Supporting Information For

Multifunctional Nanoporous Polymer Membranes from Supramolecular Assembly of Block Copolymer with Polymerizable Arginine Derivative

Yun Liang\textsuperscript{ab}, Wanlin Zhang\textsuperscript{a}, Tian Tian\textsuperscript{c}, Wanyue Ouyang\textsuperscript{a}, Peng Wang\textsuperscript{a}, Shiqiang Wang\textsuperscript{a}, Yong Ju\textsuperscript{b,*}, Guangtao Li\textsuperscript{a,*}

\textsuperscript{a}Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China. E-mail: lgt@mail.tsinghua.edu.cn

\textsuperscript{b}Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: juyong@mail.tsinghua.edu.cn

\textsuperscript{c}Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093, Switzerland
Experimental Section

1) Preparation of the block copolymer (PS-\textit{b}-P4VP)\textsuperscript{1}

\textbf{Scheme S1}. The synthetic way for the preparation of PS-\textit{b}-P4VP

\textit{RAFT chains transfer agent EDMAT}: 96.4 g (16.6 mol) acetone and 3.23 g (8.00 mmol) methyl trioctyl ammonium chloride were mixed in a 500 mL flask, and 12.4 g (0.200 mol) ethanethiol was added into the solution at 10 °C. 16.8 g (0.210 mol) NaOH solution with 50 wt% was dropped into the mixed solution within 20 min. The reaction was stirred 20 min and then a mixture of 15.2 g (0.200 mol) carbon disulfide and 20.3 g (0.350 mol) acetone was dropped into the reaction accompanying by the change of color to yellow. After 20 min, the 35.8 g (0.300 mol) CHCl\textsubscript{3} and 80.0 g (1.00 mol) 50 wt% NaOH solution were dropped into the reaction separately, and the color of the solution turned to brown. The reaction was stirred overnight at 10 °C. Then the acetone was removed by vacuum rotator and 250 mL 1M HCl aqueous solution was used to adjust the pH to 3. Then the mixture was extracted with n-hexane for three times, and the organic phase was collected as well as dried by anhydrous Na\textsubscript{2}SO\textsubscript{4}. The crude product was purified by a silica gel column with petroleum ether and ethyl acetate as eluent at the ratio of 2:1. Finally, the product was recrystallized in the n-hexane before use. (Yield: 20%) \textsuperscript{1}HNMR (CDCl\textsubscript{3}), \( \delta \) (ppm): 3.31 (q, 2H), 1.71 (s, 6H), 1.32 (t, 3H). \textsuperscript{13}C NMR (DMSO-\textit{d}\textsubscript{6}), \( \delta \)(ppm): 221.60, 173.19, 56.11, 30.71, 25.07, 12.95. ESI-MS (+): m/z [M+H\textsuperscript{+}] calcd. for C\textsubscript{7}H\textsubscript{12}O\textsubscript{2}S\textsubscript{2} 223.00, found 223.1.

\textit{PS-\textit{b}-P4VP}: 10.0 g (96.2 mmol) styrene, 10.5 mg (0.047 mmol) EDMAT and 1.5 mg (0.0091 mol) AIBN were mixed in a 50 mL Schlenk tube. The reaction system was degassed through three freeze-evacuate-
thaw cycles. And the RAFT polymerization was carried out at 90 °C for 12 h. The polymerization was stopped by the reaction exposed to air. The crude product was dissolved in THF and purified by precipitating it three times in methanol. The conversion of the monomer was characterized by $^1$HNMR. Then 1.16 g (0.017 mmol) PS-CTA, 1.13 g (10.7 mmol) 4-vinyl pyridine, 0.273 mg (0.0017 mmol) AIBN and 0.45 g THF were mixed in a 25 mL Schlenk tube. After degassed through three evacuate thaw cycle, a further degas was performed to ensure the polymerization was carried out in vacuum at 60 °C. The polymerization was stopped when the magneton could not stir and the reaction was exposed to air. It was dissolved in THF and purified by precipitation three times in n-hexane. The molecular weight of PS-b-P4VP were determined by Proton Nuclear Magnetic Resonance ($^1$H NMR) (Figure S1) and the PDI of the BCPs was performed by Gel permeation chromatography (GPC) with DMF as eluent (Figure S2).

