Electronic Supplementary Information

Hyperbranched Poly(ionic liquid) Functionalized Poly(ether sulfone) Membranes as Healable Antifouling Coatings for Osmotic Power Generation

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Experiment Section

Materials

Dopamine hydrochloride (DA, 99%), tris(hydroxymethyl)aminomethane (Tris, ≥99.8%) and triethylamine (TEA, ≥99%) were purchased from Sigma-Aldrich and used as received except for additional declaration. Polyethersulfone (PES, Solvay Advanced Polymers) was used to fabricate the hollow fiber substrate. 1,3-Phenylenediamine (MPD, >98%, TCI, Japan), sodium dodecyl sulfate (≥99%) and trimesoyl chloride (TMC, ≥98%) were utilized to form the TFC layer on the lumen side of the PES hollow fiber substrates.

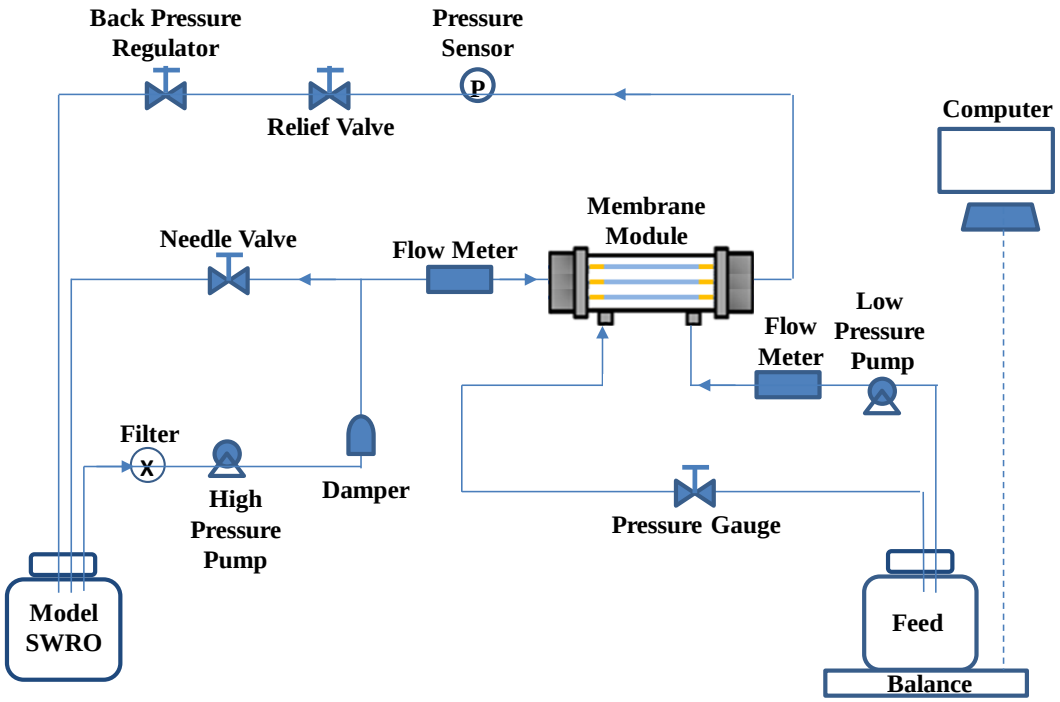
Preparation of the Thin-Film Composite (TFC) Polyamide Inner Layer

The PES hollow fiber substrate was fabricated via a dry-jet wet-spinning process as described elsewhere.[1-3] The as-spun hollow fiber substrates were soaked in water for 2 days to remove the residual solvents and posted in a 50/50 wt% glycerol/water solution for another 2 days before air-drying. To fabricate the PRO module, three pieces of hollow fiber membranes were loaded into a perfluoroalkoxy tubing connected with two Swagelok stainless steel male run tees. Both ends of the hollow fiber module were sealed with the slow curing epoxy. The effective length of the membrane module was 13 cm. A thin film polyamide selective layer was then synthesized on the lumen side of the hollow fiber substrates via interfacial polymerization. Briefly, a 2 wt% MPD and 0.1 wt% SDS aqueous solution was pumped through the lumen side of the fibers for 3 min. The excess water droplets on the inner surface were removed by continuous air blow for 5 min. Subsequently, a 0.15 wt% TMC/hexane solution was pumped through the lumen side for

