figure S18: AFM image of octadecyl rhodamine-6G (**R**) (5.0×10^{-5} M) in aqueous media (ethanol-water, 1:4, v/v).

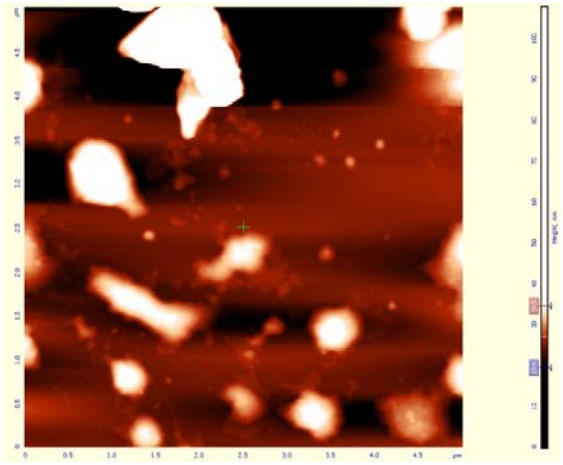


Figure S19: AFM image of propyl rhodamine-6G (5.0×10^{-5} M) in aqueous media (ethanol-water, 1:4, v/v) shows featureless aggregates.

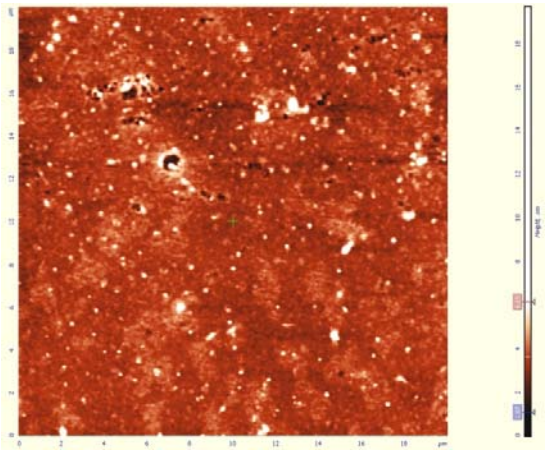


Figure S20: AFM image of the PDMA-b-PMMA-b-PDMA polymer (0.4g/L) with propyl rhodamine-6G (5.0×10^{-5} M) in water-ethanol (4:1, v/v) solvent system.

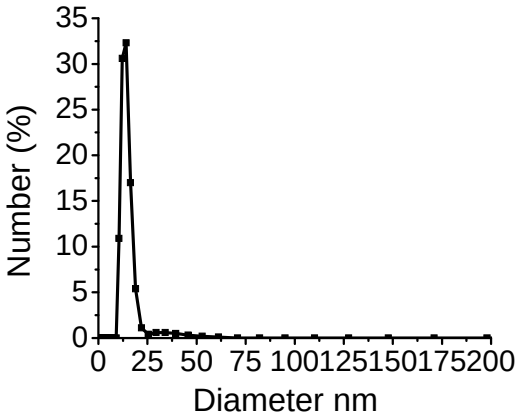


Figure S21: DLS result of PDMA-b-PMMA-b-PDMA polymer (0.4 g/L) with rhodamine-6G (0.12 g/L) in water-ethanol (4:1, v/v) solvent system. Thus, DLS result shows formation of micelles.

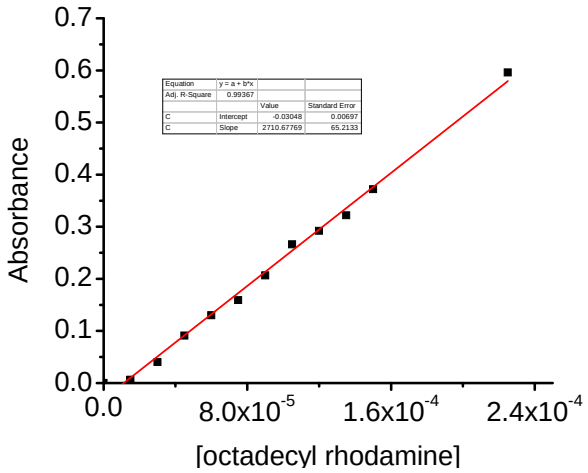


Figure S22: Standard curve of octadecyl rhodamine-6G in aqueous media (ethanol-water, 1:4, v/v) system (absorbance).

