Supporting Information

Fluorescent Supracolloidal Chains of Patchy Micelles of Diblock Copolymers Functionalized with Fluorophores

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• Synthesis of green fluorescent 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY): 4-hydroxybenzaldehyde (550 mg, 4.50 mmol) and 2,4-dimethylpyrrole (910 mg, 9.56 mmol) were dissolved in THF (120 ml) under nitrogen. After addition of several drops of trifluoroacetic acid, the mixture was stirred overnight. 2,3-dichloro-5,6-dicyano-p-benzoquinone (1.1 g, 4.8 mmol) in THF (80 ml) was added slowly into the solution and stirred for 6 h. Then, triethylamine (24 ml, 0.17 mol) was added into the solution followed by addition of boron trifluoride diethyl etherate (24 ml, 0.19 mol) cooled in an ice-water bath. The mixture was stirred for another 6 h and then filtered. After evaporation of THF, the residue was dissolved in dichloromethane (300 ml). Then, the solution was washed with water (300 ml × 3) and dried over $MgSO_4$. The product was purified by silica gel column chromatography with a mixture of ethyl acetate and hexane (1:4 v/v) as an eluent to give green fluorescent BODIPY in a red solid (760 mg, 54%).

• Synthesis of red fluorescent BODIPY: Green fluorescent BODIPY (360 mg, 1.06 mmol), p-anisaldehyde (4.1 g, 30 mmol), acetic acid (2.2 ml, 38 mmol), and piperidine (2.5 ml, 25 mmol) were dissolved in toluene (60 ml) and the solution was refluxed for 24 h with a Dean-Stark apparatus to remove the water formed during the reaction. Then, the mixture was concentrated and purified by silica gel column chromatography with dichloromethane and with a mixture of ethyl acetate and hexane (1:4 v/v) to give red fluorescent BODIPY in a dark blue solid (160 mg, 27%).

• Synthesis of blue fluorescent coumarin: 4-(diethylamino)salicylicaldehyde (2.2 g, 11 mmol), diethyl malonate (3.4 ml, 22mmol), and piperidine (1.2 ml, 12 mmol) were dissolved in ethanol (30 ml). Then, the solution was refluxed for 6 h and cooled to room temperature. After addition of an aqueous solution of NaOH (15 ml, 6 M), the mixture was refluxed again for 30 m and chilled in an ice-water bath. Then, HCl was added into the solution up to pH 2. The precipitant was filtered and recrystallized from ethanol to give blue fluorescent coumarin in an orange solid (1.2 g, 40%).

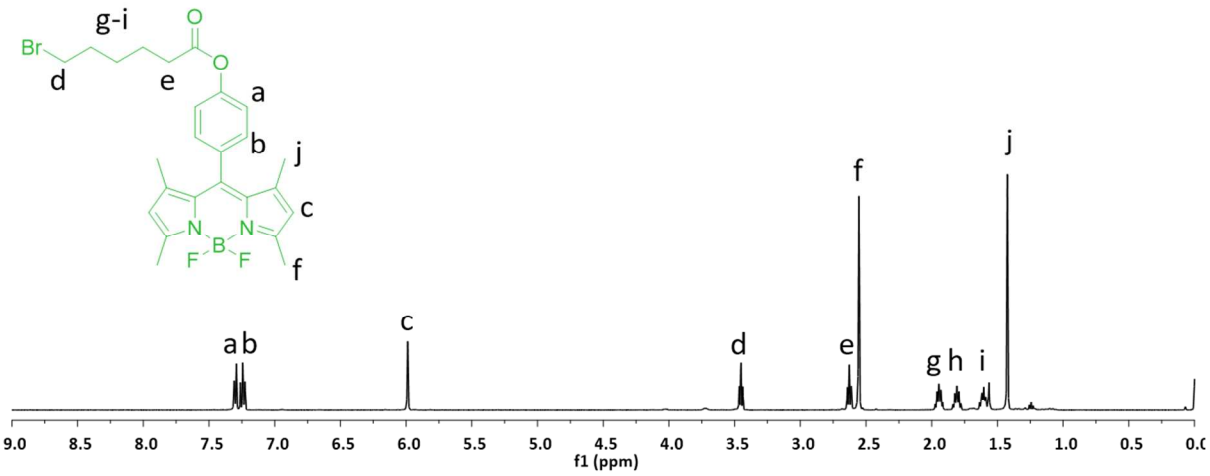

Figure S1. NMR spectrum of G dye.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 5.99 (s, 2H), 3.45, (t, J = 6.8 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.55 (s, 6H), 1.94 (quin, J = 7 Hz, 2H), 1.81 (quin, J = 7.6 Hz, 2H), 1.60 (quin, J = 7.8 Hz, 2H), 1.42 (s, 6H).

