

Supporting Information

Self-Assembling Supramolecular Polymer Membranes for Highly Effective Filtration of Water-Soluble Fluorescent Dyes

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Experimental Section

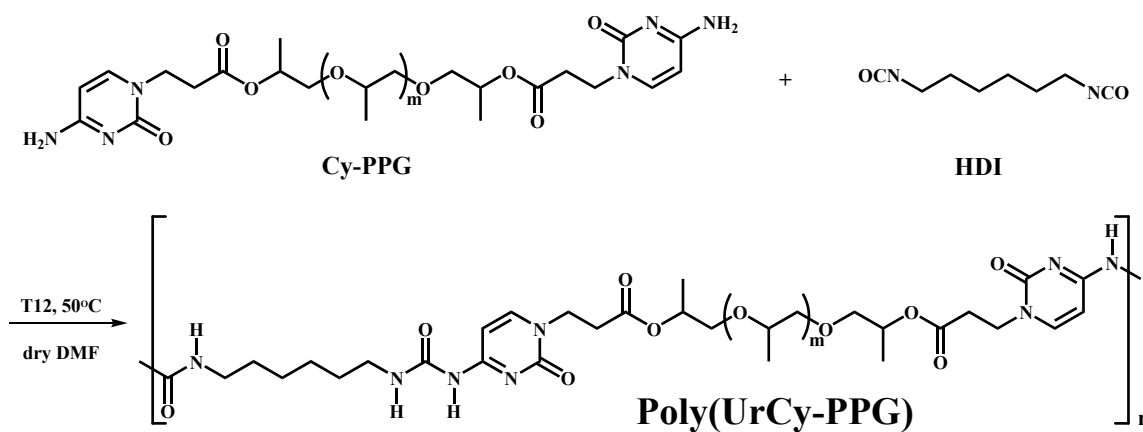
Materials

All chemicals and solvents were of analytical grade and were purchased from Sigma-Aldrich (Louis, MO, USA). All solvents used were high-performance liquid chromatography (HPLC) grade and were purchased from TEDIA (Fairfield, OH, USA). Dimethylformamide (DMF) was distilled twice over calcium hydride before use.

