Supporting Information

PhotocleavableGlycopolymer Aggregates

Sajith Menon, Rahul M. Ongungal and Suresh Das*

Photosciences and Photonics Section, Chemical Sciences and Technology Division

National Institute for Interdisciplinary Science and Technology, CSIR

Trivandrum – 19, Kerala, India.

E-mail: sureshdas55@gmail.com

Experimental Section

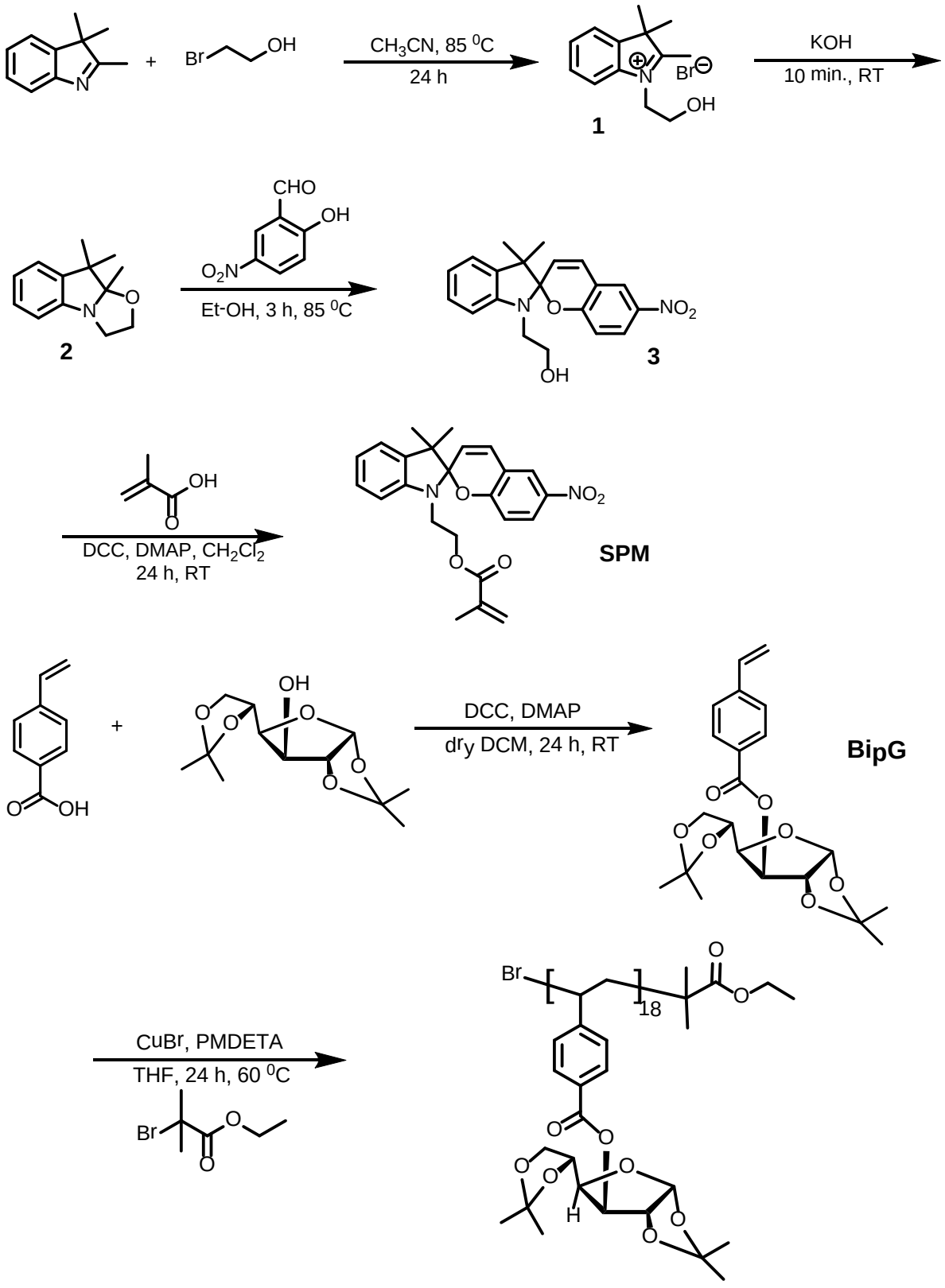
Materials.N,N,N',N",N"-Pentamethyldiethylenetriamine (PMDETA), ethyl-2-bromoisobutyrate, 1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose, 2,3,3 trimethyl-3H-indole, 2-bromoethanol,methacrylic acid, 4-vinylbenzoic acid, dicyclohexylcarbodiimide (DCC), 4-(N,N-dimethylamino)pyridine (DMAP) and Coumarin 7were purchased from Aldrich and used without further purification. CuBr (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and then it was washed with ethanol and dried under vacuum overnight. Solvents were purchased locally and purified using standard procedures before use.