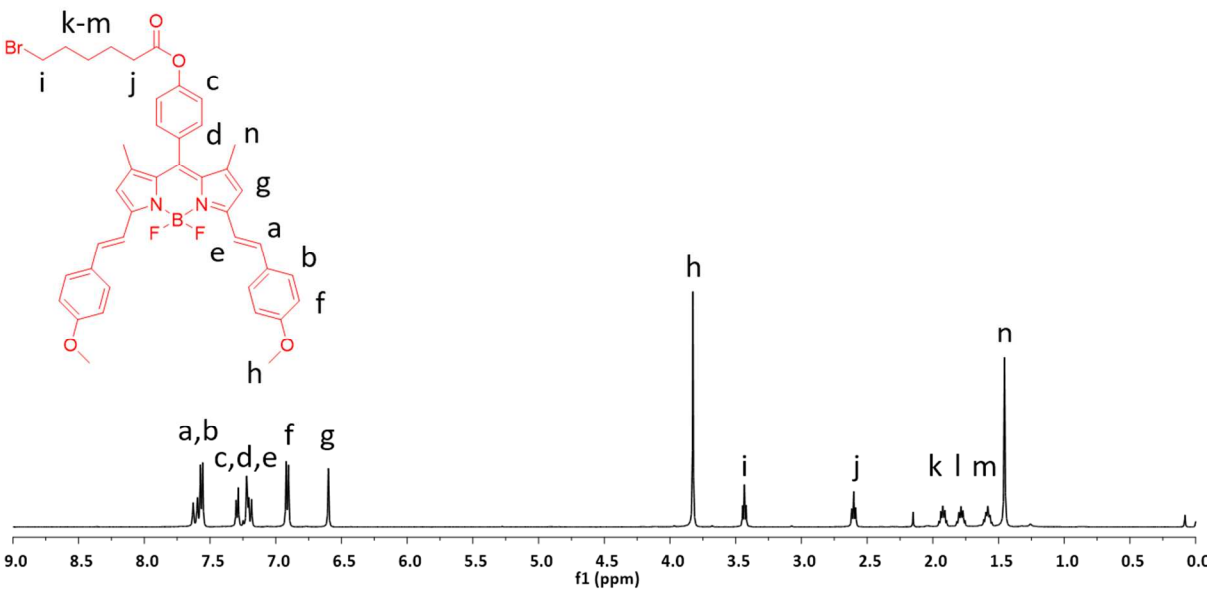

Figure S2. NMR spectrum of R dye.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, J = 16.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 4H), 7.29 (d, J = 8.5 Hz, 2H), 7.21, (d, J = 8 Hz, 2H), 7.20 (d, J = 16.5 Hz, 2H), 6.91 (d, J = 9, 4H), 6.60 (s, 2H), 3.83 (s, 6H), 3.43 (t, J = 6.5 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 1.92 (quin, 7.2 Hz, 2H), 1.79 (quin, J = 7.5 Hz, 2H), 1.58 (quin, J = 7.6 Hz, 2H), 1.45 (s, 6H).

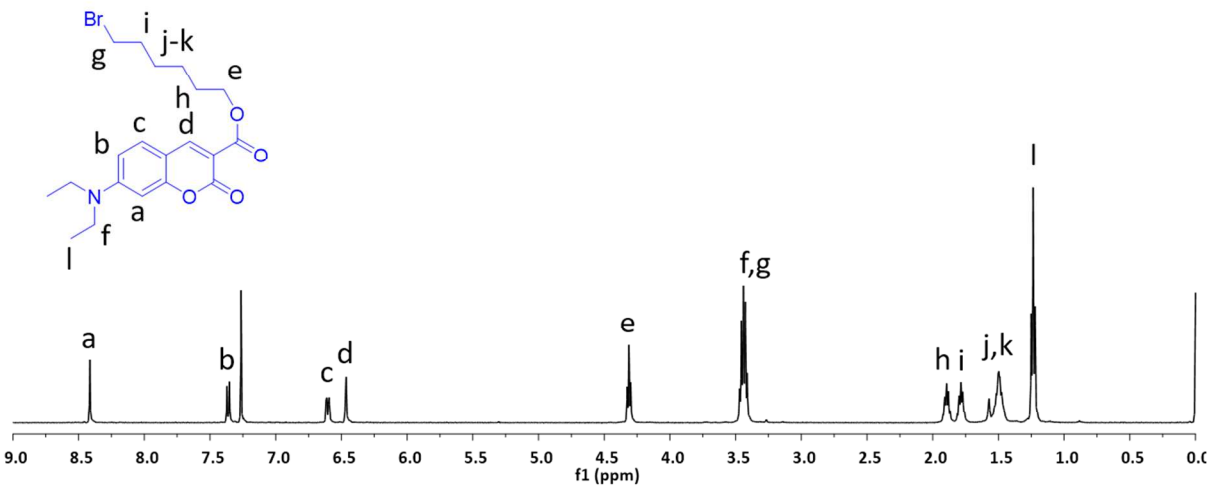

Figure S3. NMR spectrum of B dye.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 7.36 (d, J = 9 Hz, 1H), 6.61, (dd, J = 9, 2.0 Hz, 1H), 6.46 (d, J = 2 Hz, 1H), 4.31 (t, J = 6.5 Hz, 2H), 3.44 (quin, J = 7.1 Hz, 4H, 2H overlapped), 1.89 (quin, J = 6.6 Hz, 2H), 1.79 (quin, J = 6.8 Hz, 2H), 1.50 (m, 4H), 1.24 (t, J = 7 Hz, 6H).