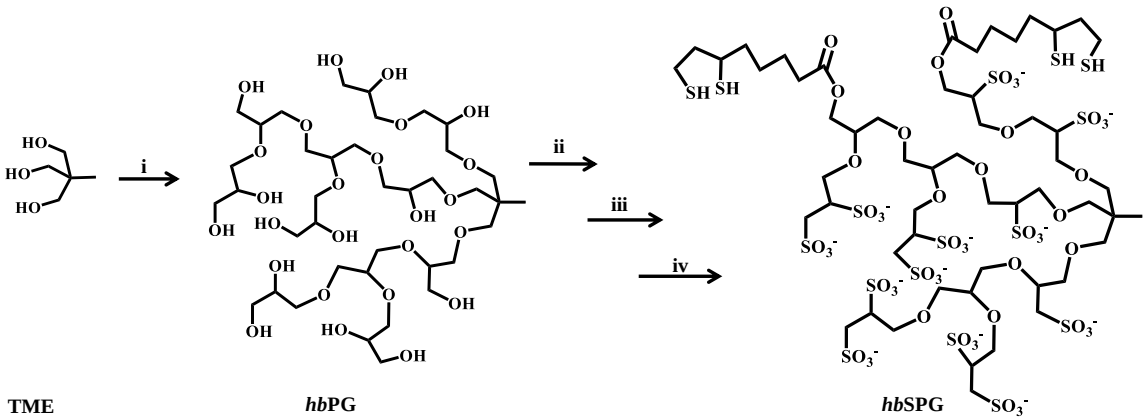
5 min. The resultant membranes were purged with air blow for 1 min to remove the excess hexane. The membranes obtained as such were labeled as PES-TFC.

Characterization

Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) were used to characterize the molecular weights and chemical structures of the synthesized polymers. ^{1}H NMR spectroscopy were recorded on a Bruker ARX operating at 400 MHz for ^{1}H using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and internal reference with chemical shifts (δ) reported in ppm. GPC profiles were conducted on a Waters GPC system equipped with an isocratic pump model 1515, a differential refractometer model 2414, a dual-wavelength UV detector model 2487 and Styragel columns. The number-average molecular weight ($M_{n,GPC}$) and polydispersity index ($Đ = M_{w,GPC}/M_{n,GPC}$) were measured with narrow molecular weight distribution poly(ethylene oxide) (PEO) as the standards and water as the eluent at a flow rate of 1.0 mL/min. Surface compositions of the membranes were characterized by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra^{DLD} spectrometer (Kratos Analytical Ltd) sourcing with a monochromatized Al Kα X-ray source (1468.71 eV). Water contact angle was measured by a goniometer (Dataphysics OCA20, Germany) in static mode. Three μL of water was dropped on the membrane surface by an automatic piston syringe and photographed by a video capture.



Scheme S1. Schematic diagram of the lab-scale PRO set-up.



Scheme S2. Reagents and conditions: (i) slow monomer addition, glycidol (GLY), 1,4-dioxane, 100 ºC, 36 h; (ii) lipoic acid (LA), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), *N*,*N'*-dicyclohexylcarbodiimide (DCC), DMF, 24 h; (iii) sulfamic acid (SA), NMP, 90 ºC, 24 h; (iv) DL-dithiothreitol (DTT), 50 ºC, 24 h.