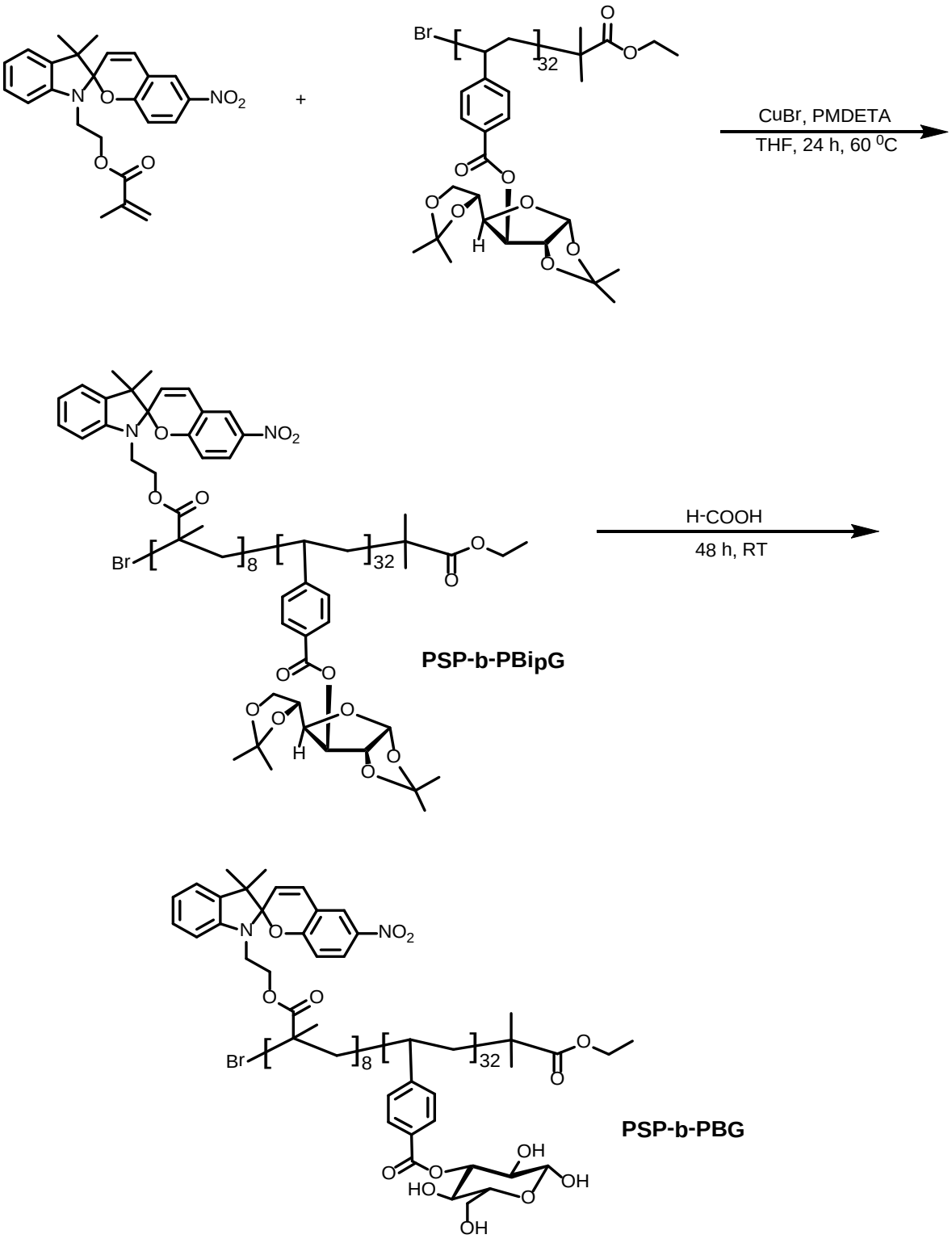
Analysis and Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 500 MHz Spectrometer using tetramethylsilane (TMS) as the internal standard. chloroform-d ($CDCl_3$) and DMSO-d_6 were used as solvents.The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene standards for the calibration. The GPC was calibrated with different polystyrene standards having molecular weights ranging from 2950 to 177,000 g/mol (Polymer Standards Service).Waters 515 pump connected through three series of StyragelHR