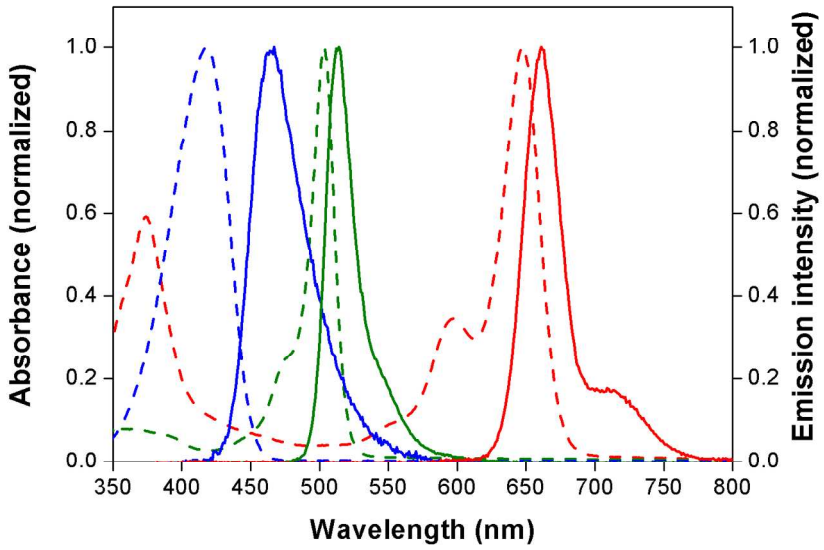

Figure S4. Absorption (dashed) and emission (solid) spectra of R, G, and B dyes in DMF. The excitation wavelength was 365 nm.

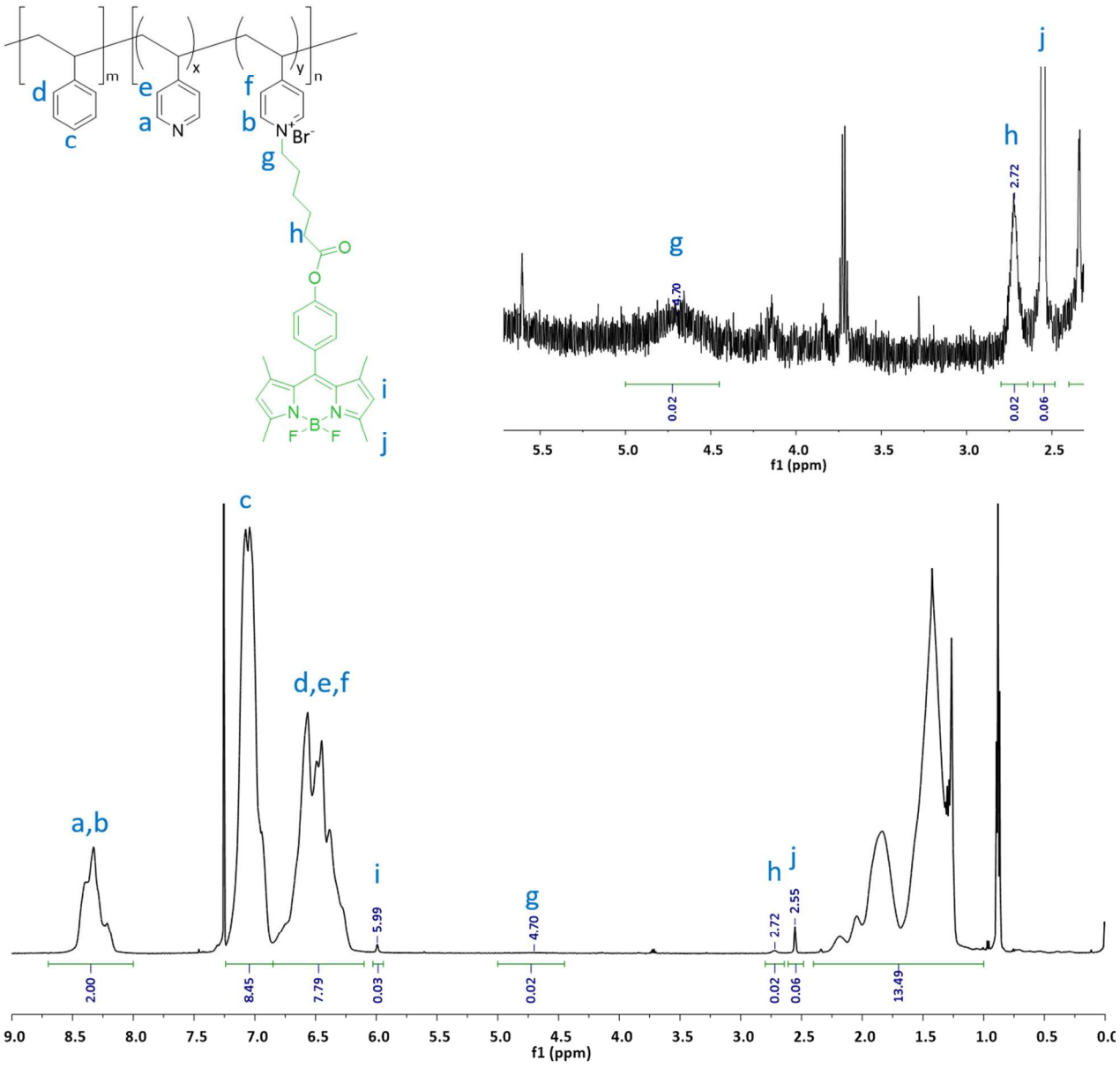

Figure S5. NMR spectrum of PS-*b*-P4VP functionalized with G dyes. The amount of G dyes in the P4VP block was calculated by comparing the signals of G dye (g, h, i, j) to those of 4-vinylpyridine (a, b).

