

Supporting Information

Photoresponsive Fluorescent Glycopolymer

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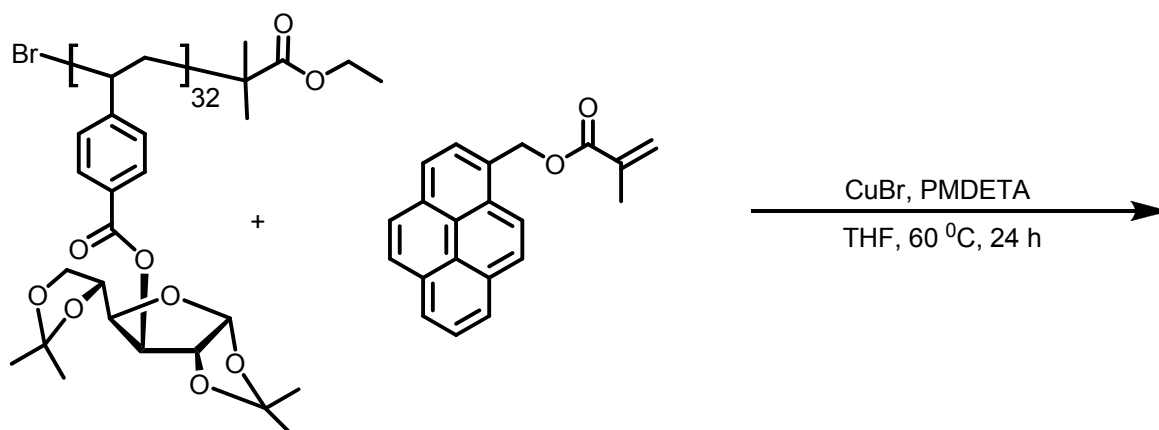
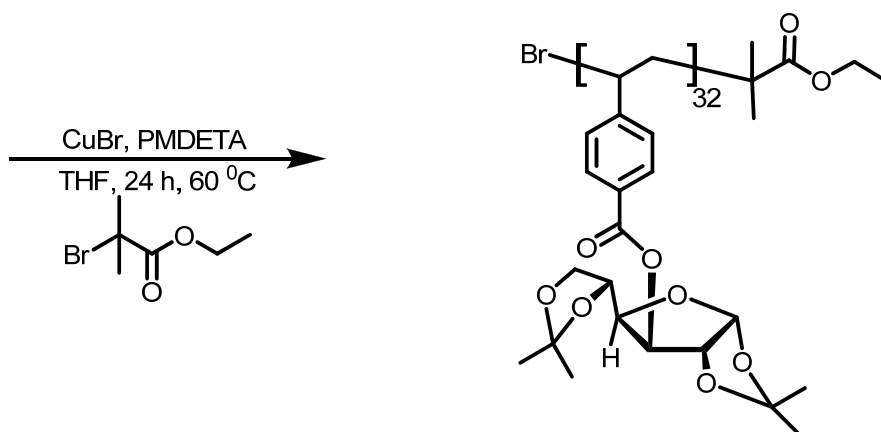
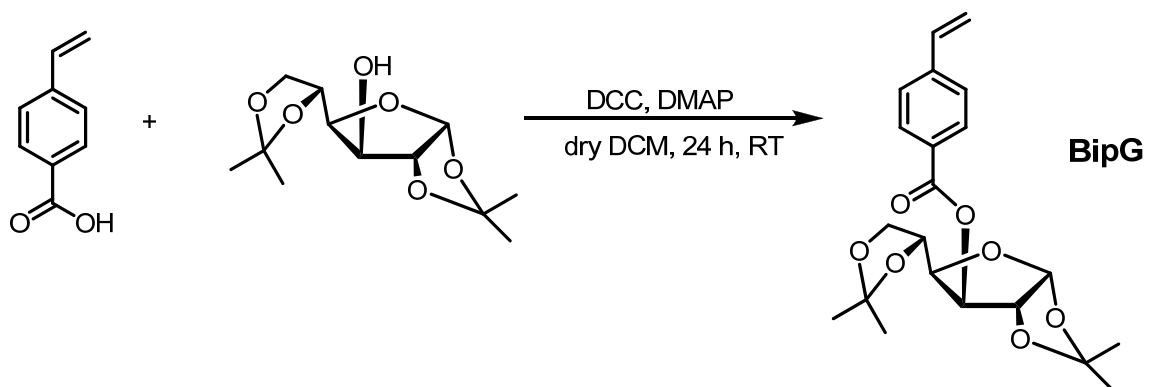
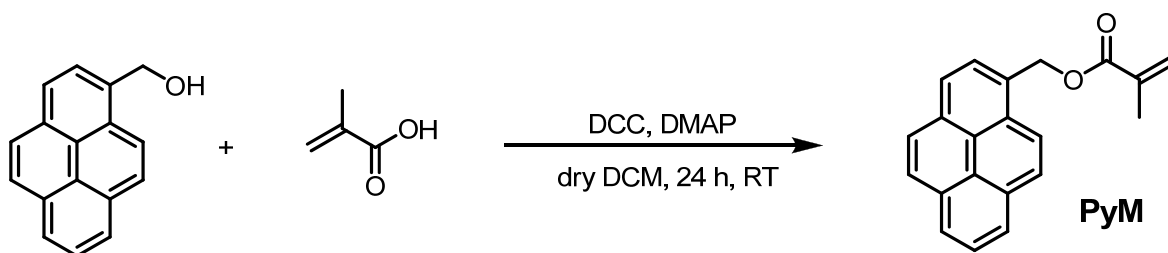
Experimental Section