![Figure S1. $^1$H NMR of PS-CTA without any treatment; inset is the $^1$H NMR of PS-b-P4VP for 77S-16P](image-url)
Figure S2. GPC spectra of the prepared PS-b-P4VP

2) Synthesis of the additive (Py3-Arg)

Scheme S2. The synthetic schematic for the preparation of the additive (Py3-Arg)
**Compound 1:** 20 g (60.9 mmol) 1,12-dibromododecane, 1.7 g NaH (dispersion in Paraffin Liquid) and 120 mL DMF were mixed in 250 mL flask and stirred for 30 min. Then 1.5 g (22.4 mmol) pyrrole was added drop-wisely into the reaction under ice bath conditions. The mixture was reacted for 24 h, and then excessive NaH was eliminated by water (500 mL). The solution was extracted three times with CH$_2$Cl$_2$, and then the organic extracts were collected and dried with anhydrous Na$_2$SO$_4$. The crude product was purified by a silica column with petroleum ether as eluent. (Yield: 43%) $^1$H NMR (CDCl$_3$), $\delta$(ppm): 6.65(d, 2H), 6.14(d, 2H), 3.88(t, 2H), 3.39(t, 2H), 1.86(m, 2H), 1.76(m, 2H), 1.43(m, 2H), 1.27(m, 14H). $^{13}$C NMR (CDCl$_3$), $\delta$(ppm): 120.44, 107.99, 49.61, 34.10, 32.79, 31.56, 29.47, 29.45, 29.38, 29.18, 28.73, 28.14, 26.74. ESI-MS (+): m/z [M+H]$^+$ calcd. for C$_{16}$H$_{28}$BrN 314.14, found 314.2.

**Compound 2:** 9 g (28.7 mmol) Py-Br, 1.14 g (7.9 mmol) methyl gallate, 6.62 g (47.9 mmol) K$_2$CO$_3$ and 0.146 g (0.5 mmol) tetrabutylammonium iodide were dissolved in 50 mL DMF and the reaction was refluxed under the N$_2$ atmosphere at 80 °C for 12 h. Then the reaction mixture was poured into 500 mL water and the solution was extracted three times with CH$_2$Cl$_2$. Organic phase was collected and dried with anhydrous Na$_2$SO$_4$. The crude product was purified by a silica column with petroleum ether/ethyl acetate 30:1 as eluent. The mild product was recorded as Py$_3$-GA-COOMe. $^1$H NMR (CDCl$_3$), $\delta$(ppm): 7.25(s, 2H), 6.65(dd, 6H), 6.14(dd, 6H), 4.01(t, 6H), 3.89(s, 3H), 3.86(t, 6H), 1.70-1.85(m, 12H), 1.47(m ,6H), 1.26(m, 42H). $^{13}$C NMR (CDCl$_3$), $\delta$(ppm): 167.04, 152.88, 142.31, 124.74, 120.55, 107.95, 107.82, 73.55, 69.19, 52.25, 49.73, 31.70, 30.41, 29.80, 29.76, 29.73, 29.68, 29.62, 29.47, 29.37, 29.34, 26.89, 26.15. ESI-MS (+): m/z [M+H]$^+$ calcd. for C$_{56}$H$_{89}$N$_3$O$_5$ 884.68, found 884.9.

**Compound 3:** 12 g (13.6 mmol) Py$_3$-GA-COOMe was dissolved in 110 mL methanol and 4.35 g (108 mmol) NaOH aqueous solution was added drop-wisely into the mixture. The reaction was refluxed at 70 °C for 12 h, and then poured into 1M HCl solution (500mL) to adjust the pH to 3. The solution was extracted three times with CH$_2$Cl$_2$, and then the organic phase was collected and dried with anhydrous Na$_2$SO$_4$. Product could be obtained by evaporation of the organic solvent. (Yield: 86%) $^1$H NMR (CDCl$_3$), $\delta$(ppm): 7.35(s, 2H), 6.66(d, 6H), 6.15(d, 6H), 4.03(t, 6H), 3.87(t, 6H), 1.72-1.85(m, 12H), 1.47(m, 6H), 1.26(m,
$^{13}$C NMR (CDCl$_3$), $\delta$(ppm): 171.95, 152.96, 143.27, 123.73, 120.56, 108.67, 107.86, 73.65, 69.29, 49.74, 31.71, 30.45, 29.81, 29.75, 29.69, 29.64, 29.49, 29.39, 29.35, 26.91, 26.18. ESI-MS (+): $m/z$ [M+H]$^+$ calcd. for C$_{55}$H$_{87}$N$_3$O$_5$ 870.66, found 870.8.