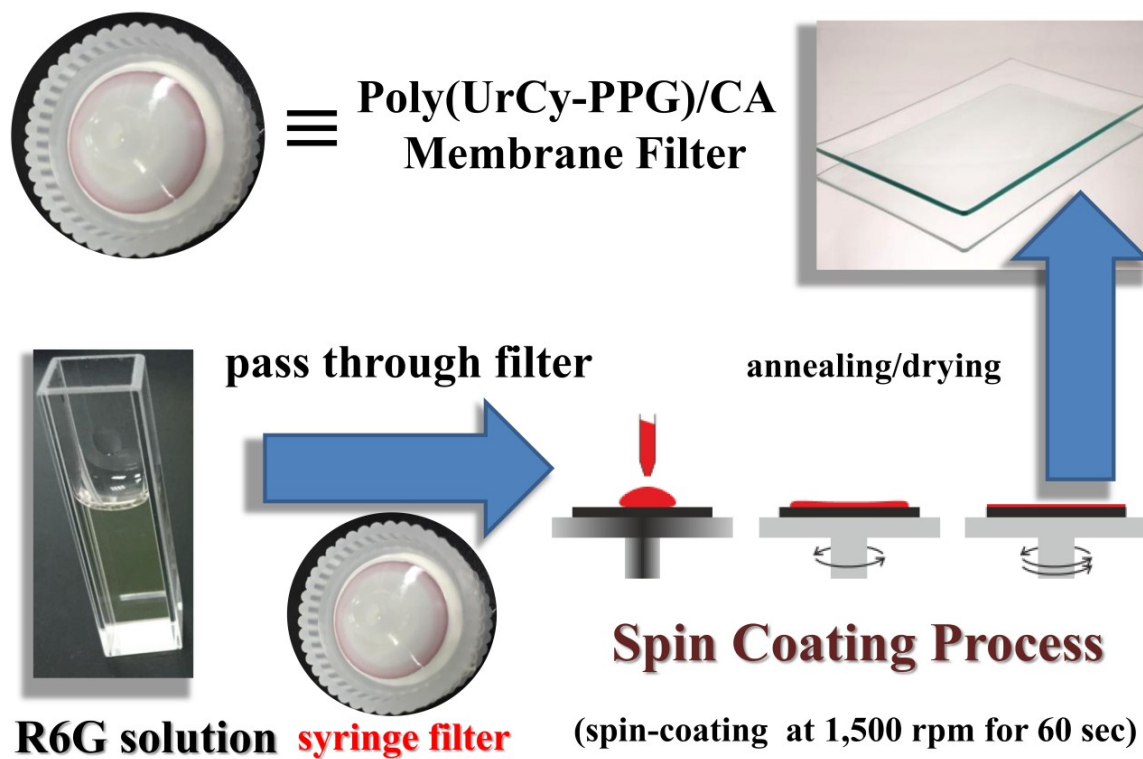
Characterization

Proton Nuclear Magnetic Resonance (¹H NMR). ¹H NMR spectra were recorded on a 500 MHz Bruker AVIII spectrometer (Bruker Biospin AG, Fällanden, Zürich, Switzerland) at different temperatures from 25 to 100 °C. Samples (ca. 20 mg) were dissolved in 0.8 mL of deuterated tetrachloroethane for ¹H NMR analysis. *Size Exclusion Chromatography (SEC).* Molecular weight information was analyzed using a Waters GPC system at 40 °C. The mobile phase for SEC was tetrahydrofuran (THF) solvent at a flow rate of 1.0 mL/min. The system was calibrated against narrow distribution polystyrene standards (Polymer Standards Service, Silver Spring, MD, USA). *Ultraviolet-Visible (UV-Vis) and Photoluminescence (PL) Spectroscopy.* The UV-Vis spectra of samples in solution were recorded at 25 °C using a Jasco V-730 Spectrophotometer (Hachioji, Tokyo, Japan) between 200 and 800 nm at 0.5 nm intervals at 1000 nm/min. PL spectra were obtained at 25 °C using a Jasco FP-8300 Spectrofluorometer (Hachioji) from 525 nm to 800 nm in 1 nm increments at an excitation wavelength of 520 nm. *Zeta potential measurements.* Zeta potentials of aqueous solution samples were measured at 25 °C using a Malvern Zetasizer Nano ZS (Herrenberg, Germany). *Differential Scanning Calorimetry (DSC).* DSC was

performed under a dry nitrogen atmosphere at a scanning rate of 10 °C over the temperature range from -70 to 200 °C. DSC results for the second heating scan of Cy-PPG and poly(UrCy-PPG) are presented in Fig. S4. *Small and Wide-Angle X-ray Scattering (SAXS and WAXS)*. SAXS data were generated using the BL17A1 wiggler beamline of the National Synchrotron Radiation Research Center, Taiwan. Each sample was sealed between two Kapton windows (thickness: 12 μm) and analyzed at 25 °C using X-ray photons (wavelength = 0.113 nm) and an overall q -range from 0.05 to 3.5 nm⁻¹ (beam diameter: ~1.0 mm). WAXS patterns of samples were obtained using a Rigaku D/MAX-2500 diffractometer with a Ni-filtered Cu K α radiation at a wavelength of 0.154 nm; data were collected over the q range from 60 to 300 Å at a rate of 15 Å/min. Variable-temperature Fourier transform infrared (VT-FTIR) experiments were carried out using a PerkinElmer Spectrum Two system (PerkinElmer, Buckinghamshire, UK) over a broad range of wavenumbers from 600 to 4000 cm⁻¹. *Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)*. Field emission SEM (JSM-6500F, JEOL, Tokyo, Japan) and tapping-mode AFM (NX10, AFM Park Systems, Suwon, South Korea) were carried out to analyze sample morphology and microstructure. All samples were solubilized in methanol, the solutions were directly spin-coated onto a silicon wafer substrate, then dried under vacuum at 40 °C.



Scheme S1: Synthesis of poly(UrCy-PPG).



Scheme S2: Preparation of R6G thin films by the spin coating deposition process.

Synthesis of Poly(UrCy-PPG)

Cy-PPG was synthesized from commercial poly(propylene glycol) diacrylate (average molecular weight ~800, ca. 14 repeat units) and cytosine according to procedures described previously.⁴¹ Cy-PPG (69.8 g, 0.068 mol) and 1,6-hexamethylene diisocyanate (11.44 g, 0.068 mol) were dissolved in dry DMF (150 mL) and three drops of dibutyltin dilaurate were added via a syringe. The reaction was carried out at 60 °C under a nitrogen atmosphere. After 24 h, an excess of methanol (10 mL) was added to the reaction mixture, then the solvents were removed by vacuum distillation. Finally, the residue was purified by pouring the reaction mixture into a large amount of acetone (300 mL) to generate a slightly yellow solid product. Yield: 84% (68 g).