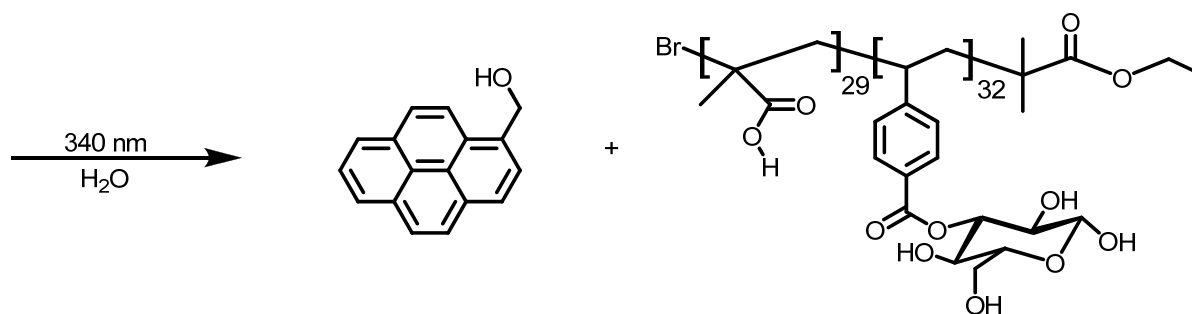
Materials. N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA), ethyl-2-bromoisobutyrate, 1,2:5,6-Di-o-isopropylidene- α -D-glucofuranose, 1-pyrene methanol, methacrylic acid, 4-vinylbenzoic acid, dicyclohexylcarbodiimide (DCC), 4-(N,N-dimethylamino)pyridine (DMAP) and Nile Red were purchased from Aldrich 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. ^1H 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-d₆ 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 Styragel HR 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 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 °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 II melting 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 340 nm Oriel band-pass filter. Irradiation was carried out on stirred solutions in a cuvette at 21 °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 ($\lambda = 632.8$ nm) and equipped with a thermo stated sample chamber. 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 10 nm. The scan rate was 1 Hz. To prepare samples for 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 using a JEOL JEM 1011 instrument with an accelerating voltage of 100 kV. Samples were prepared by drop-casting aqueous solutions of PPy-b-PBG on 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 PPy-b-PBG





Scheme S1. Synthesis of PPy-b-PBG and its photosolvolytic cleavage

Synthesis of (1-pyrene)methylmethacrylate (PyM). To a mixture of 1-pyrenemethanol (5.0 g, 21.5 mmol), methacrylic acid (2.15 g, 25 mmol) and 1,3-dicyclohexylcarbodiimide (5.16 g, 25 mmol) in dichloromethane (100 mL) was added dimethylaminopyridine (305 mg, 2.5 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, 3% EtOAc-hexane as eluent).