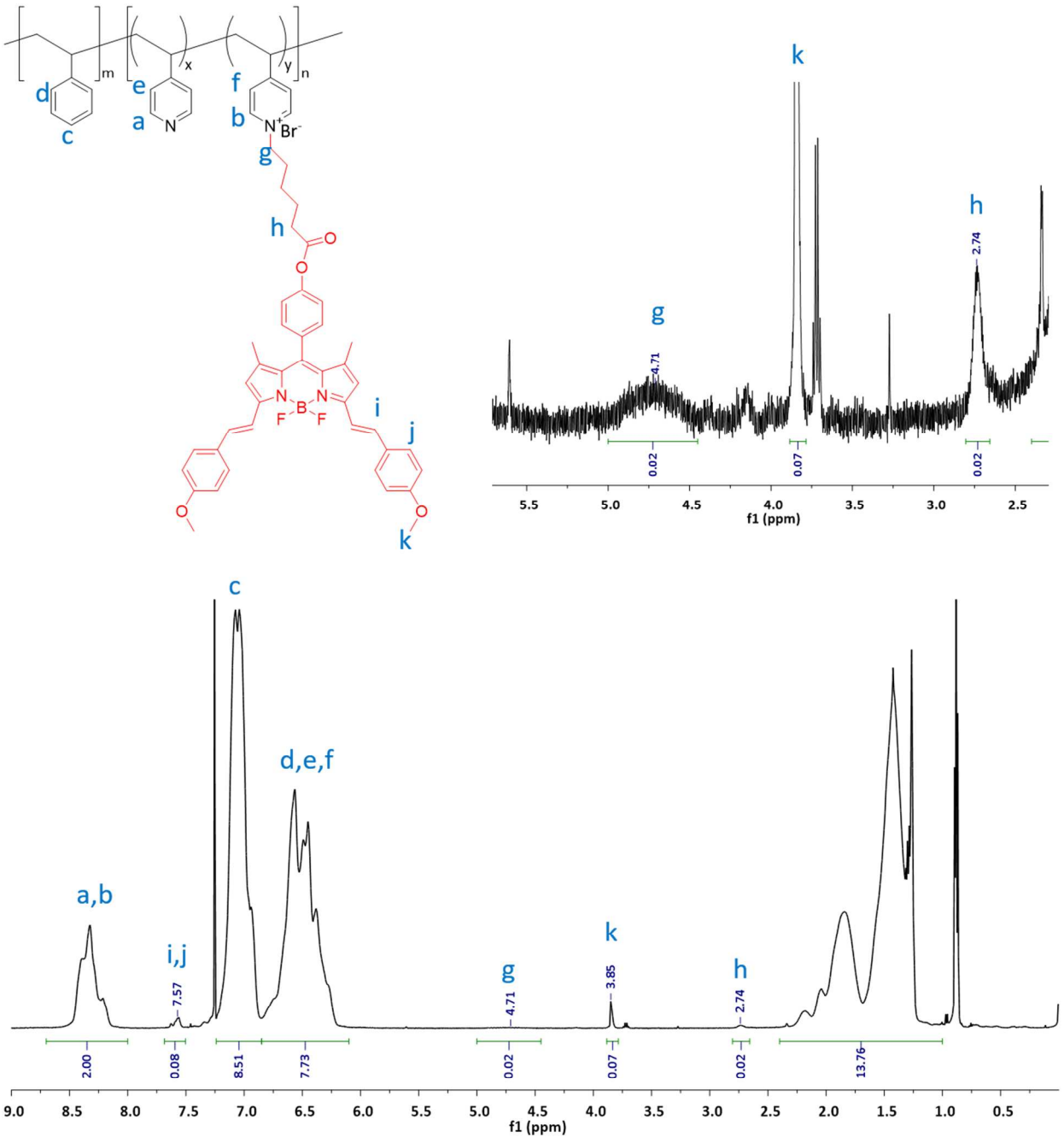

Figure S6. NMR spectrum of PS-*b*-P4VP functionalized with R dyes. The amount of R dyes in the P4VP block was calculated by comparing signals of R dye (g, h, i, j, k) to those of 4-vinylpyridine (a, b).

