Electronic Supplementary Information

Permselective 2D-Polymer-Based Membrane Tuneable by Host-guest Chemistry

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General Methods. All the reagents and solvents employed were commercially available and used as supplied without further purification. PerallyloxyCB[6], N^1,N^4,N^8,N^{12}-tetra(*tert*-butoxycarbonyl)spermine, N^1-(3-ammoniopropyl)-N^4-(3-(dodecylammonio)propyl)butane-1,4-diammonium chloride (C12-Spm), N^1-(3-ammoniopropyl)-N^4-(3-((2-carboxyethyl)-ammonio)propyl)butane-1,4-diammonium chloride (Acid-Spm), and 1-chloro-2-(2-2-methoxyethoxy)ethoxy)ethane were synthesized by following the previously reported methods.[1-5] All the NMR data were recorded on a Bruker DRX500 spectrometer. All chemical shifts are reported in parts per million downfield from internal tetramethylsilane (TMS). All fluorescence measurements were performed with 10 mm^2 quartz cells on a Shimadzu RF-5301PC spectrofluorometer. UV-Visible absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrophotometer. SEM images were collected using a Phillips XL30S FEG scanning electron microscope operating at 5 kV. AFM images were collected using a DI Nanoscope IIIa and VEECO Dimension 3100. High-purity deionized water was obtained with a Milli-Q water system (Millipore). High-resolution mass (ESI) data was obtained with a SYNAP G2 mass spectrometer (Waters) at the Korean Basic Science Institute (Ochang). Nanoindentation experiments were performed with a PI85 Picoindenter (Hysitron) equipped with a FEI Helios 600 at the National Institute for Nanomaterials Technology (Pohang).

Synthesis of TEG-Spm. N^1,N^4,N^8,N^{12}-tetra(*tert*-butoxycarbonyl)spermine (100 mg, 166 μmol) was added to a suspension of sodium hydride (4.00 mg, 166 μmol) in dry DMSO (10 mL) at 0 °C. 1-chloro-2-(2-2-methoxyethoxy)ethoxy)ethane (30 mg, 166 μmol) was added dropwise to the reaction mixture, and stirred for 12 h at room temperature. After termination of the reaction by adding water at 0 °C, the crude product was extracted with ethyl acetate, and dried over Na_2SO_4. After removal of the solvent, a yellowish oil was obtained. A white powder of TEG-Spm (54 mg, 67 %) was obtained by de-protection of *tert*-butoxycarbonyl groups using 4M hydrochloric acid in 1,4-dioxane for 3 h. ^{1}H NMR (D_2O, 500 MHz): δ = 3.61-3.78 (m, 10H), 3.40 (s, 3H), 3.30 (t, 2H), 3.08-3.14 (m, 12H), 2.02-2.27 (m, 4H), 1.76 (m, 4H). ^{13}C NMR (D_2O, 125 MHz): δ = 72.7, 71.0, 70.3, 69.1, 58.6, 47.7, 46.3, 45.1, 39.0, 38.3, 28.5, 26.3, 23.1. HR-ESI-MS calcd. for $C_{17}H_{41}N_4O_3$ $[M+H-4HCl]^+$: 349.3173, found: 349.3177.

Preparation of CB[6]-based 2D polymer. A solution of perallyloxyCB[6] (10.0 mg, 4.98 μmol) and 1,2-ethanedithiol (20 μL, 240 μmol) in DMA (10 mL) was sonicated until it became clear. After the solution was purged with N_2 gas for 30 min, the mixture was irradiated with UV light (254 nm and 300 nm) for 6 h. The polymerization reaction was terminated by treating the reaction mixture with ethyl vinyl ether (2.3 mL, 24 mmol) under UV irradiation for 6 h. The reaction mixture was then purified by dialysis against DMA using a membrane (MWCO: 10,000) to give a dispersion of 2D polymer in DMA. The resulting CB[6]-based 2D polymer has a quasi-hexagonal 2D network structure with an average distance between neighbouring CB[6] units of ~3 nm. There may be some "defect" sites in the 2D polymer network; however, layer-on-layer stacking of the 2D polymer films on the supporting membrane may compensate for any defects and prevent unwanted permeation through the membrane.