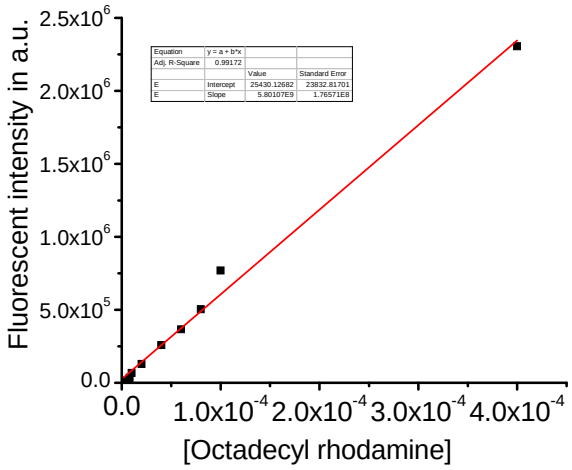


Figure S23: Standard curve of release of octadecyl rhodamine-6G in aqueous media (ethanol-water, 1:4, v/v) system at a pH < 2 for 24 h.

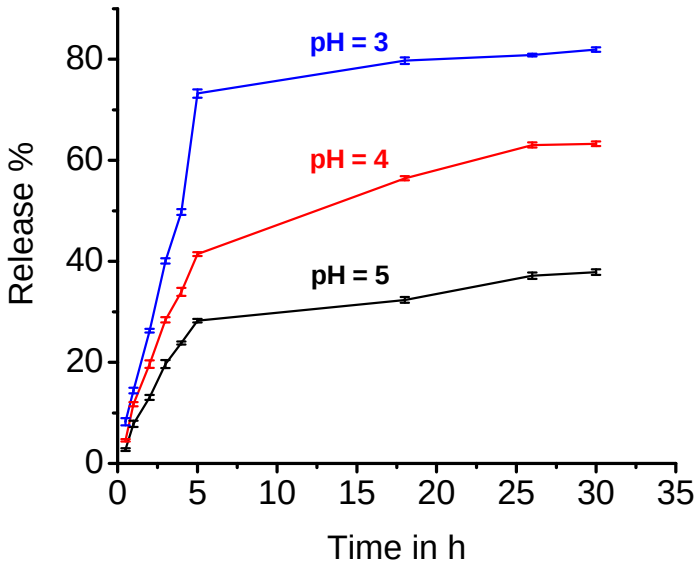


Figure S24: Plot for the release of total ring opened octadecyl rhodamine-6G released from the vesicle after dialysis in suitable pH, followed by the addition of 2N HCl for 30 min. in water-ethanol (4:1, v/v) solvent system.

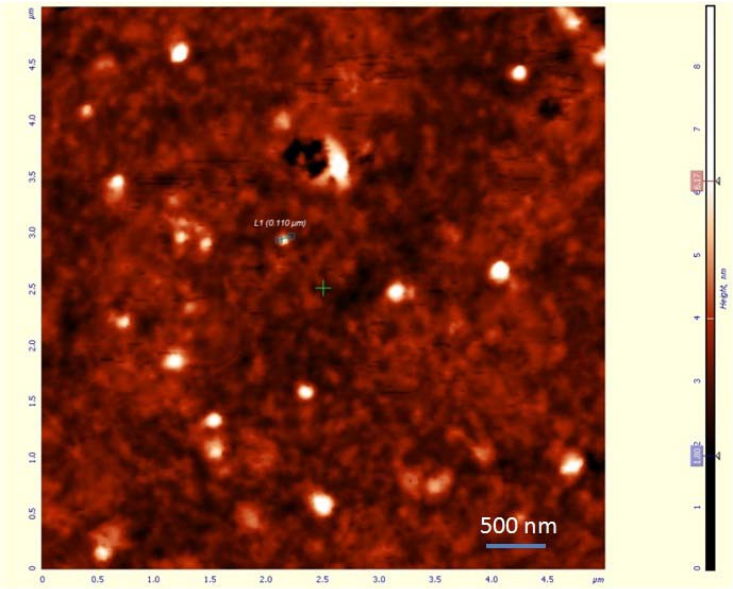


Figure S25: AFM image of the PDMA-b-PMMA-b-PDMA polymer (0.4g/L) with octadecyl rhodamine-6G (0.12 g/L) in water-ethanol (4:1, v/v) solvent system when drop casted over mica substrate.