Yield = 5.60 g (86.6%) m.p. = 99 °C ; FABMS : $m/z = 301.40 [M+H]^+$; $^1\text{H-NMR}$ (CD_3Cl): $\delta = 7.98\text{-}8.31$ (m, 9H, pyrene aromatic), 6.15 (s, 1H, $\text{CH}_2=\text{C}$), 5.89 (s, 2H, $-\text{CH}_2\text{O}-$), 5.55 (s, 1H, $\text{CH}_2=\text{C}$), 1.96 (s, 3H, $-\text{CH}_3$); $^{13}\text{C-NMR}$ (CD_3Cl): $\delta = 167.65, 143.99, 136.60, 135.42, 134.58, 132.63, 132.03, 130.07, 128.61, 128.15, 127.99, 127.12, 126.87, 126.35, 126.04, 124.76, 124.10, 121.09, 120.56, 66.75, 17.20$.

Synthesis of 3-O-4-vinylbenzoyl-1,2:5,6-di-O-isopropylidene-D-glucofuranose (BipG). To a mixture of 4-vinylbenzoic acid (2.85 g, 19.3 mmol), 1,2:5,6-di-O-isopropylidene-D-glucofuranose (5.00 g, 19.2 mmol) and 1,3-dicyclohexylcarbodiimide (4.20 g, 20.4 mmol) in dichloromethane (100 mL) was added dimethylaminopyridine (250 mg, 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 : $m/z = 413.38 [M+Na]^+$; $^1\text{H-NMR}$ (CDCl_3): $\delta = 7.99$ (d, 2H, aromatic), 7.47 (d, 2H, aromatic), 6.75 (m, 1H, $-\text{CH}=\text{CH}_2$), 6.00 (dd, 1H, $-\text{CH}=\text{CH}_2$), 5.89 (dd, 1H, $-\text{O}-\text{CH}(\text{O})-\text{CH}-$), 5.52 (dd, 1H, $-\text{CH}=\text{CH}_2$), 4.71 (m, 1H, $-\text{CH}(\text{COOAr})-\text{CH}(\text{O})-\text{CH}-$), 4.34 (m, 2H, $-\text{CH}-\text{CH}(\text{COOAr})-\text{CH}-$, $-\text{CH}-\text{CH}(\text{O})-\text{CH}(\text{COOAr})-$), 4.10 (m, 1H, $-\text{CH}_2(\text{O})-\text{CH}(\text{O})-\text{CH}-$), 3.77 (m, 2H, $-\text{O}-\text{CH}_2-\text{CH}(\text{O})-$), 1.32-1.42 (m, 12H, $-\text{O}-\text{C}(\text{CH}_3)_2-\text{O}-$); $^{13}\text{C-NMR}$ (CD_3Cl): $\delta = 165$, 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-isopropylidene-D-glucofuranose) (PBipG). CuBr (10.00 mg, 0.07 mmol) was added to a 10 mL round bottom flask containing BipG (1.0 g, 2.7 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 $60\text{ }^\circ\text{C}$ for 24 hours. 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%); $^1\text{H-NMR}$ (CDCl_3): $\delta = 7.59$ (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, $-\text{CH}_2\text{CH}-$), 1.25-1.38 (m, 12H, $-\text{O}-\text{C}(\text{CH}_3)_2-\text{O}-$); GPC (THF): $M_n = 12,297$, $M_w/M_n = 1.19$.

Synthesis of poly(pyrenylmethyl methacrylate)-b-poly(3-O-4-vinylbenzoyl-1,2:5,6-di-O-isopropylidene-D-glucofuranose) (PPy-b-PBipG). CuBr (11.00 mg, 0.08 mmol) was added to a 10 mL round bottom flask containing PPy (500 mg, 1.67 mmol),

PBipG (500 mg, 0.04 mmol) and PMDETA (12.50 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 °C for 24 hours. 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 = 550 mg (55%); ¹H-NMR (CDCl₃): δ = 7.49 (m, 11H, aromatic), 6.40 (m, 2H, aromatic), 5.97 (m, 1H), 5.37 (m, 1H), 5.27 (m, 2H, -OCOCH₂-Py), 4.69 (m, 1H), 4.31 (m, 2H), 4.06 (m, 2H), 1.55-1.60 (m, 3H, -CH₂CH-), 1.25-1.38 (m, 12H, -O-C(CH₃)₂-O-), 0.69-0.88 (m, 5H, -(CH₃)C(COOCH₂Py)CH₂-); GPC (THF): M_n = 21,194, M_w/M_n = 1.46.

Synthesis of poly(pyrenylmethyl methacrylate)-b-poly(3-O-4-vinylbenzoyl-D-glucopyranose) (PPy-b-PBG). 120 mg of the protected polymer PPy-b-PBipG was dissolved in 80% formic acid (12 mL) and stirred for 48 hours at room temperature. Additional 6 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 PPy-b-PBG in quantitative yield.