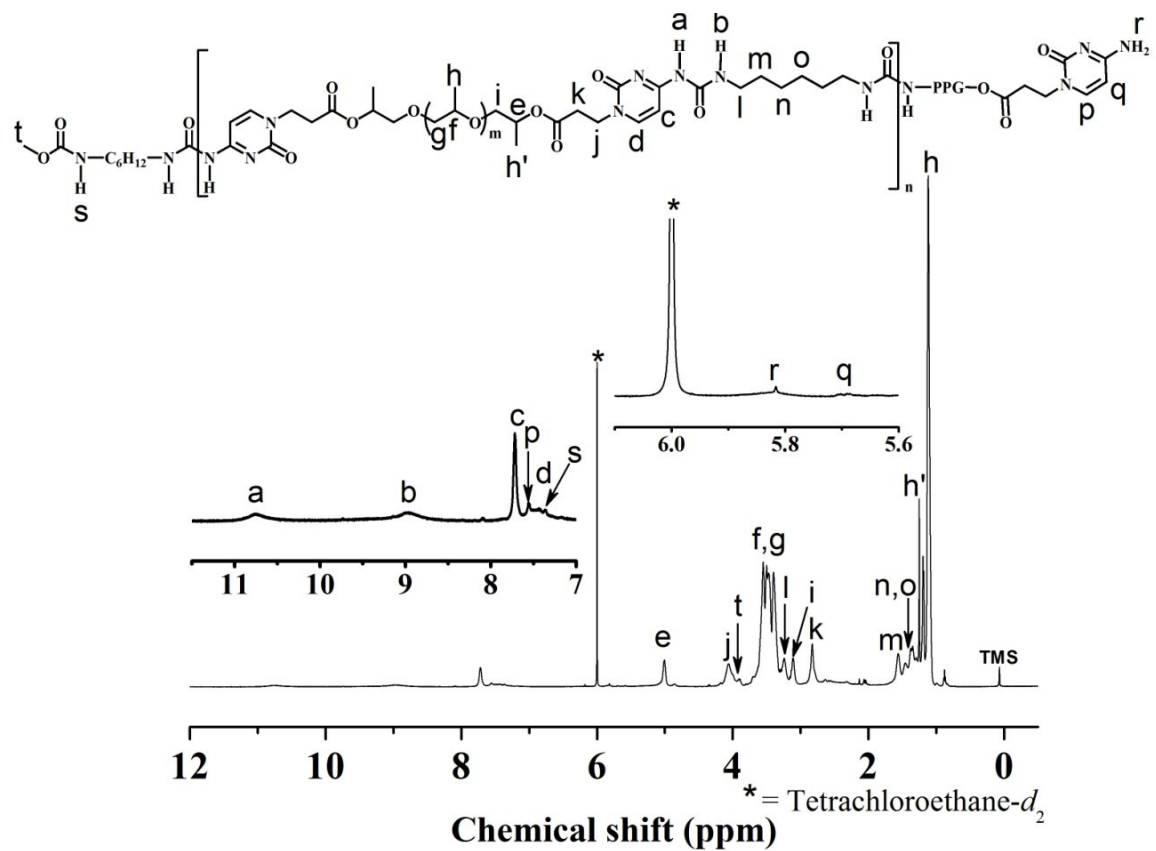


Fig. S1: ^1H NMR spectroscopy of poly(UrCy-PPG) in tetrachloroethane- d_2 .

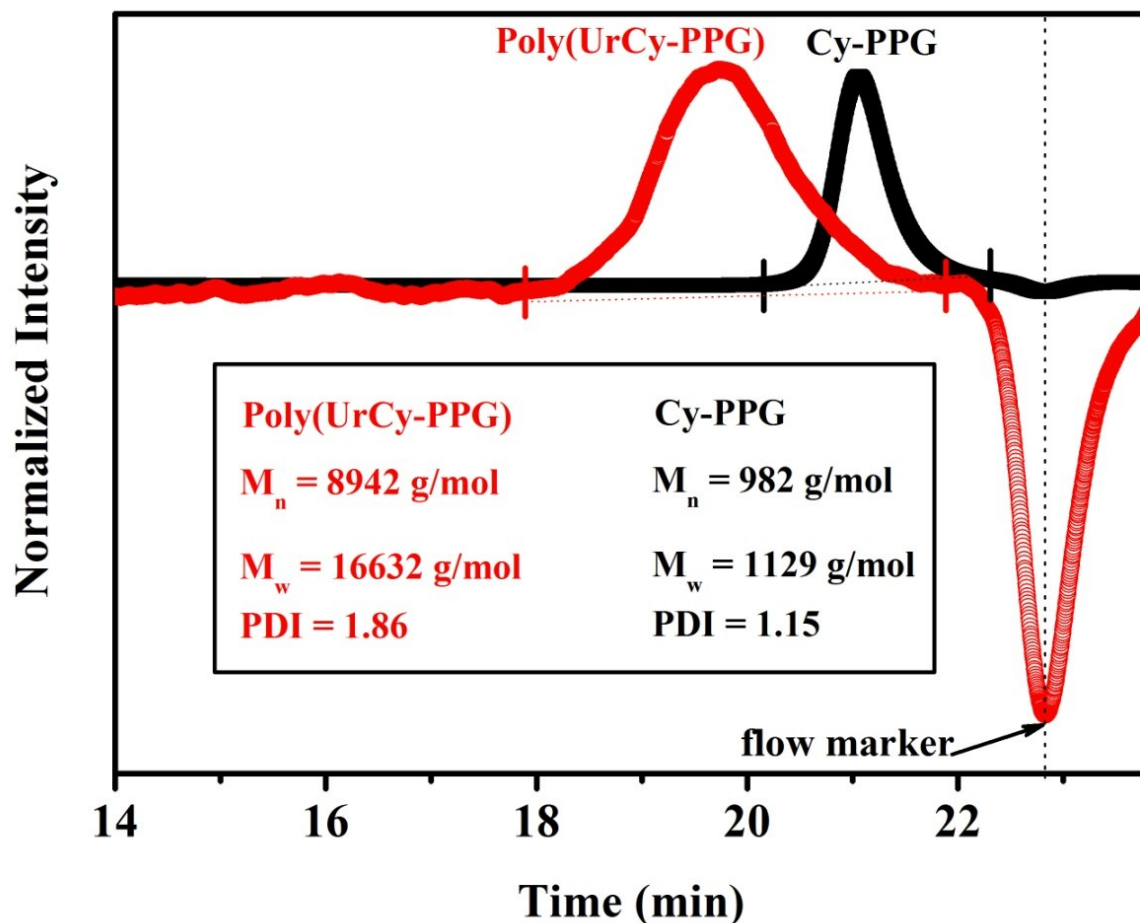


Fig. S2: GPC traces of poly(UrCy-PPG) in THF.