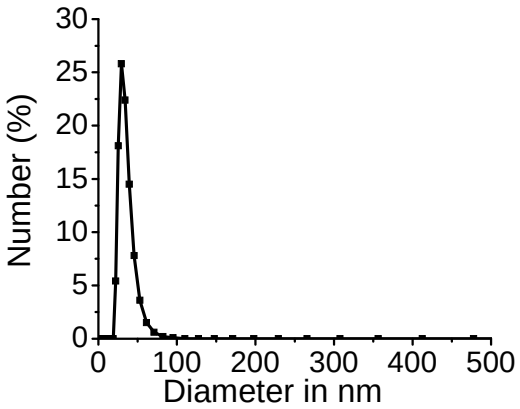


Figure S 26: DLS result of PDMA-b-PMMA-b-PDMA polymer (0.4 g/L) with octadecyl rhodamine-6G (0.12 g/L) in water-ethanol (4:1, v/v) solvent system at a pH = 3. Thus, DLS result shows rapture of the vesicle and generation of miceller structures with an average diameter of > 35 nm at this low pH.

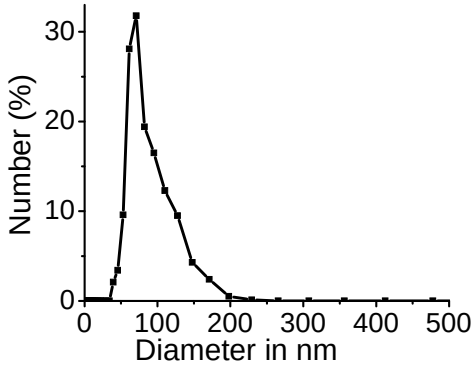


Figure S27: DLS result of PDMA-b-PMMA-b-PDMA polymer (0.4 g/L) with octadecyl rhodamine-6G (0.12 g/L) in water-ethanol (1:4, v/v) solvent system at a pH = 7 with continuous removal of organic solvent by dialysis for 24 h.

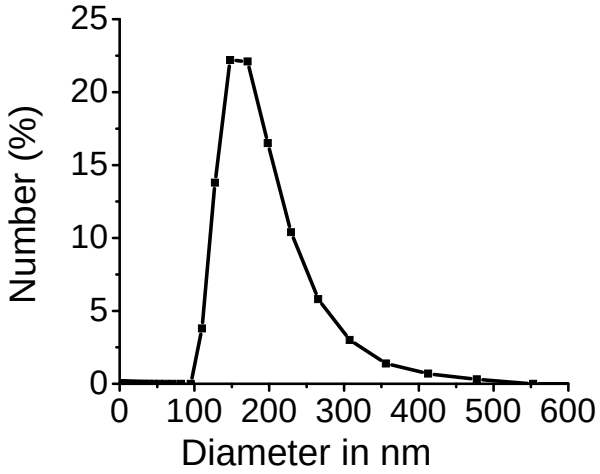


Figure S 28: The size distribution of the octadecyl rhodamine-6G (5.0×10^{-5} M) in water-ethanol (4:1, v/v) media.