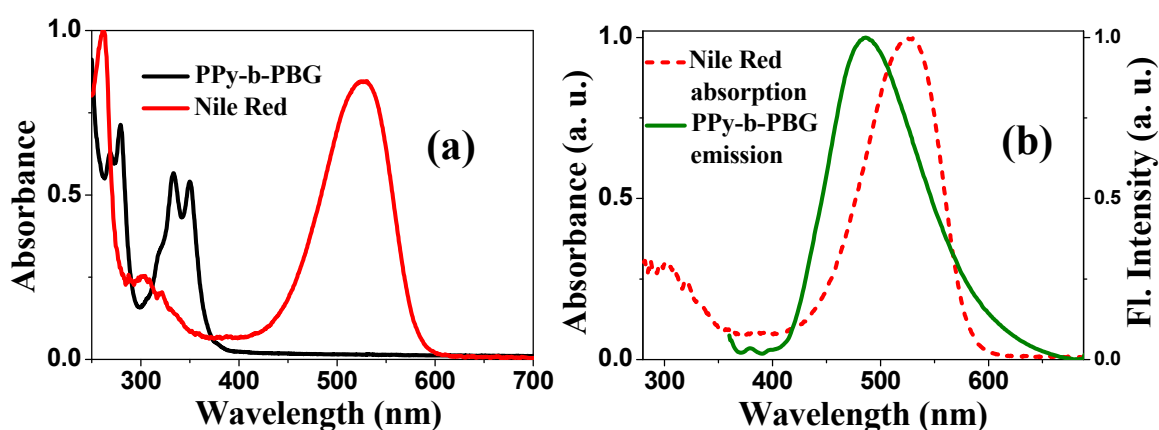


Figure S1. (a) Absorption spectra of Nile Red and PPy-b-PBG in THF and water respectively. (b) Comparison of the absorption spectra of Nile Red in THF with the fluorescence spectra of PPy-b-PBG in water.

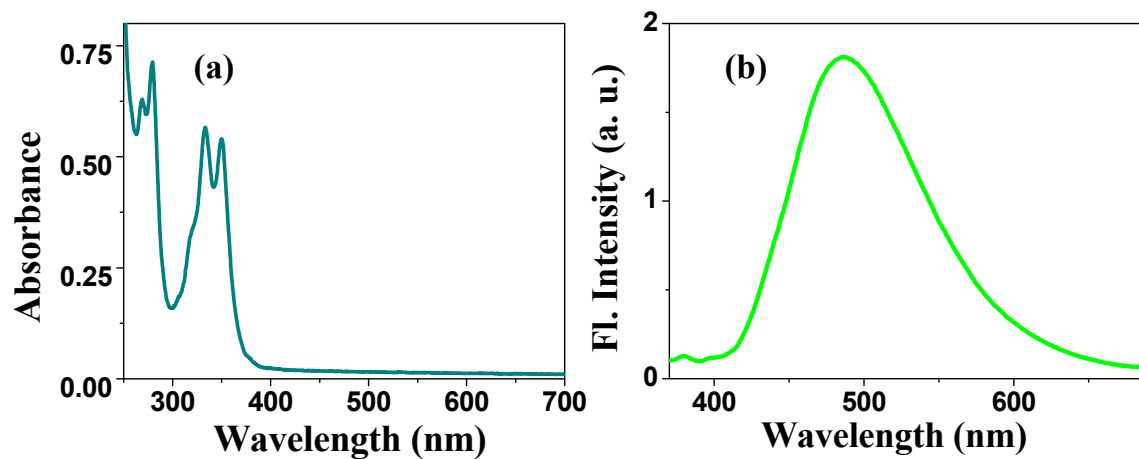


Figure S2. (a) Absorption spectra of PPy-b-PBG in water (b) emission spectra of PPy-b-PBG in water.