**Compound 4:** 10.93 g (12.6 mmol) Py$_3$-GA-COOH, 2.89 g (15.1 mmol) EDCI, 0.307 g (2.5 mmol) DMAP were dissolved in 100 mL anhydrous CH$_2$Cl$_2$, and then 2.17 g (18.9 mmol) N-Hydroxysuccinimide was added drop-wisely into the mixture. The reaction was stirred overnight at room temperature and then poured into 1M HCl aqueous solution (250 mL). The mixture was extracted three times with CH$_2$Cl$_2$ and successively washed with saturated NaHCO$_3$ aqueous solution and saturated brine. The organic extract was collected and dried with anhydrous Na$_2$SO$_4$. The crude product was purified by a silica column with CH$_2$Cl$_2$ as eluent. The product was recorded as Py-NHS. (Yield: 75%) $^1$H NMR (CDCl$_3$), $\delta$(ppm): 7.39(s, 2H), 6.69(d, 6H), 6.17(d, 6H), 4.11(t, 2H), 4.05(t, 4H), 3.87(t, 6H), 2.88 (s, 4H), 1.78-1.88(m, 12H), 1.52(m, 6H), 1.33(m, 42H). $^{13}$C NMR (CDCl$_3$), $\delta$(ppm): 169.55, 161.85, 153.23, 144.24, 120.56, 119.29, 109.04, 107.89, 73.75, 69.39, 49.74, 31.74, 30.45, 29.82, 29.79, 29.77, 29.70, 29.66, 29.47, 29.40, 29.36, 26.92, 26.26, 25.80. ESI-MS (+): $m/z$ [M+H]$^+$ calcd. for C$_{59}$H$_{90}$N$_4$O$_7$ 967.68, found 967.9.

**Compound 5:** 1 mL NaHCO$_3$ aqueous solution with 66 mg (0.62 mmol) was added into the 5 mL DMF solution with 37 mg (0.21 mmol) L-arginine. This solution was stirred 30 min, and then 0.1 g (0.1 mmol) Py$_3$-NHS DMF solution was added drop-wisely into the reaction. It was stirred overnight and then adjusted with the equally HCl aqueous solution. The mixture was extracted with CH$_2$Cl$_2$ three times and organic phase was collected. Anhydrous Na$_2$SO$_4$ was used to dry the organic extract. The crude product was purified by a silica column with CH$_2$Cl$_2$/MeOH 10:1 as eluent. (Yield: 63%) $^1$H NMR (DMSO-d$_6$), $\delta$(ppm): 12.65(s, 1H), 8.25(s, 1H), 7.78(s, 1H), 7.18(s, broad), 7.18(s, 2H), 6.68(d, 6H), 5.93(d, 6H), 4.39(t, 1H), 3.80-3.97(m, 12H), 3.12(t, 2H), 1.86, 1.81(m, 2H), 1.22-1.71(m, 62H). $^{13}$C NMR (DMSO-d$_6$), $\delta$(ppm): 180.08, 165.30, 157.98, 152.20, 139.27, 129.53, 120.78, 107.84, 105.67, 77.02, 72.53, 68.62, 64.56, 45.87, 31.70, 30.53, 29.86, 29.76, 29.65, 29.21, 26.66, 26.31, 26.00. ESI-MS (+): $m/z$ [M+H]$^+$ calcd. for C$_{61}$H$_{90}$N$_7$O$_6$ 1026.77, found 1027.2.
3) **Electrochemical characterization:** The prepared membranes for the CV characterization were immersed into solution with the pH of 1, 7, and 13 for 2 h and washed with pure water three times before use. Then the membrane was mounted on the Au electrode with a Teflon shell as the working electrode.

4) **Dye adsorption:** The membranes were immersed into solution with the pH of 1 for at least 3 h, and then they were repeatedly washed with pure water until the pH value of filtration was 7. Then the 6 mg positively-charged nanoporous membranes was immersed into 3 mL 100 ppm mixed solution of Methyl orange (MO) and Rhodamine 6G (R6G). Then it was incubated for 48 h until the solution became pink.