columns (HR-3, HR-4E, and HR-5E) and Waters Model 2487 Dual wavelength UV-Vis Detector and a Waters 2414 Differential Refractometer were used for analyzing the samples. The flow rate of the THF was maintained as 1 mL/min throughout the experiments, and the sample solutions at very dilute concentration were filtered and injected for recording the GPC chromatograms at 30 ^{0}C.Mass spectral analyses were carried out using a JEOL JMS600 instrument in FAB ionization mode. Melting points are uncorrected and were determined on a Mel-Temp IImelting point apparatus.Absorption spectra were recorded on a Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer. The excitation and emission spectra were recorded on a SPEX Fluorolog F112X spectrofluorimeter. Steady-state photolysis was carried out using the output from a 200 W high-pressure mercury lamp filtered through a 360 nmor 560nmOriel band-pass filter. Irradiation was carried out on stirred solutions in a cuvette at 21 ^{0}C. No change in sample temperature was observed during the irradiation period. Dynamic light scattering (DLS) measurements were done by using a Nano ZS Malvern instrument employing a 4-mW He-Ne laser (λ = 632.8 nm) and equipped with a thermo stated sample chamber. Samples for scanning electron microscopy (SEM) were provided with a thin gold coating using JEOL JFC-1200 fine-coater. SEM images were recorded using a JEOL JSM-5600 LV instrument.Atomic force microscopy (AFM) images were recorded under ambient conditions using NTEGRA Prima - NT-MDT, Russia Scanning probe microscope operated in tapping mode. Micro-fabricated silicon cantilever tips (NSG 20) with a resonance frequency of 260-630 kHz and a force constant of 20-80 Nm^{-1} were used. The tip curvature radius was 10nm. The scan rate was 1 Hz. To prepare samples for SEM and AFM measurements, a drop of the polymer colloidal solution was placed on a freshly cleaved mica sheet and the solution was allowed to evaporate at room temperature in air. Transmission electron microscopy (TEM) images were recorded JEOL JEM 1011 with an accelerating voltage of 100kV. Samples were prepared by drop-casting aqueous solutions of PSP-b-PBG on a carbon coated

copper grids under ambient conditions. The solvent was allowed to evaporate at room temperature. TEM images were obtained without staining.

Synthesis and Characterization of PSP-b-PBG





Scheme S1. Synthesis of PSP-b-PBG.

Synthesis of 1-(-2-hydroxyethyl)-2,3,3-trimethyl-3H-indolium bromide (1). A solution of 2,3,3 trimethyl-3H-indole (2.83 g, 17.75 mmol) and 2-bromoethanol (3.31 g,26.50 mmol) in MeCN(20 mL) was heated for 24 hours under reflux and nitrogen. After cooling down to ambient temperatures, the solvent was distilled off under reduced pressure. The residue was suspended in hexane (25 mL) and the mixture was sonicated and filtered. The resulting solid was precipitated from chloroform by adding hexane to give a pink solid.