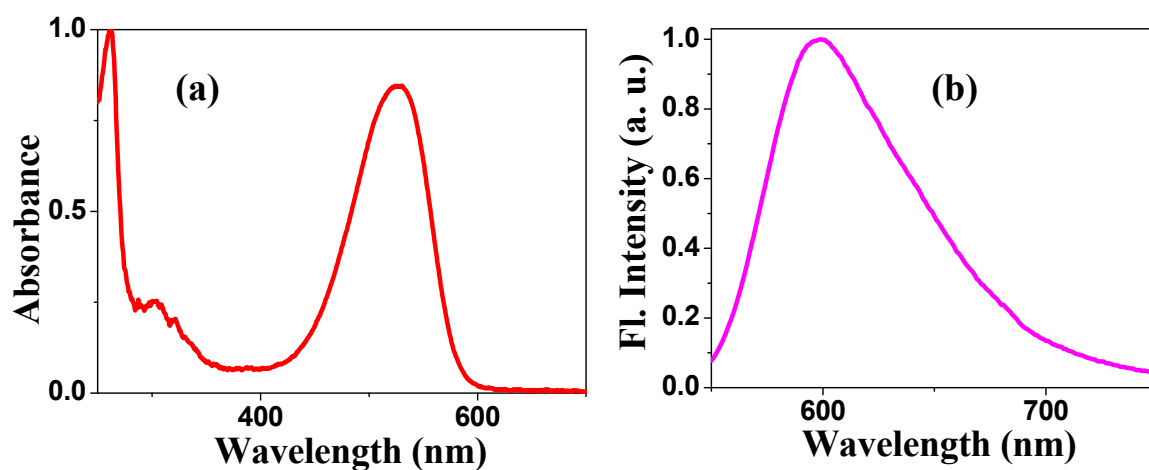


Figure S3. (a) Absorption spectra of Nile Red in THF (b) Emission spectra of Nile Red in THF.

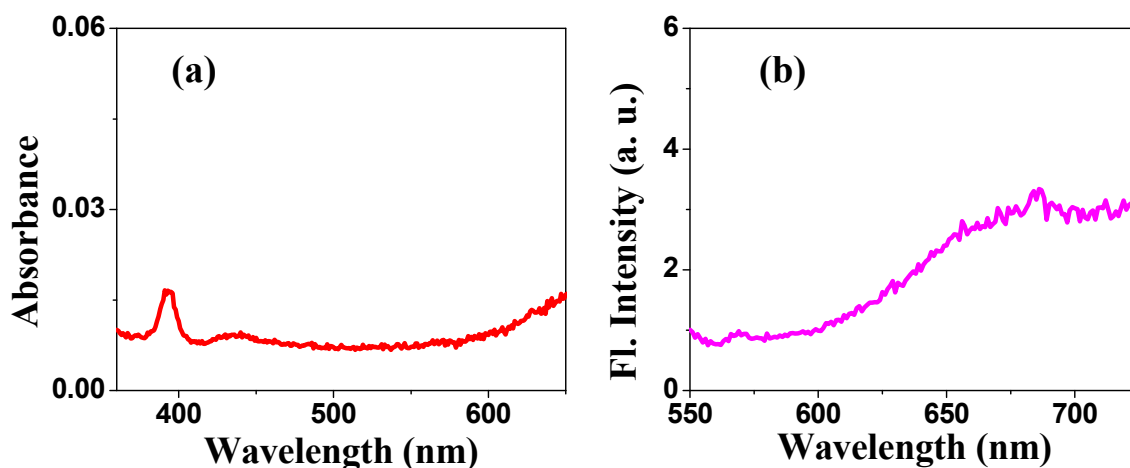


Figure S4. (a) Absorption spectra of Nile Red in water (b) Emission spectra of Nile Red in water (Solubility of Nile Red in water is very poor).