Preparation of double-layered poly(UrCy-PPG)/CA filters

Cellulose acetate (CA, ADVANTEC Toyo, Ltd., Tokyo, Japan; pore size, $0.45 \mu\text{m}$; effective filtration area, 4.0 cm^2) was chosen as a support membrane, as it is inexpensive, allows high flow rates for water solutions and cannot be dissolved by methanol. We directly spin-coated poly(UrCy-PPG) films onto CA filters using a sample solution of 10 mg/mL in methanol with a constant spin speed for different periods of time, as presented in Fig. 5a. After air drying for 1 h at ambient temperature, the resulting filters were dried at $40 \text{ }^\circ\text{C}$ under vacuum for 1 h.

Fabrication of spin-coated rhodamine 6G (R6G) thin films

Aqueous solution containing 5 ppm R6G was filtered through the CA or poly(UrCy-PPG)/CA filters. The resulting R6G filtrates were directly spin-coated onto a quartz surface at 1500 rpm for 60 sec, as shown in **Scheme S2**. The substrates generated were dried in a vacuum oven at 25 °C for 24 h.

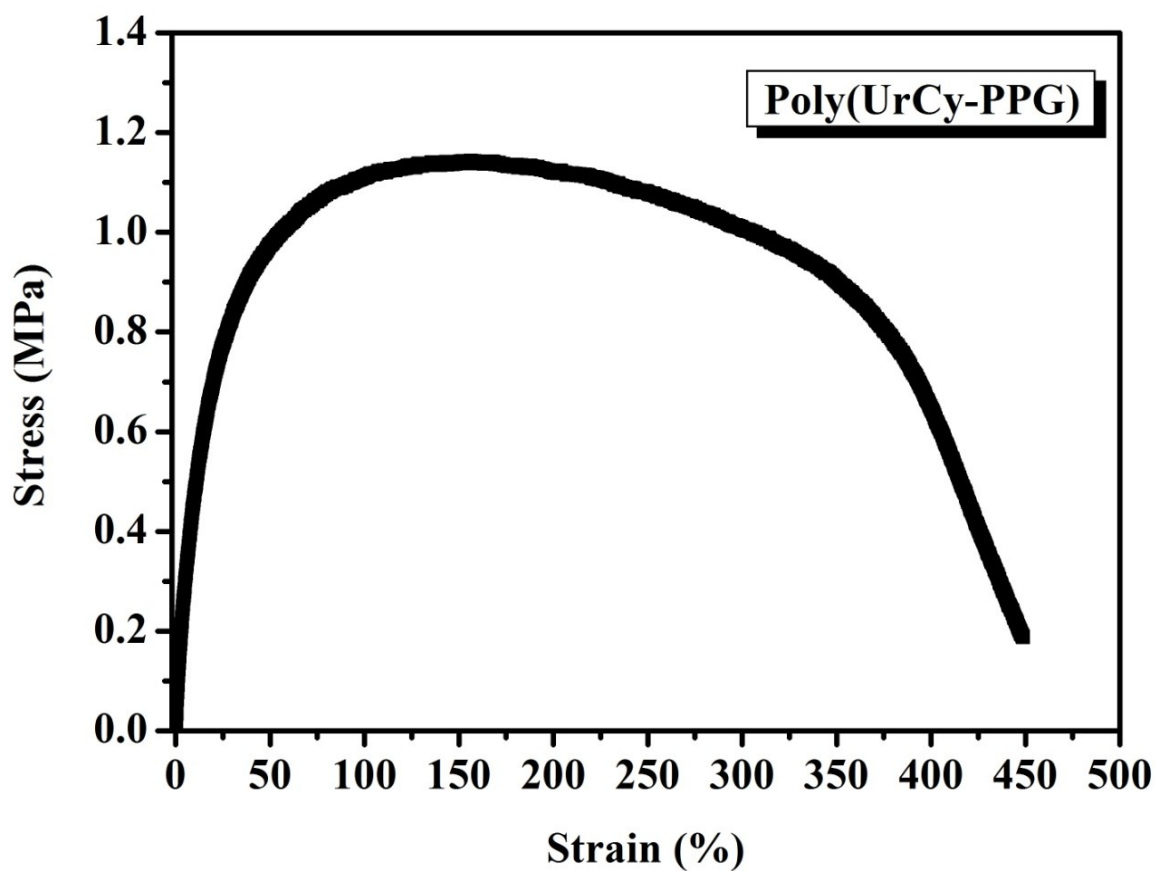


Fig. S3: Stress-strain curve for poly(UrCy-PPG) membrane.