Yield = 4.69g(93.43%); mp = 191^{0}C ; FABMS : *m/z* = 204.35 $[M\text{-}Br]^+$; ^{1}H-NMR ($CDCl_3$):δ = 7.79 (m, 1H, aromatic), 7.58-7.27 (m, 3H, aromatic), 4.90 (t, 2H, =N-C**H$_2$**-CH_2-), 4.19 (t, 2H, N-CH_2-C**H$_2$**-), 2.18 (s, 3H, -N=C-C**H$_3$**), 1.65 (s, 6H, -C(C**H$_3$**)$_2$-) ; ^{13}C-NMR (CD_3CN): δ = 197.37, 141.27, 140.74, 129.77, 128.51, 122.99, 110.86, 58.06, 51.44, 50.72, 22.91, 15.78.

Synthesis of 9,9,9a-trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a] indole (2). A solution of **4** (4.30 g, 15.90 mmol) and KOH (0.93 g, 16.57 mmol) in water (50 mL) was stirred at ambient temperature for 10 min. and, then, it was extracted with ether (3X20 mL). The organic phase was concentrated under reduced pressure to afford **2** as yellow oil.

Yield = 3.11g(96.23%); FABMS : *m/z* = 204.39 $[M+H]^+$; ^{1}H-NMR ($CDCl_3$):δ = 7.14-7.03 (m, 2H, aromatic), 6.90 (t, 1H, aromatic), 6.74 (d, 1H, aromatic), 3.81-3.65 (m, 2H, -CH_2-C**H$_2$**-O-), 3.57-3.46 (m, 2H, -N-C**H$_2$**-CH_2-), 1.41 (s, 3H, -C-C**H$_3$**), 1.36 (s, 3H,-C-(C**H$_3$**)$_2$), 1.18(s, 3H,-C-(C**H$_3$**)$_2$) ; ^{13}C-NMR ($CDCl_3$): δ = 150.33, 139.77, 127.31, 122.20, 121.51, 111.77, 108.75, 62.75, 49.84, 46.73, 27.90, 15.12.

Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-yl)ethanol (3). A solution of 2-hydroxy-5-nitrobenzaldehyde (3.70 g, 22.15mmol) and **2** (3.0 g, 14.77mmol) in EtOH (35 mL) was maintained under N_2 and heatedunder reflux for 3 hours. After being cooled to ambient temperature,the mixture was filtered. The resulting purple solid waswashed with EtOH (10 mL) and dried to afford **3** as shining purple crystals.

Yield = 3.73g(71.72%); mp = 171^{0}C ; FABMS : *m/z* = 353.26 $[M+H]^+$; ^{1}H-NMR ($CDCl_3$):δ = 8.04 (d, 1H, aromatic), 7.99 (dd, 1H, aromatic), 7.14 (pt, 1H, aromatic), 7.10 (1H, d, aromatic), 6.92 (d, 1H, -O-C-CH=C**H**-), 6.78(pt, 1H, aromatic), 6.68 (d, 1H, aromatic), 6.65 (d, 1H, aromatic), 5.90 (d, 1H, -O-C-C**H**=CH-), 3.81-3.70 (m, 2H, -N-CH_2-C**H$_2$**-OH), 3.45-3.31 (m, 2H,-N-C**H$_2$**-CH_2-OH), 1.24 (s, 3H, -C-(C**H$_3$**)$_2$), 1.19 (s, 3H, -C-(C**H$_3$**)$_2$); ^{13}C NMR (CD_3CN) *δ* 166.09, 146.95, 141.00, 135.78, 129.76, 128.15, 127.77, 125.86, 122.70, 121.95, 119.85, 118.93, 115.45, 106.81, 106.31, 60.75, 52.76, 46.02, 25.82, 19.93.

Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]-1'-yl)ethyl methacrylate (SPM). To a mixture of **3** (3.52 g, 10 mmol), methacrylic acid (1.03g, 11.61 mmol) and 1,3-dicyclohexylcarbodiimide (2.5 g, 12 mmol) in dichloromethane(55 mL) was added dimethylaminopyridine (0.15 g, 1.20 mmol), and stirred at room temperature for 24 hours. After the reaction the solid was filtered off, washed several times with dichloromethane and the filtrate was concentrated and finally purified by column chromatography (basic alumina, 10% EtOAc-hexane as eluent).

Yield = 3.43g(81.70%); mp = 85^{0}C ; FABMS : *m/z* = 421.94 $[M+H]^+$; ^{1}H-NMR ($CDCl_3$):δ = 8.03 (d, 1H, aromatic), 8.00 (dd, 1H, aromatic), 7.21 (t, 1H, aromatic), 7.10 (d, 1H, aromatic), 6.92 (d, 1H, -O-C-CH=C**H**-), 6.88 (t, 1H, aromatic), 6.74 (d, 1H, aromatic), 6.70 (d, 1H, aromatic), 6.07 (s, 1H,-OCO-C(CH_3)=C**H$_2$**), 5.87 (d, 1H, -O-C-CH=C**H**-), 5.56 (s, 1H, -OCO-C(CH_3)=C**H$_2$**), 4.30 (t, 2H, -N-CH_2-C**H$_2$**-), 3.50 (m, 2H, N-C**H$_2$**-CH_2-), 1.92 (s, 3H,-OCO-C(C**H$_3$**)=CH_2), 1.28 (s, 3H, -C-(C**H$_3$**)$_2$), 1.17 (s, 3H, -C-(C**H$_3$**)$_2$) ;^{13}C-NMR ($CDCl_3$): δ = 167.17, 159.36, 146.62, 141.04, 136.00, 135.66, 128.26, 127.81, 125.88, 122.74, 121.77, 119.89, 118.39, 115.53, 106.72, 106.49, 62.60, 52.77, 42.39, 29.66, 26.87, 25.80, 19.79, 18.32.

Synthesis of 3-O-4-vinylbenzoyl-1,2:5,6-di-O-isopropyliden-D-glucofuranose (BipG). To a mixture of 4-vinylbenzoic acid (2.85 g, 19.25 mmol), 1,2:5,6-di-O-isopropyliden-D-glucofuranose (5.00 g, 19.21 mmol) and 1,3-dicyclohexylcarbodiimide (4.20 g, 20.36 mmol) in dichloromethane (100 mL) was added dimethylaminopyridine (0.25 g, 2.05 mmol), and stirred at room temperature for 24 hours. After the reaction the solid was filtered off, washed several times with dichloromethane and the filtrate was concentrated and finally purified by column chromatography (Silica gel, 10% EtOAc-hexane as eluent).

Yield = 6.17 g (81.9%); FABMS : *m/z* = 413.38 $[M+Na]^+$; ^{1}H-NMR ($CDCl_3$):δ = 7.99 (d, 2H, aromatic), 7.47 (d, 2H, aromatic), 6.75 (m, 1H, -C**H**=CH_2), 6.00 (dd, 1H, -CH=C**H$_2$**), 5.89 (dd, 1H, -O-C**H**(O)-CH-), 5.52 (dd, 1H, -CH=C**H$_2$**), 4.71 (m, 1H, -CH(COOAr)-C**H**(O)-CH-), 4.34 (m, 2H, -CH-C**H(**COOAr)-CH-, -CH-C**H**(O)-CH(COOAr)-), 4.10 (m, 1H, -CH_2(O)-C**H**(O)-CH-), 3.77 (m, 2H, -O-C**H$_2$**-CH(O)-), 1.32-1.42 (m, 12H, -O-C(C**H$_3$**)$_2$-O-) ; ^{13}C-NMR (CD_3Cl): δ = 165, 142.50, 135.8, 130.29, 130.04, 126.26, 117, 112.50, 109.40, 105.50, 83.13, 76.81, 72.59, 68.27, 64.23, 26.82, 25.20.