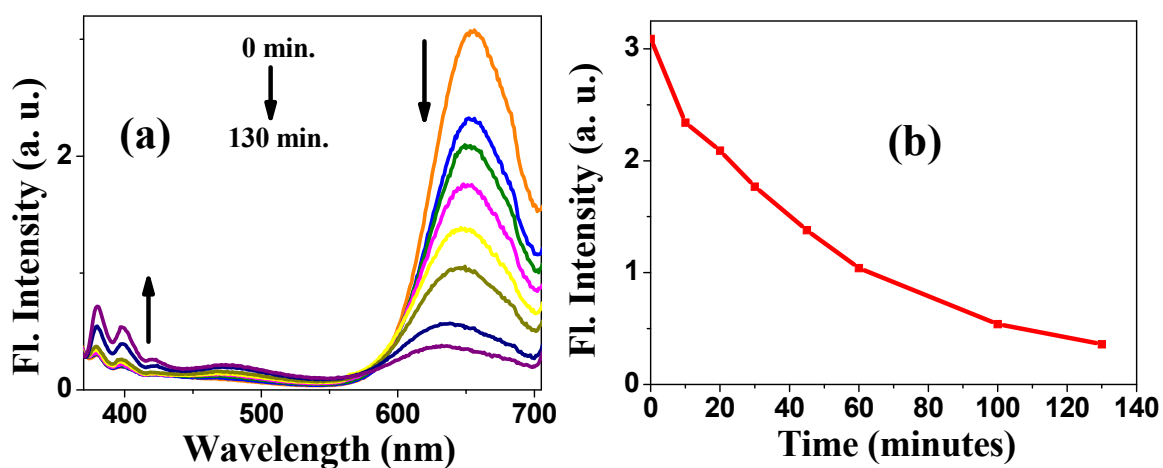


Figure S5. Changes in the fluorescence emission spectra ($\lambda_{\text{ex}} = 350 \text{ nm}$) of Nile Red loaded polymer aggregates in water upon UV irradiation. (b) Systematic changes in the fluorescence intensity at 656 nm upon UV irradiation.

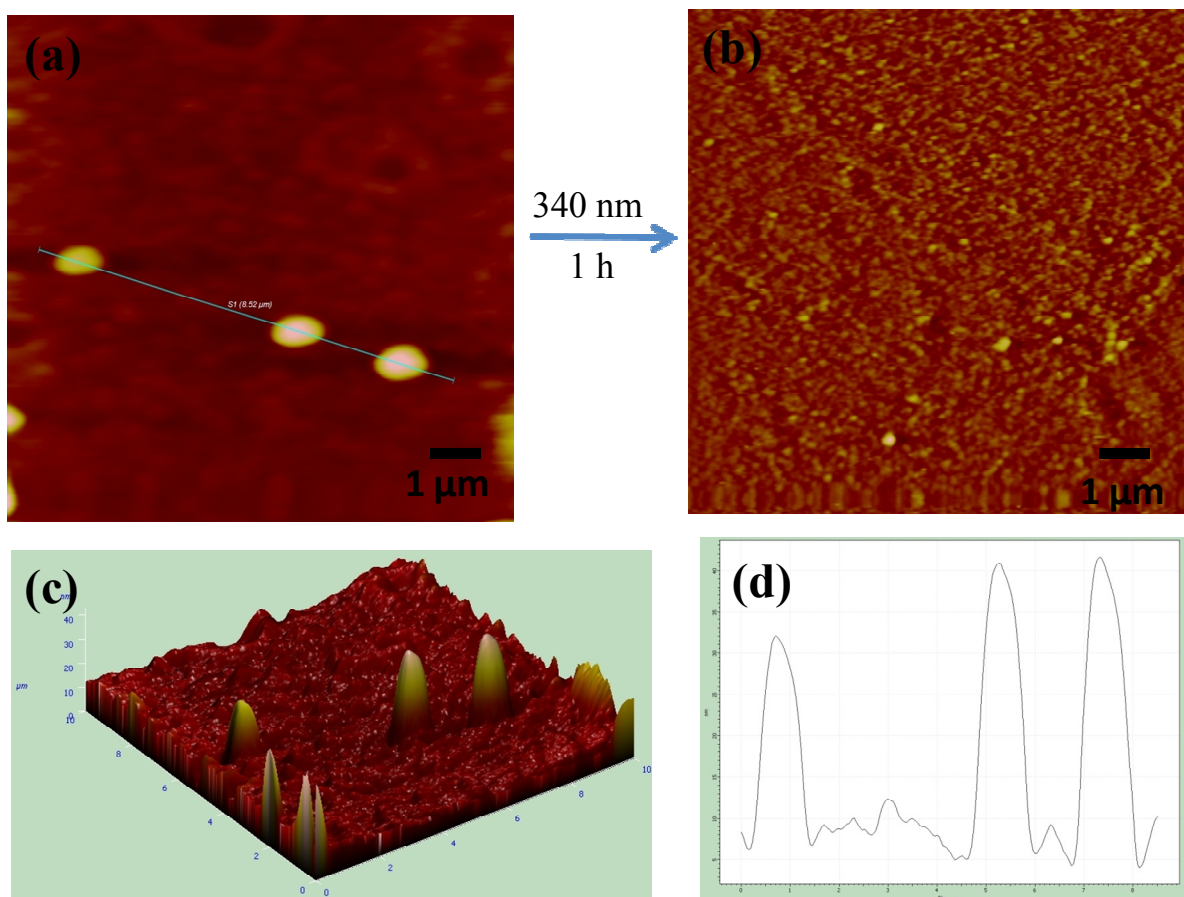


Figure S6. (a) AFM image showing aggregates formed by PPy-b-PBG in water (b) Dissociation of the aggregates after UV irradiation (c) 3D image of fig 4(a) (d) Height profile of fig 4(a).