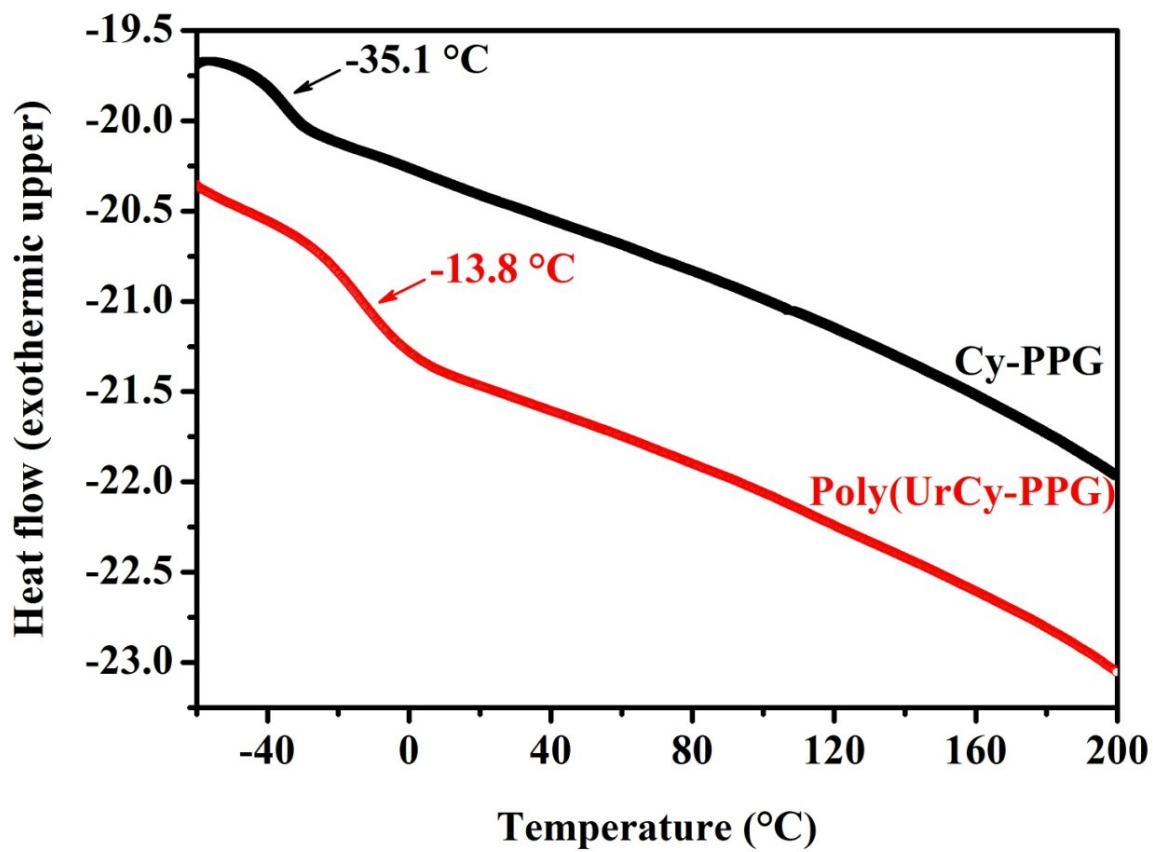


Fig. S4: DSC curves for Cy-PPG and poly(UrCy-PPG).