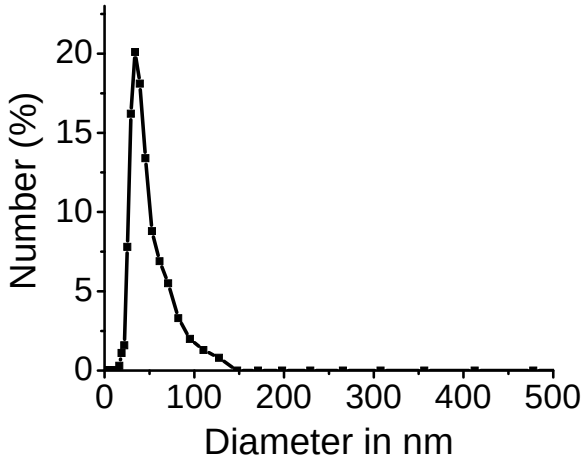


Figure S 29: The size distribution of the PDMA-b-PMMA-b-PDMA polymer (0.4 g/L) with propyl rhodamine-6G (5.0×10^{-5} M) in water-ethanol (4:1, v/v) media.

Synthesis of **PDMA-b-PMMA-b-PDMA** copolymers.

$PDMA_{11k}$-$PMMA_{6k}$-$PDMA_{11k}$ (subscripts indicate the M_n) copolymer was synthesized by the reported procedure.[1] A typical example for the synthesis of $PDMA_{11k}$-$PMMA_{6k}$-$PDMA_{11k}$ copolymer with M_n 28000 g/mol and a polydispersity index (PDI) 1.20 is as follows. Briefly, a difunctional Cl–PMMA–Cl was prepared at 35 ºC using CuCl/bpy as the catalyst and 1,2-bis(bromoisobutyryloxy)ethane as the initiator with the following recipe: MMA (7 g, 0.07 mol), acetone (4.2 mL), CuCl (0.1 g, 0.00094 mol), bpy (0.3 g, 0.0019 mol) and 1,2-bis(bromoisobutyryloxy)ethane (0.34 g, 0.00094 mol). After 12 h the conversion was 80% and the M_n and PDI values were 6300 g/mol and 1.30 respectively. In the next step the dried and purified Cl–PMMA–Cl macroinitiator was used to polymerize DMA. The recipe was as follows: DMA (4.66 g, 0.03 mol), acetone (4.2 mL), CuCl (0.016 g, 0.00016 mol), bpy (0.05 g, 0.00032 mol) and Cl–PMMA–Cl (1.1 g, 0.00017 mol) (M_n= 6300 and PDI = 1.30). After 12 h, the conversion was 78%. The polymer was purified by passing its solution through a silica gel column using toluene as an eluent. The copper free solution was concentrated by rotary evaporator and precipitated in petroleum ether. The polymer was re-dissolved in acetone and re-precipitated with petroleum ether again. The precipitated mass was dried in air for 12 h and then in vacuum oven at 60 ºC for 48 h. The M_n and PDI values were determined to be 28,400 g/mol and 1.2 respectively.

The M_ns and PDIs of the copolymer were determined by GPC. The GPC was performed at room-temperature using a Waters model 2695 separation module coupled with Waters 2414 refractive index detector and Waters Ultra-Styragel columns of 10000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF was used as the eluent at a flow rate of 1 mL/min. Before injection into the GPC system the polymer solutions were filtered through a pre-filter-filter combination system compatible with organic solvents. Polystyrene standards were used for calibration.

Quantum Yield calculation

Fluorescence quantum yield of **R**, $\mathbf{R_1}$ and $\mathbf{R_v}$ was determined in Ethanol-H_2O (1:4, v/v) using optically matching solutions of Rhodamine-6G (Φ_F = 0.94 in ethanol)[2] as standard at an excitation wavelength of 500 nm and quantum yield was calculated using equation 1.

$$\Phi_F = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2) \quad \text{---------- 1}$$

where As and Ar are the absorbances of the sample and reference solutions respectively at the same excitation wavelength, Fs and Fr are the corresponding relative integrated fluorescence intensities and η is the refractive index of the solvent used.

1. U. Chatterjee, S. K. Jewrajka and B. M. Mandal, *Polymer*., 2005, **46**, 10699.
2. (a) M. Fischer and J. George, *Chem. Phys. Lett*., 1996, **260**, 115; (b) D. Wu, W. Huang, Z. Lin, C. Duan, C. He, S. Wu and D. Wang, *Inorg. Chem*., 2008, **47**, 7190.