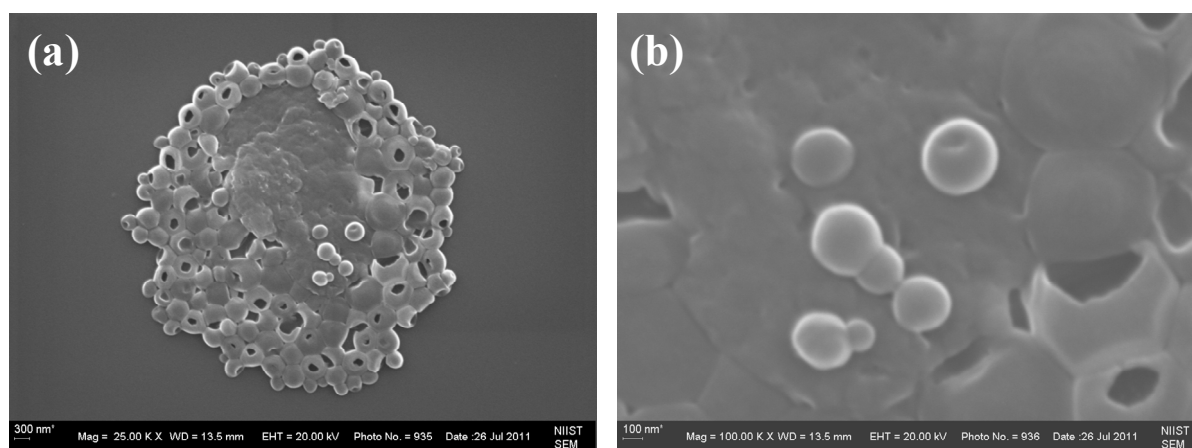


Figure S7. (a, b) SEM images showing vesicular aggregates formed by PPy-b-PBG in water.

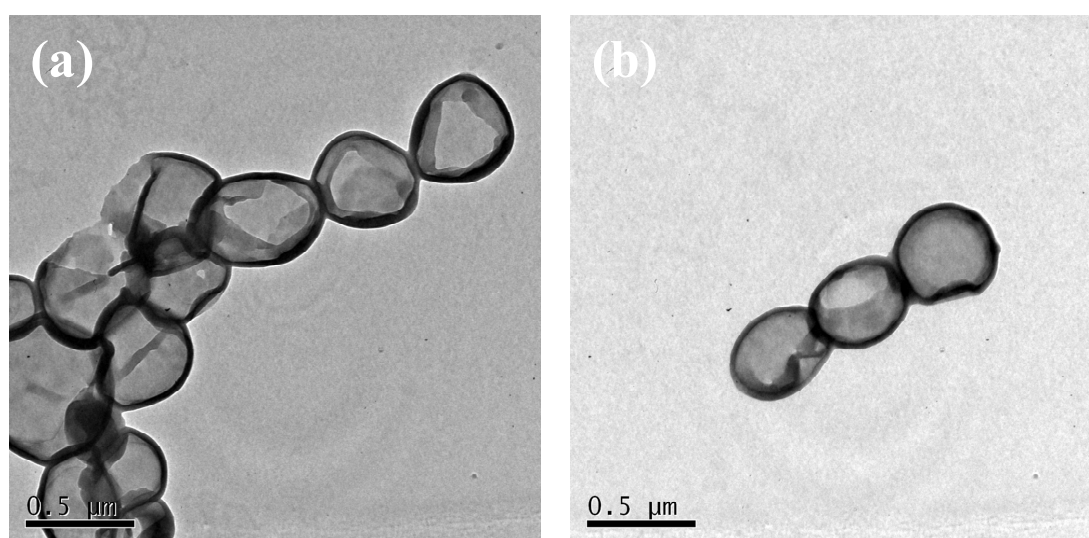


Figure S8. (a, b) TEM images showing vesicular aggregates formed by PPy-b-PBG in water.