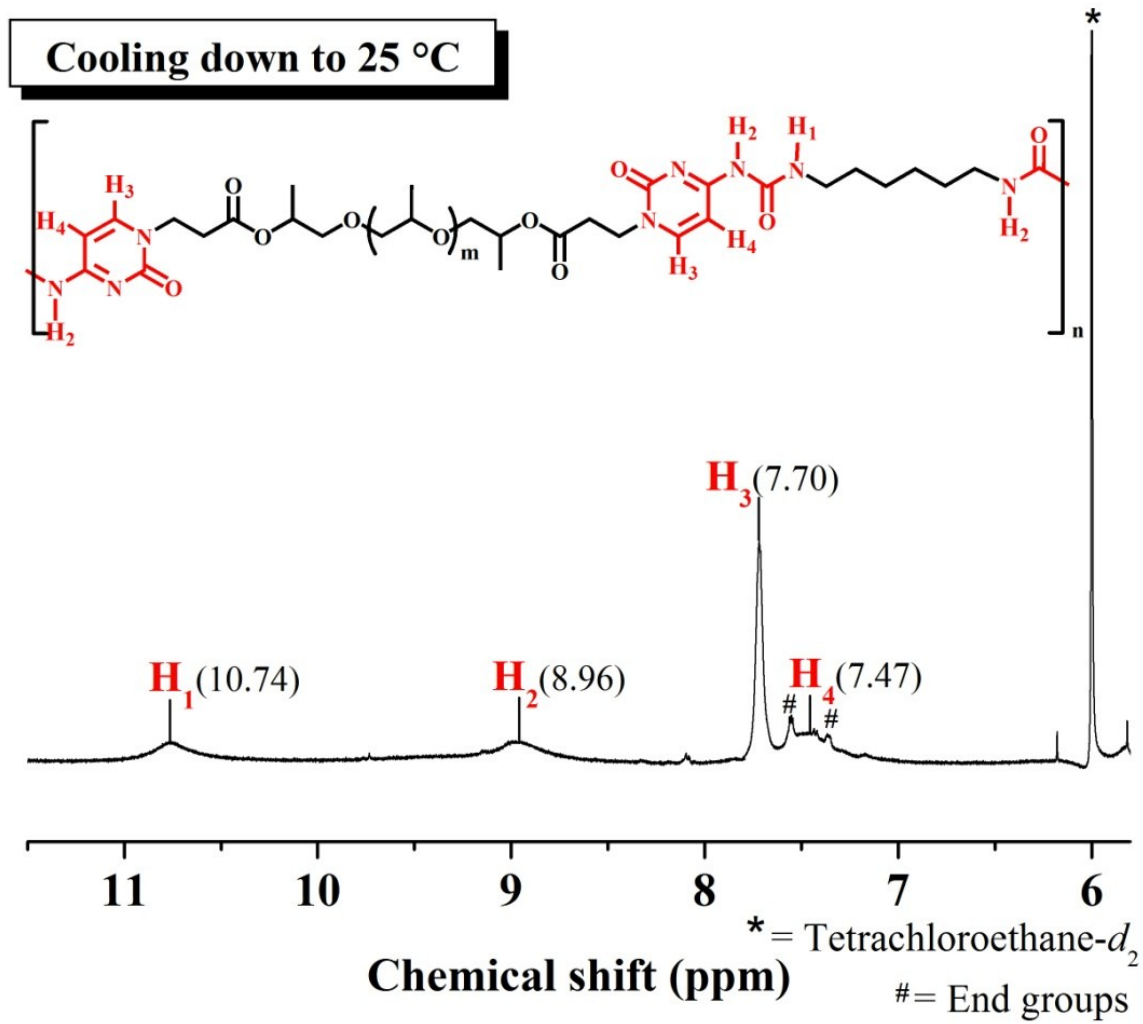


Fig. S5: ¹H NMR spectroscopy of poly(UrCy-PPG) after heat treatment followed by cooling back down to 25 °C in tetrachloroethane-*d*₂

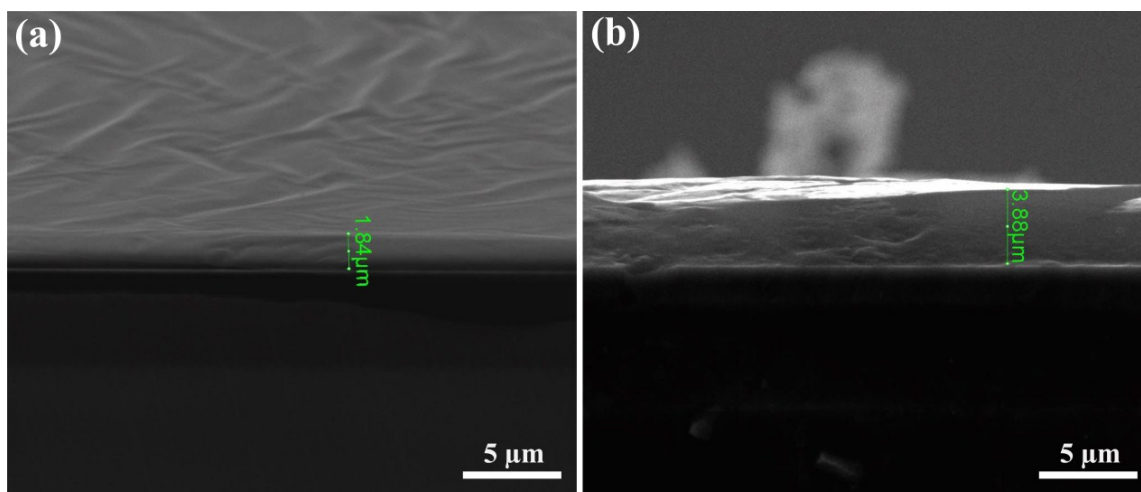


Fig. S6: Cross-section SEM images of poly(UrCy-PPG) membranes with different thicknesses: **(a)** 1.84 μm and **(b)** 3.88 μm on cellulose acetate (CA) supports.