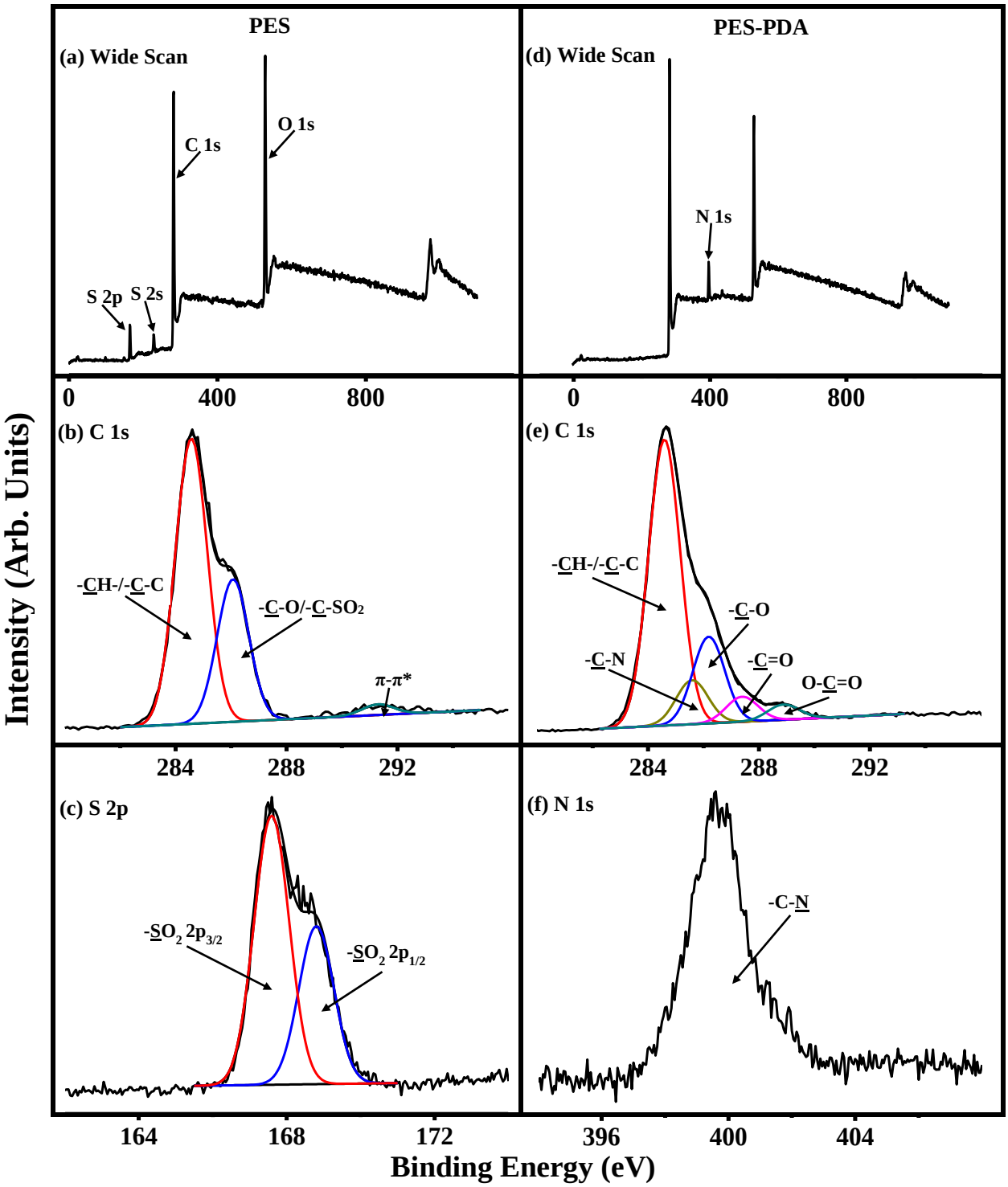


Figure S1. XPS wide-scan, C 1s, N 1s and S 2p core-level spectra of the (a,b,c) PES-TFC and (d,e,f) PES-PDA hollow fiber membranes.

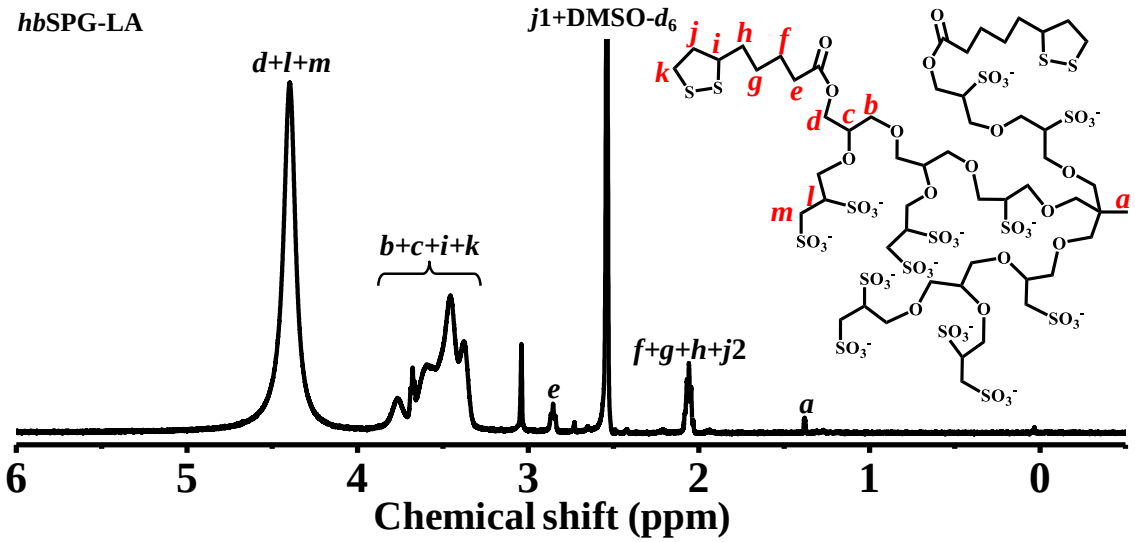


Figure S2. ^{1}H NMR spectrum of *hb*SPG-LA polymers in DMSO-d_6.