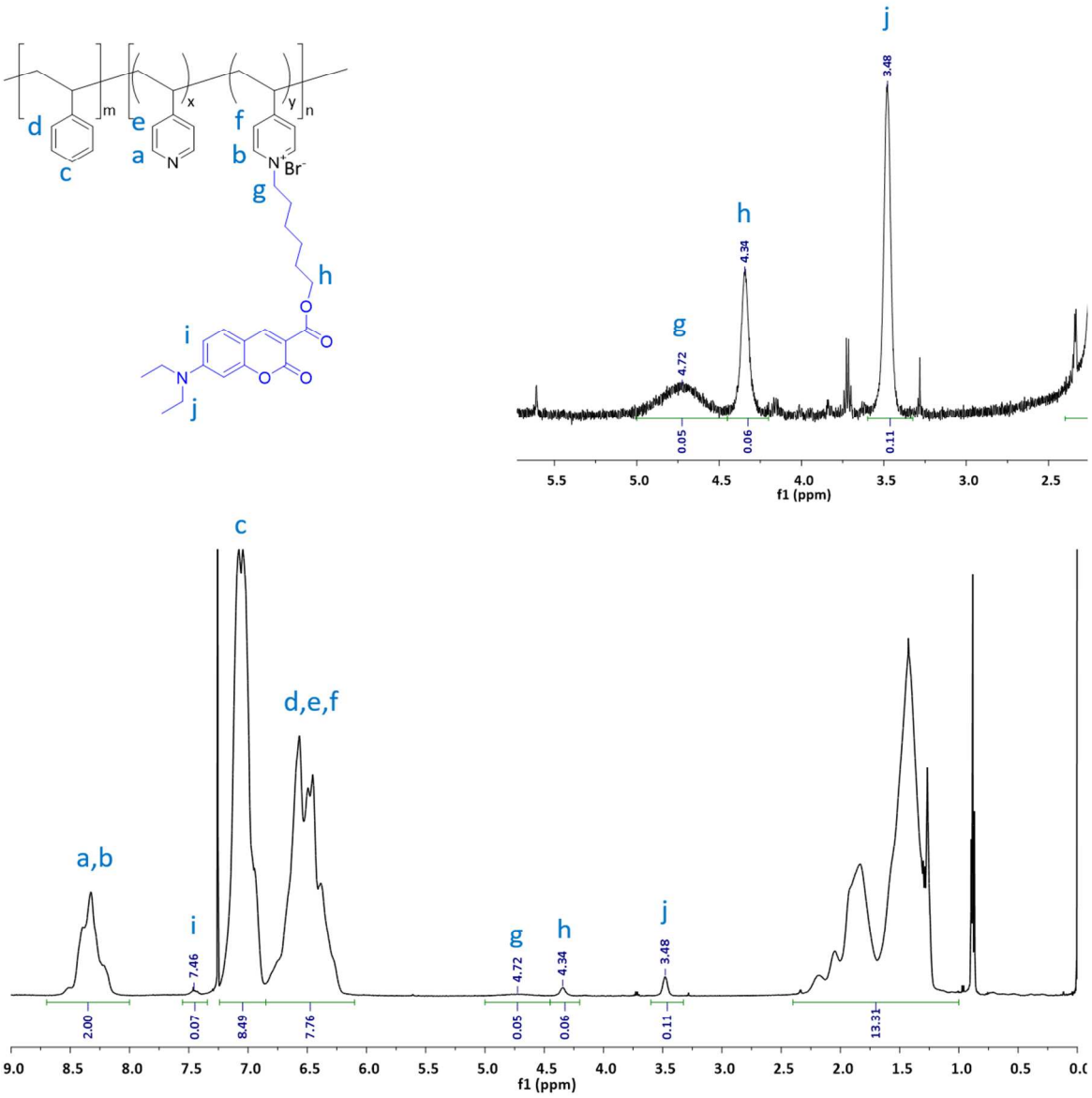

Figure S7. NMR spectrum of PS-*b*-P4VP functionalized with B dyes. The amount of B dyes in the P4VP block was calculated by comparing the signals of B dye (g, h, i, j) and 4-vinylpyridine (a, b).

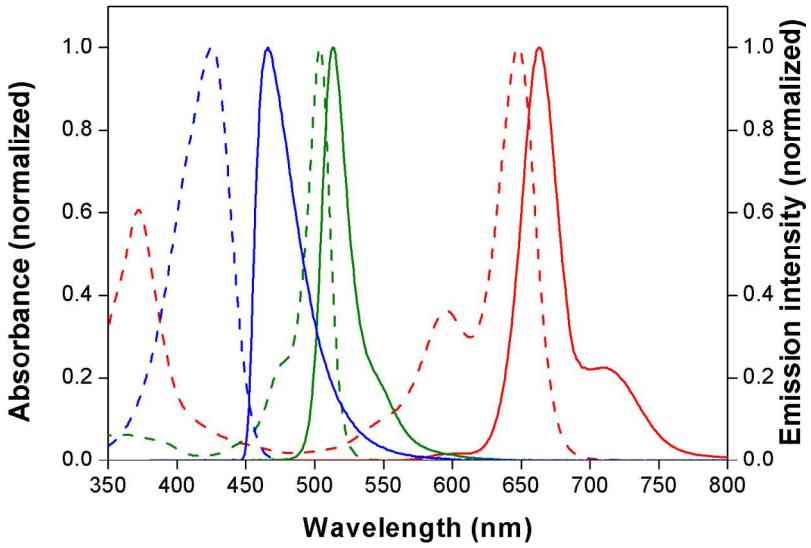

Figure S8. Absorption (dashed) and emission (solid) spectra of PS-*b*-P4VP functionalized with R, G, and B dyes in chloroform. The excitation wavelength was 365 nm.