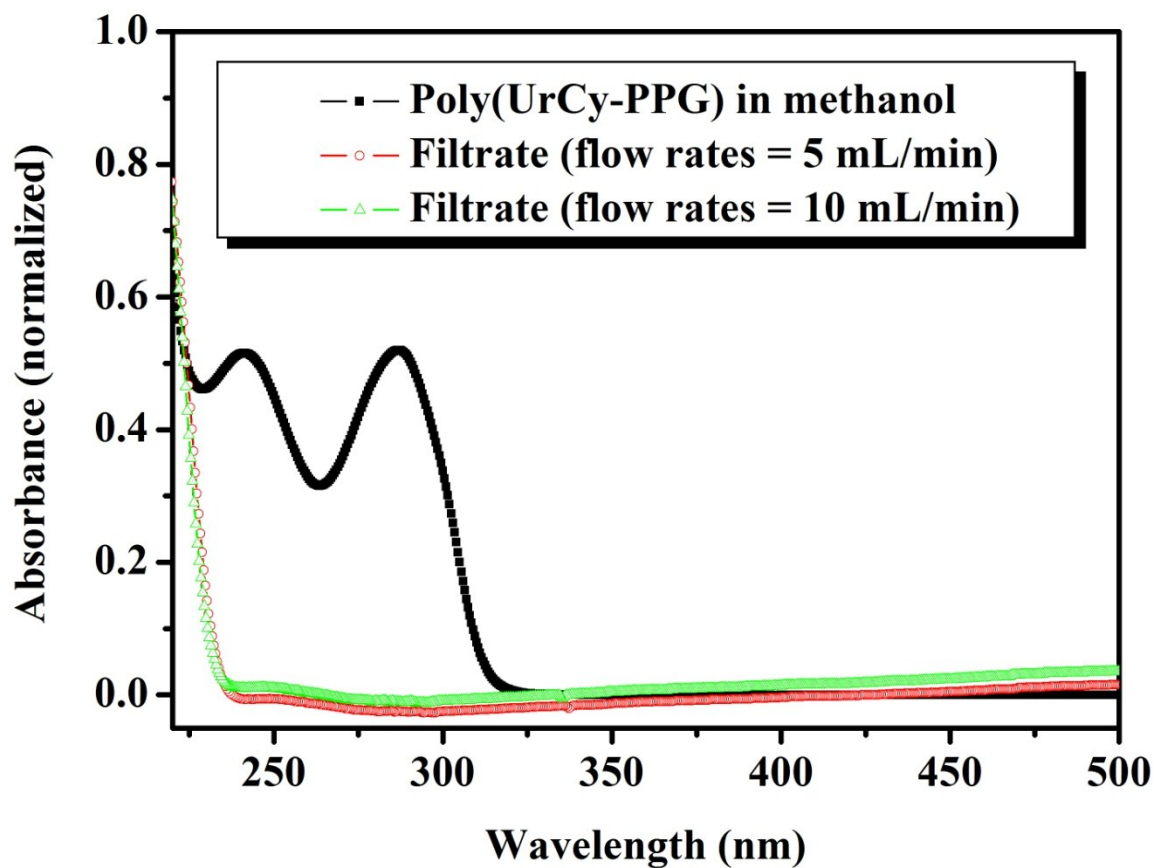


Fig. S7: UV-Vis spectra of poly(UrCy-PPG) solution in methanol (2×10^{-3} mg/mL), the filtrates were obtained by flowing deionized water through a double-layered poly(UrCy-PPG)/CA filter at different flow rates (5 and 10 mL/min).

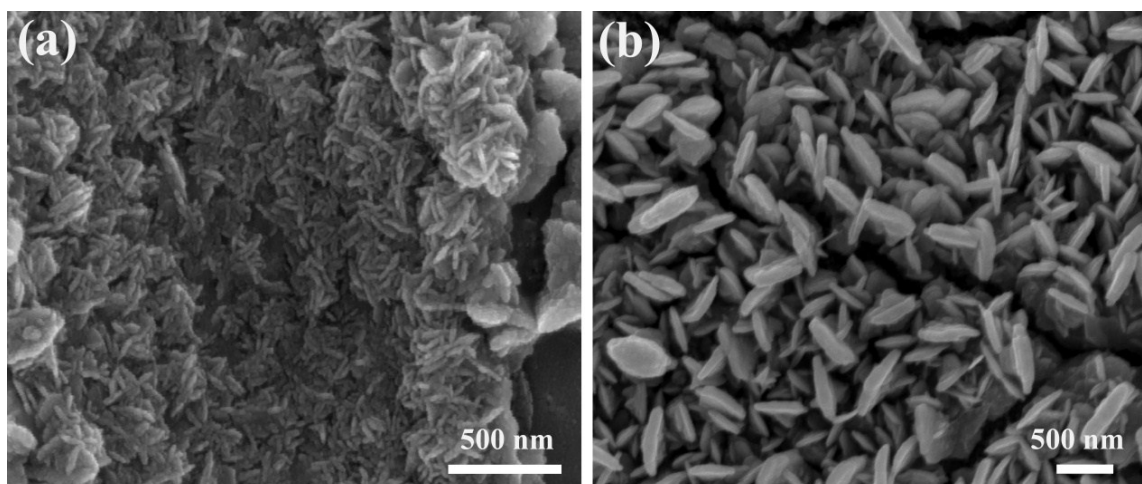


Fig. S8: SEM images of the spin-coated R6G films: **(a)** unfiltered R6G film and **(b)** R6G film filtered through the cellulose acetate (CA) filter.