5) **Dopamine polymerization:** The membrane was immersed into 1 M NaOH solution for at least 3 h, and then it was repeatedly washed with pure water until the pH value of filtration was 7. Then the obtained membrane was immersed into 2 mg/mL dopamine solution for 72 h. The control experiment was carried out at 2 mg/mL dopamine solution for 72 h without obtained membranes.

6) **Flux measurements:** The experimental protocol for the determination of solvent flux was used similar to that previously described (Adv. Mater. 2015, 27, 7349-7355). The nanoporous membrane with effective testing area ca. 0.785 cm² was fixed in a homemade equipment (Figure S11a). The solvents were poured onto the membrane surface with the pressure of 0.1 MPa, and the temperature was constant at 25 °C. After the permeate flux reaches a steady state, we recorded the experiment time required to collect 4 mL of the permeating solvent. The flux values for different solvents were calculated by dividing the volumetric permeate rate by the membrane area. For water, the experiment time was 13.4 h and the calculated flux of membranes was 3.8 L m⁻² h⁻¹. For ethanol, the experiment time was 3.2 h and the calculated flux of membranes was 16 L m⁻² h⁻¹.
Figure S3. (a) $^1$H NMR spectra of supramolecular ensemble of PS-b-P4VP-R(Py$_3$-Arg) and their parent molecules; (b) The chemical shift of the H belonging to the pyridine and Py$_3$-Arg; (c) The chemical shift of the H belonging to the Py$_3$-Arg.

Figure S4. (a) SEM image of the as-casting lamella-structured supramolecular membrane without any treatment; (b-f) SEM images of the membrane in (a) after being washed with ethanol in 55 °C for 30 min, 60 min, 90 min, 120 min and 150 min, respectively. Scale bars are 200 nm.
Figure S5. SAXS characterization of the lamella-structured supramolecular membrane before and after the ethanol rinsing process.

Figure S6. SEM images of the surface (a₁-d₁) and (a₂-d₂) cross-section of the neat PS-b-P4VP were obtained at \( f_{P4VP} \) of 0.06, 0.12, 0.17 and 0.23, after the ethanol rinsing process. Scale bars are 500 nm.
Figure S7. The SEM images of the supramolecular membranes of PS-$b$-P4VP-R(Py$_3$-Arg) annealed in
(a) THF; (b) 1,4-dioxane; (c) toluene; (d) THF/1,4-dioxane mixture. Scale bars are 500 nm.

Figure S8. Chemical structures of the block copolymer PS-$b$-P4VP, the monomer Py$_3$-Arg, and the
corresponding PPy$_3$-Arg after the BCP-templated topochemical polymerization of the supramolecular
ensemble PS-$b$-P4VP-R(Py$_3$-Arg).
Figure S9. (a₁-e₁) SEM images of the resultant nanoporous polymer membranes after immersed in the methanol, chloroform, 1,4-dioxane, toluene, DMF; (a₂-e₂) photographs of the resultant nanoporous polymer membranes immersed in the methanol, chloroform, 1,4-dioxane, toluene, DMF. Scale bars are 200 nm.

Figure S10. (a-c) Photographs of the resultant nanoporous polymer membranes at different bending. (d-f) SEM images of the cross-section of the nanoporous membrane at different magnifications. The scale bars correspond to 20 µm (d), 500 nm (e) and 100 nm (f).
Figure S11. The permeability of the membrane was determined using a homemade equipment at ambient pressure: (a) The prepared nanoporous membrane was fixed between a commercial filter; which was attached with tube of syringe; (b) the fluxes of water and ethanol through the prepared porous membrane.

Figure S12. SEM images of (a) supramolecular film from PS-b-P4VP-1.0(Py$_3$-Arg), (b) the film after annealed in 1,4-dioxane and (c) the resultant nanoporous polymer membranes. Scale bars are 500 nm.

Figure S13. (a) Zwitterionic feature of arginine grafted to the nanochannels of the membrane; (b) Chemical structure of Methyl orange and Rhodamine, as well as the corresponding aqueous solution; (c) Chemical reaction for polymerization of dopamine.
REFERENCES