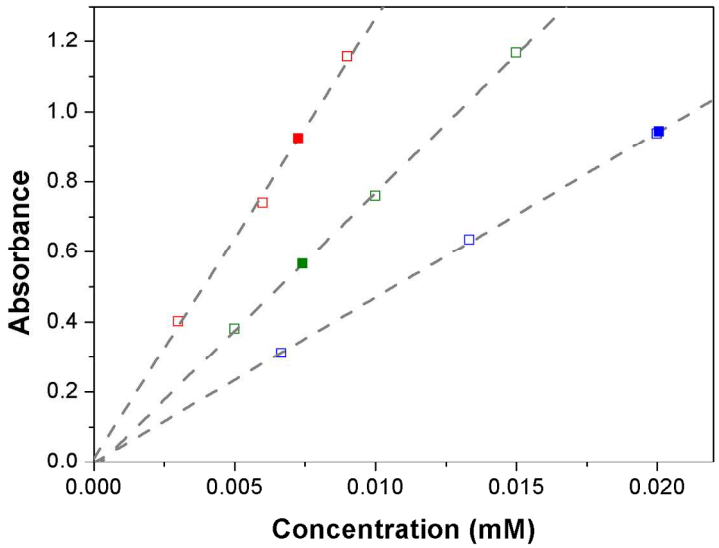

Figure S9. Absorbance vs. concentration plots for R, G, and B dyes themselves in chloroform before attached to PS-*b*-P4VP (open symbols in red, green, and blue). The amount of dyes attached to PS-*b*-P4VP was evaluated from the absorbance of dye-functionalized PS-*b*-P4VP in chloroform (0.3 mg/L), which is marked as solid symbol in red, green, and blue for R, G, and B dye-functionalized PS-*b*-P4VP, respectively.

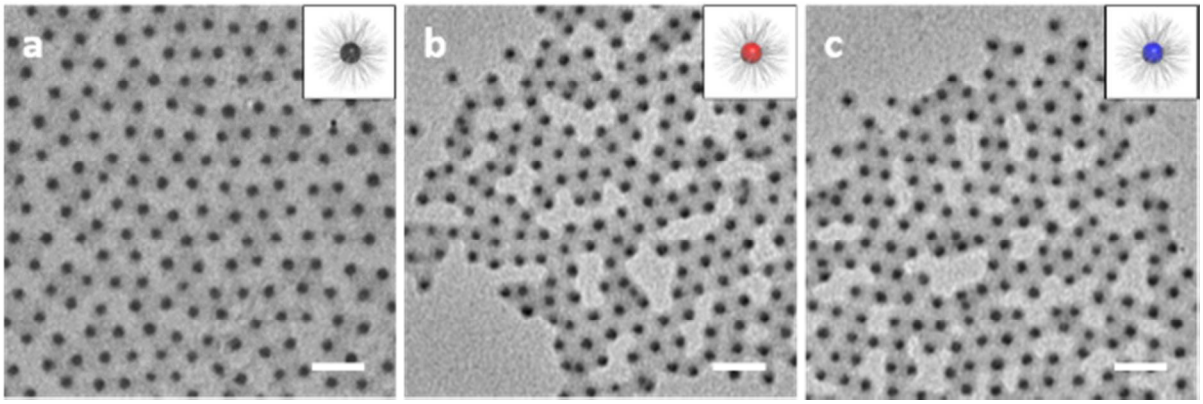

Figure S10. TEM images of spherical micelles of PS-*b*-P4VP: (a) pristine; (b) functionalized with R dyes; (c) functionalized with B dyes. All samples were stained with I_2. The scale bars are 100 nm.

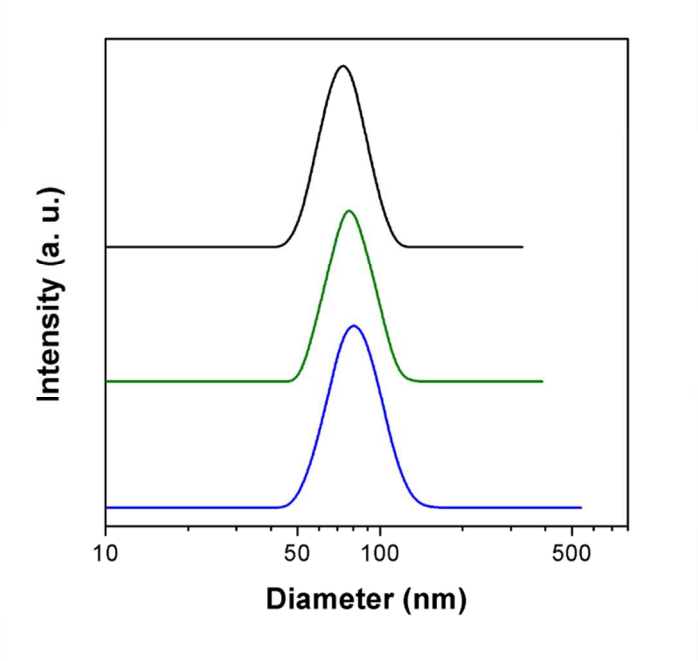

Figure S11. Diameter distributions by DLS measurements for spherical micelles of pristine PS-*b*-P4VP (black), functionalized with G dyes (green), and with B dyes (blue). PS-*b*-P4VP functionalize with R dyes was not suitable for DLS analysis because R dyes absorbed the laser light of 632 nm.