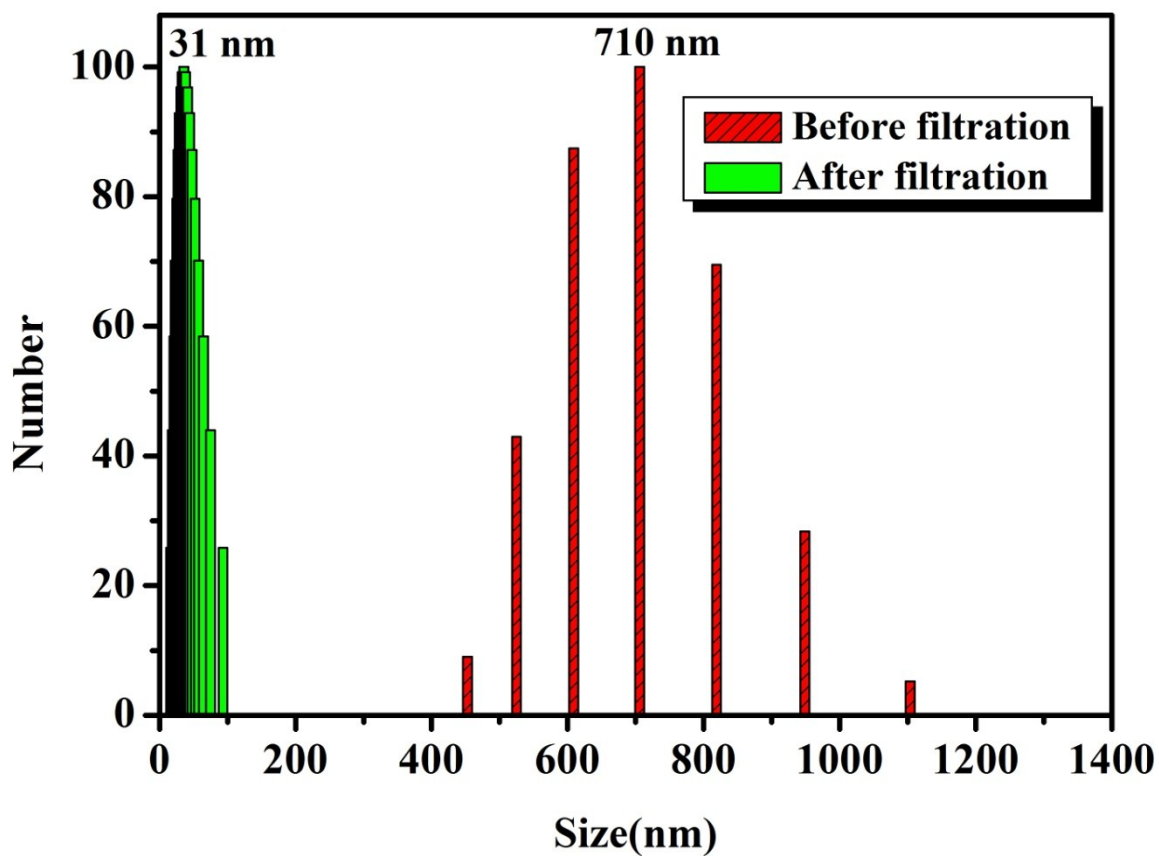


Fig. S9: Particle size distribution measured at 90° for aqueous solution containing 5 ppm R6G before and after passing through a double-layered poly(UrCy-PPG)/CA filter.

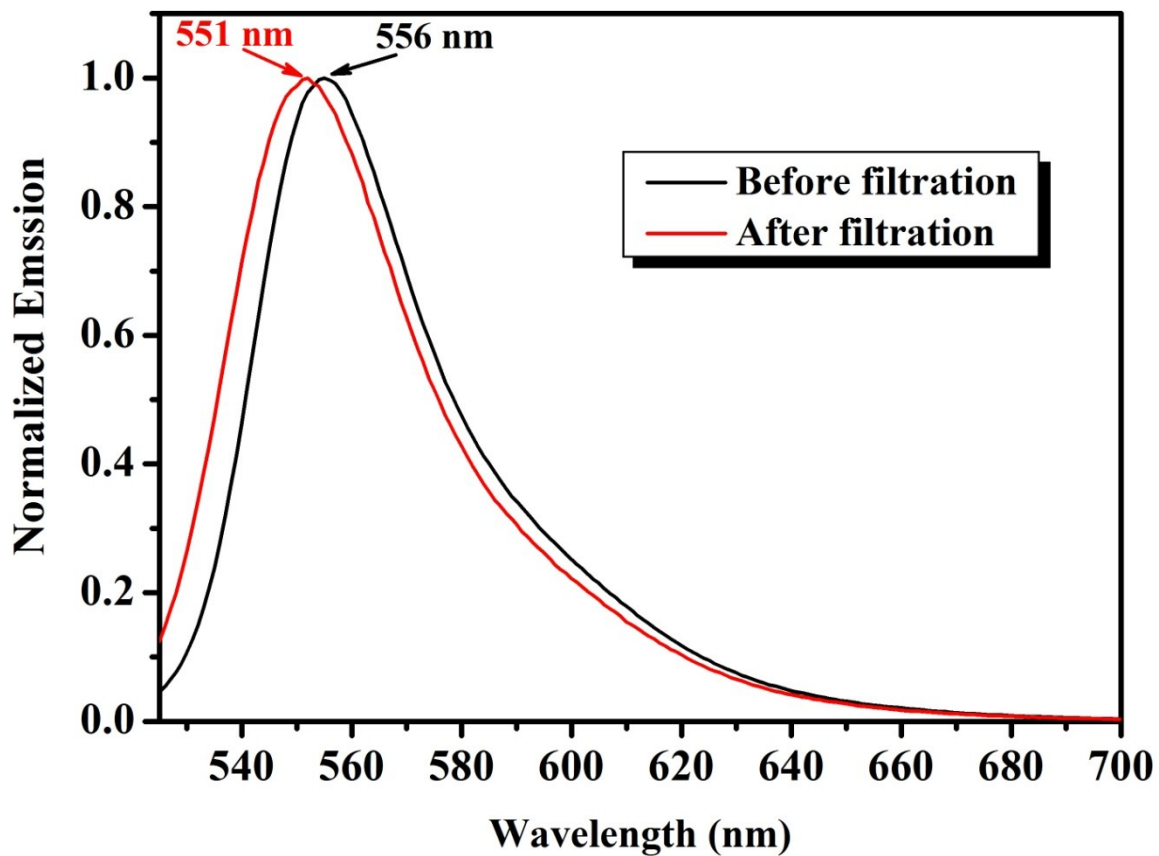


Figure S10: PL spectra of 5 ppm R6G in aqueous solution before and after passing through a double-layered poly(UrCy-PPG)/CA filter.

Table S1: Zeta potentials of R6G and related samples in aqueous solution at 25 °C.

| R6G aqueous solution | Zeta potential (mV) |
|--|----------------------------|
| Unfiltered R6G solution | -7.42 ± 1.7 |
| Filtered through a CA filter | -7.76 ± 2.7 |
| Filtered through a CA filter containing a poly(UrCy-PPG) layer of 1.84 μm | -7.18 ± 1.4 |
| Filtered through a CA filter containing a poly(UrCy-PPG) layer of 3.88 μm | -7.25 ± 1.6 |