Synthesis of poly(3-O-4-vinylbenzoyl-1,2:5,6-di-O-isopropyliden-D-glucofuranose)(PBipG). CuBr (10.00 mg, 0.07 mmol) was added to a 10 mL round bottom flask containing BipG (1 g, 2.65 mmol), ethyl-2-bromoisobutyrate (10.60 mg, 0.06 mmol) and PMDETA (9.13 mg, 0.05 mmol) in THF (3.0 mL). The flask was sealed with rubber septum and was purged with argon for 20 minutes before adding the catalyst. The flask was placed in a preheated oil bath at 60^0C for 24hours. The viscous liquid was dissolved in THF and was passed through a neutral alumina column to remove the catalyst and was then concentrated and precipitated in methanol twice.

Yield = 675 mg (67.5%); ^{1}H-NMR ($CDCl_3$):δ = 7.59 (m, 2H, aromatic), 6.40 (m, 2H, aromatic), 5.97 (m , 1H), 5.37 (m, 1H), 4.69 (m, 1H,), 4.31 (m, 2H),4.06 (m, 2H), 1.55-1.60 (m, 3H, -C**H$_2$**C**H**-), 1.25-1.38 (m, 12H, -O-C(C**H$_3$**)$_2$-O-); M_n = 12,499, M_w/M_n = 1.23.

Synthesis of poly(spiropyran)-b-poly(3-O-4-vinylbenzoyl-1,2:5,6-di-O-isopropyliden-D-glucofuranose)(PSP-b-PBipG). CuBr (11.00 mg, 0.08 mmol) was added to a 10 mL round bottom flask containing SPM (500mg, 1.19 mmol), PBipG (500 mg, 0.04 mmol) and PMDETA (12.45 mg, 0.07 mmol) in THF (3.0 mL). The flask was sealed with rubber septum and was purged with argon for 20 minutes before adding the catalyst. The flask was placed in a preheated oil bath at 60^{0}C for 24hours. The viscous liquid was dissolved in THF and was passed through a neutral alumina column to remove the catalyst and was then concentrated and precipitated in methanol thrice.

Yield = 612 mg (61.20%); ^{1}H-NMR ($CDCl_3$):δ = 7.89 (m, 2H, aromatic), 7.63 (m, 2H, aromatic), 7.03 (m, 2H, aromatic) , 6.80 (m, 2H, aromatic, -O-C-CH=C**H**-), 6.58 (m, 2H, aromatic), 6.41 (m, 2H, aromatic), 5.97 (m , 1H),5.77 (m, 1H, -O-C-C**H**=CH-), 5.40 (m, 1H), 4.72 (m, 1H), 4.32 (m, 2H),4.08 (m, 2H), 3.94 (m, 2H, -N-CH_2-C**H$_2$**-), 3.41 (m, 2H, -N-C**H$_2$**-CH_2-), 1.55-1.60 (m, 3H, -C**H$_2$**C**H**-), 1.25-1.38 (m, 12H, -O-C(C**H$_3$**)$_2$-O-), 0.77-1.08 (m, 5H, -(C**H$_3$**)C(COOSP)C**H$_2$**-); M_n = 15,791, M_w/M_n = 1.45.

Synthesis of poly(spiropyran)-b-poly(3-O-4-vinylbenzoyl-D-glucopyranose) (PSP-b-PBG).100 mg of the protected polymer PSP-b-PBipG was dissolved in 80%formic acid (10 mL) and stirred for 48hours at room temperature. Additional 5 mL water was added and stirred for another 3 hours. The solution was dialyzed against distilled water for 2 days, concentrated in-vacuum and finally lyophilized to give **PSP-b-PBG** in quantitative yield.