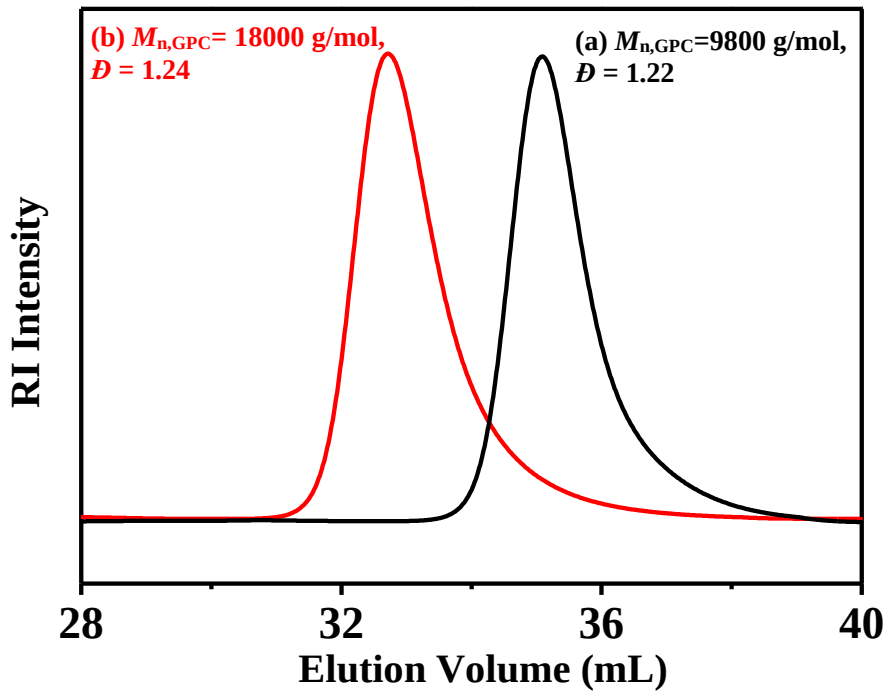


Figure S3. GPC elution curves of the (a) *hb*SPG and (b) QPEI polymers.

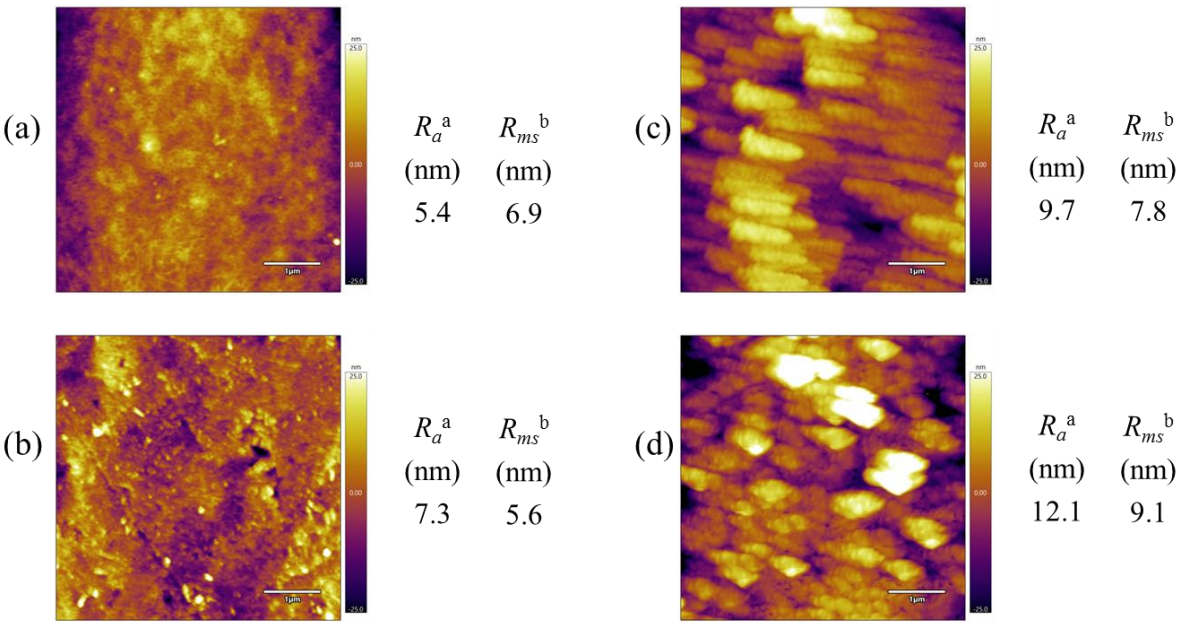


Figure S4. AFM images of outer surfaces of (a) PES-TFC, (b) PES-PDA, (c) PES-*g*-*hb*SPG and (d) PES-*g*-*hb*SPG-QPEI membranes. R_a is the mean roughness and R_{ms} is the root mean square of Z values.

References

(1) X. Chen, J. Lawrence, S. Parelkar and T. Emrick, *Macromolecules*, **2013**, *46*, 119-127.

(2) S. Zhang, P. Sukitpaneenit and T. S. Chung, *Chem. Eng. J.*, 2014, **241**, 457-465.

(3) C. F. Wan, B. Li, T. Yang and T. S. Chung, *Sep. Purif. Technol.*, 2017, **172**, 32-42.