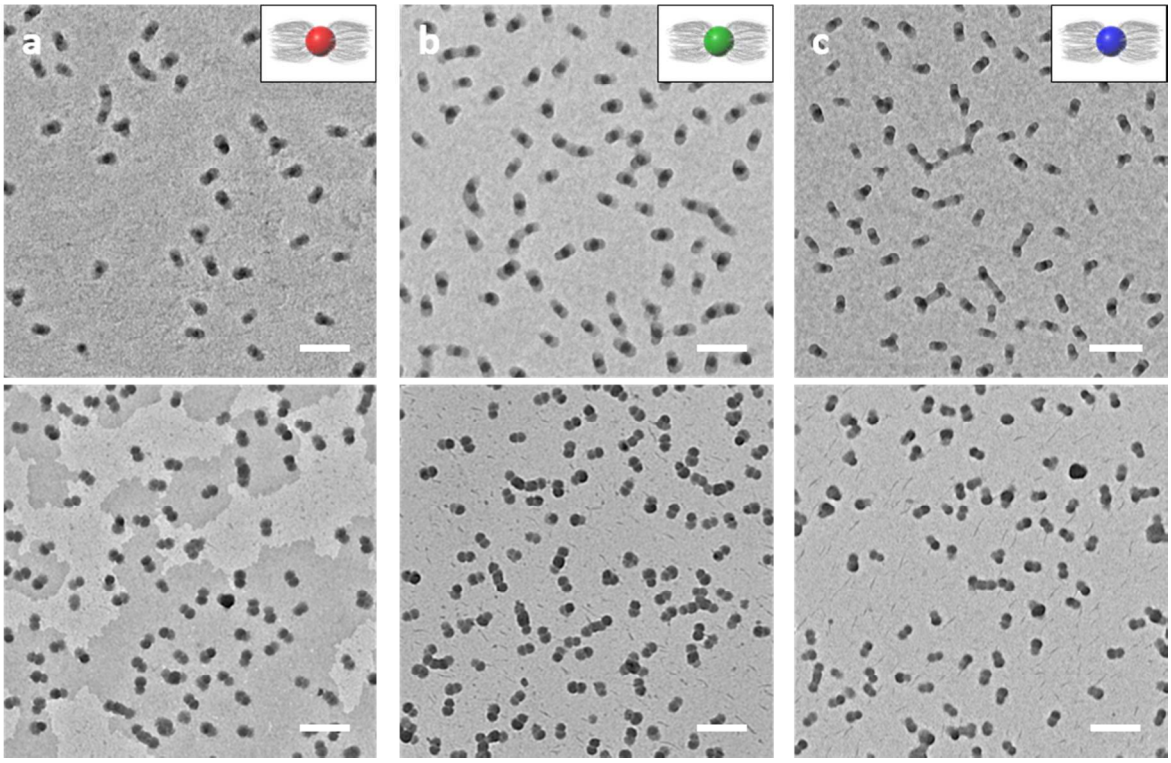

Figure S12. TEM images of patchy micelles of PS-*b*-P4VP functionalized with dyes: (a) R dyes; (b) G dyes; (c) B dyes. The images were obtained after staining with I_2 (upper row) and with RuO_4 (bottom row). The scale bars are 100 nm.

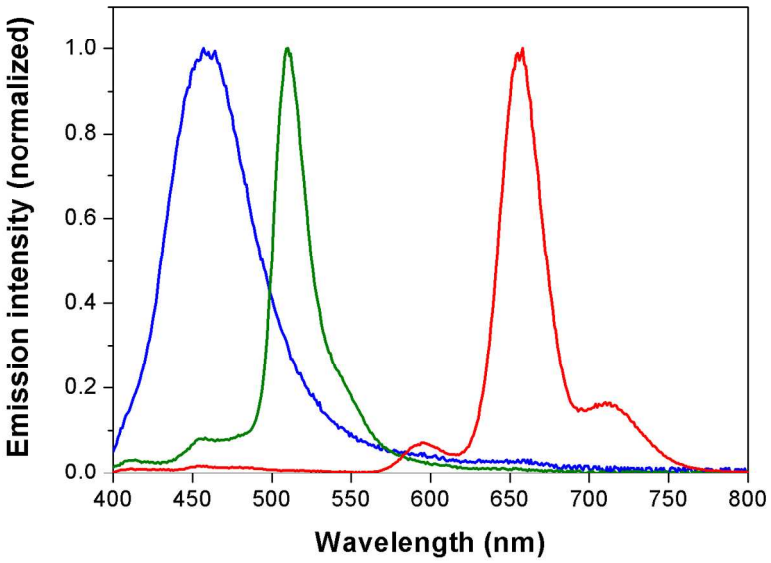

Figure S13. Emission spectra of patchy micelles of PS-*b*-P4VP functionalized with R, G, and B dyes, shown in red, green, and blue curves, respectively. The excitation wavelength was 365 nm.