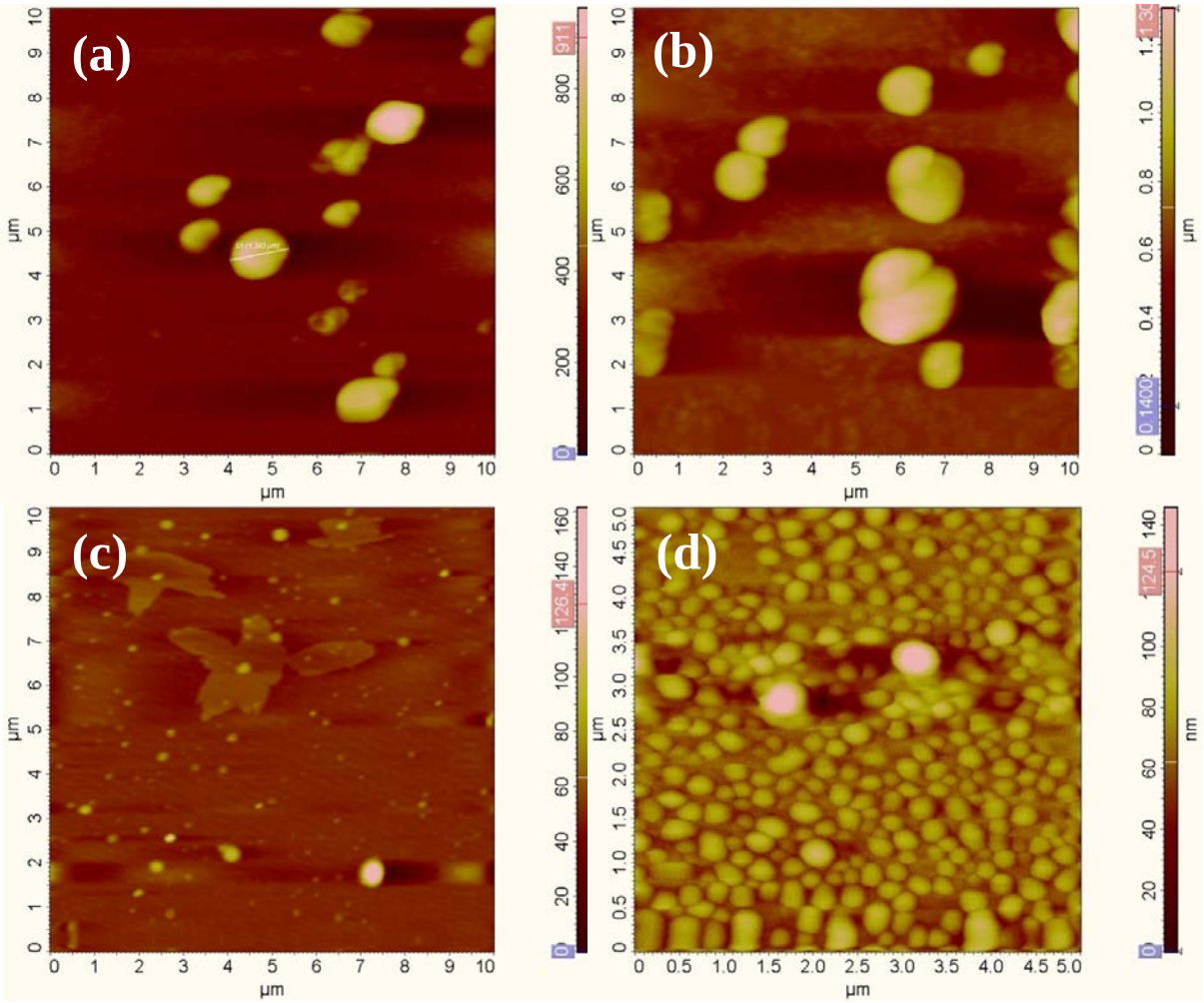
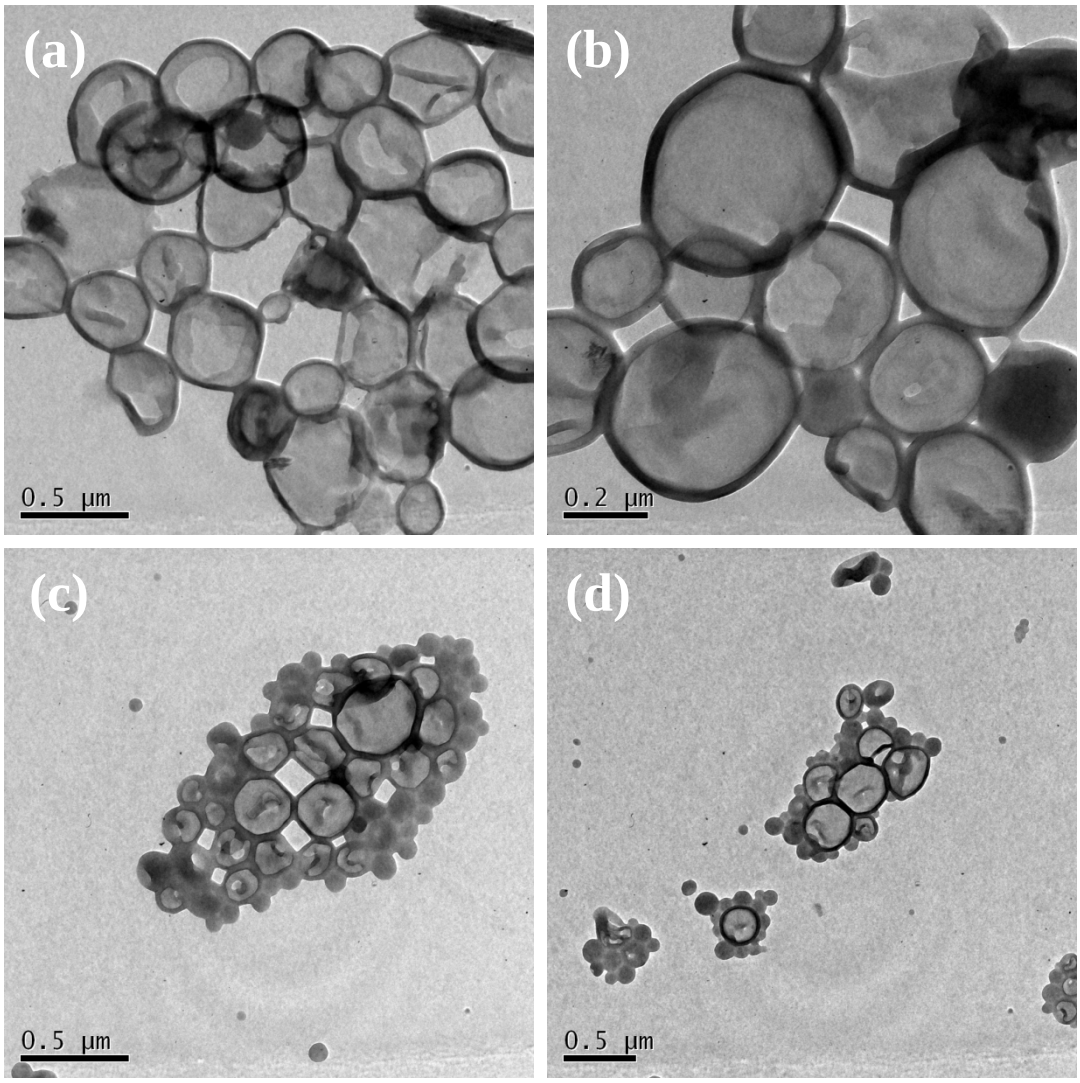


Figure S2. AFM images of PSP-b-PBG aqueous solutions drop-cast and air-dried on mica under various conditions: (a, b) before exposure to 360 nm UV light (c) after exposure to 360 nm UV light for 2 h (d) after exposure to 360 nm UV light for 2 h followed by exposure to 560 nm visible light for 2 h.



FigureS3.(a, b) TEM images showing vesicular aggregates of PSP-b-PBG obtained from its aqueous solution. (c, d) TEM images obtained after exposure to 360 nm UV light for 2 h followed by exposure to 560 nm visible light for 2 h.