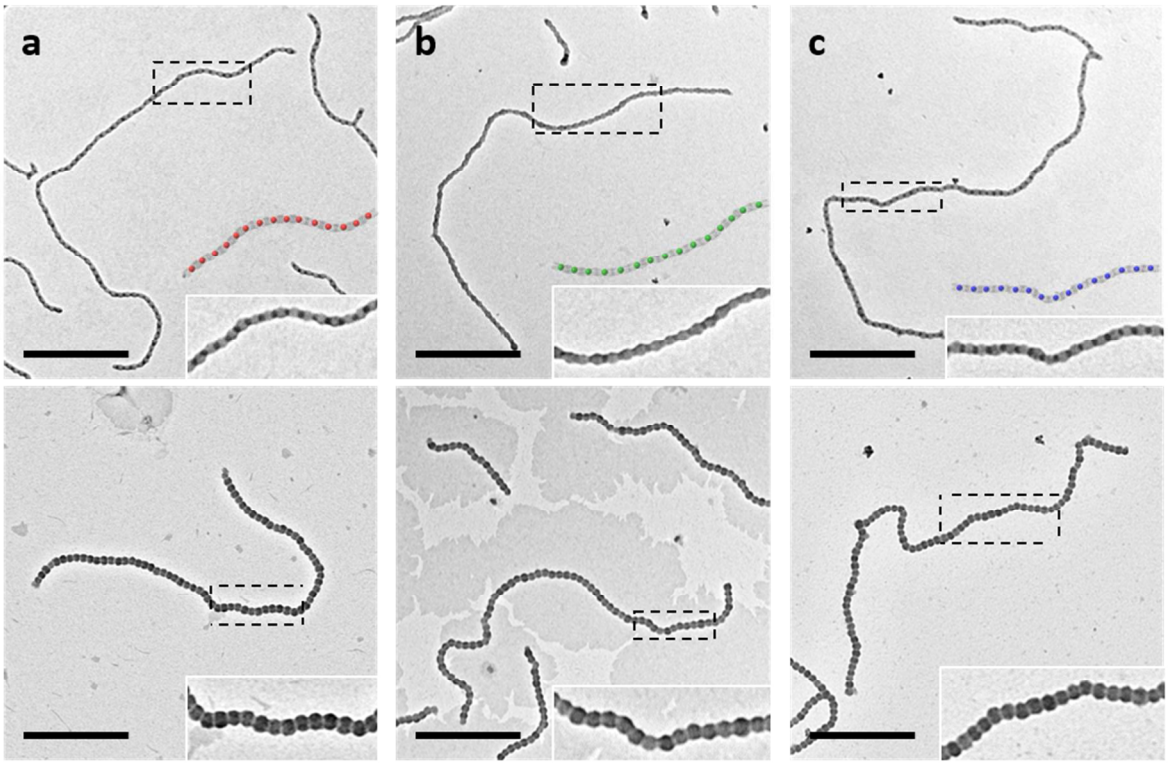

Figure S14. TEM images of supracolloidal chains with dyes: (a) R dyes; (b) G dyes; (c) B dyes. The images were obtained after staining with I_2 (upper row) and with RuO_4 (bottom row). The scale bars are 500 nm. The inset of each image is an enlarged image of the marked area.

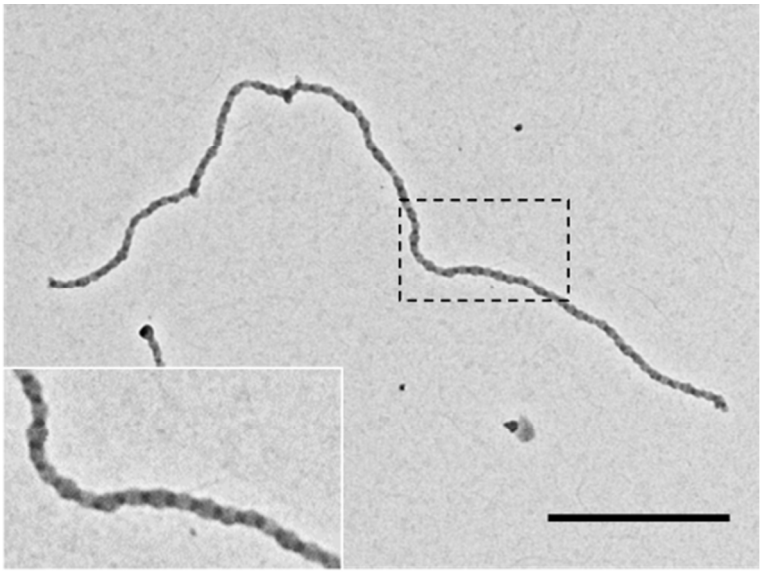

Figure S15. TEM image of a supracolloidal chain by mixing the patchy micelles containing R, G, and B dyes independently. The image was obtained after staining with I_2. The scale bar is 500 nm. The inset is a 2-fold enlarged image of the marked area.