Nano-indentation of the CB[6]-based 2D polymer. The CB[6]-based 2D polymer was deposited on a Si wafer. The samples were mounted in a Hysitron PI85 Picoindenter (Hysitron) equipped with a FEI Helios 600; a Berkovich probe tip with angle of 120° was used to indent the samples. The force and displacement curves were used to identify the elastic modulus and hardness of the CB[6]-based 2D polymer.

Preparation of CB[6]-based 2D polymer deposited permselective membrane on PTFE membrane in a syringe filter. In a typical experiment, a dispersion solution of 2D polymer in DMA (1 mL) was gently filtered through a commercially available syringe filter (Whatman, PTFE; pore size, 0.2 μm). Subsequently, the resulting membrane was gently washed with 1 mL of water to the remove the residual solvent, DMA, and to pre-wet the membranes for the following experiments. The deposition of the CB[6]-based 2D polymer on the PTFE membrane was confirmed by SEM and FT-IR studies (Fig. S1 and S2). The CB[6]-based 2D polymer deposited permselective membrane was used directly for size-selective filtration experiments. To modify the 2D polymer membrane with guest molecules, the permselective membrane was incubated with an aqueous solution of each guest molecule (1 mM) overnight. Then, the modified permselective membrane was used for charge-selective filtration. To recycle the membrane, the membrane-containing syringe filter used was immersed and gently shaken in water for 1 min, 3 times.

Preparation of CB[6]-based 2D polymer deposited permselective membrane on AAO membrane. In a typical experiment, a dispersion solution of 2D polymer in DMA (1 mL) was gently filtered through a commercially available AAO membrane (Whatman; pore size, 0.2 μm). Subsequently, the resulting membrane was gently washed with 1 mL of water to remove the residual solvent, DMA, and pre-wet the membranes for the following experiments. The deposition of the CB[6]-based 2D polymer on the AAO membrane was confirmed by SEM and FT-IR studies (Fig. S1 and S2). The CB[6]-based 2D polymer deposited permselective membrane was used directly for hydrophobic-dependent permeation experiment..

Size- and charge selective permeation experiment. An aqueous solution of each dye (3 ml, 1 μM) was filtered through the permselective membrane; then, dye content in the filtrate of each solution was measured by fluorescence (R6G, MB, and Cal) or UV-Vis (NpS) spectroscopy.

Measurement of the surface zeta potential of the permselective membranes with Spm and Acid-Spm. The surface zeta potential of the CB[6]-based 2D polymer with Spm and Acid-Spm was recorded with respect to that of the unmodified 2D polymer on a Otsuka ELSZ-2000. All the 2D polymer membranes were deposited on a glass cover slip (1 x 3 cm^2). The surface zeta potential of the unmodified 2D polymer membranes was -21.04 mV. The 2D polymer membranes modified with Spm and Acid-Spm exhibited a less negative surface zeta potential of -2.44 mV and a more negative surface zeta potential of -29.74 mV, respectively. Considering a typical zeta potential of a pristine glass cover slip (-60 to -80 mV), this result suggests that the 2D polymer membrane itself seems to have relatively positive surface zeta potential, and the surface modification of the 2D polymer membrane with spermine derivatives containing either positive (Spm) or negative charges (Acid-Spm) was successfully performed.

Hydrophobicity-dependent permeation experiment. The CB[6]-based 2D polymer deposited AAO membrane was connected to the middle of a U-shaped tube with a feed cell and a permeate cell. The feed cell was filled with a solution of Rubpy or RB (1 mM), and the permeate cell was filled with pure water. The amount of the diffused dye molecules, which had passed through the permselective membrane, to the permeate cell was measured by UV-Vis spectrophotometer every 5 hours for 15 hours. The concentration of the diffused Rubpy molecules in the permeate cell increased linearly from 0 to 79 μM for the pristine AAO membrane, to 38 μM for the unmodified 2D polymer deposited AAO membrane, to 22 μM for the TEG-Spm decorated one, and to 16 μM for the C12-Spm decorated one, respectively. Similarly, the concentration of the diffused RB molecules in the permeate cell increased linearly from 0 to 83 μM, to 3.1 μM, to 7.7 μM, and to 0.8 μM, respectively.

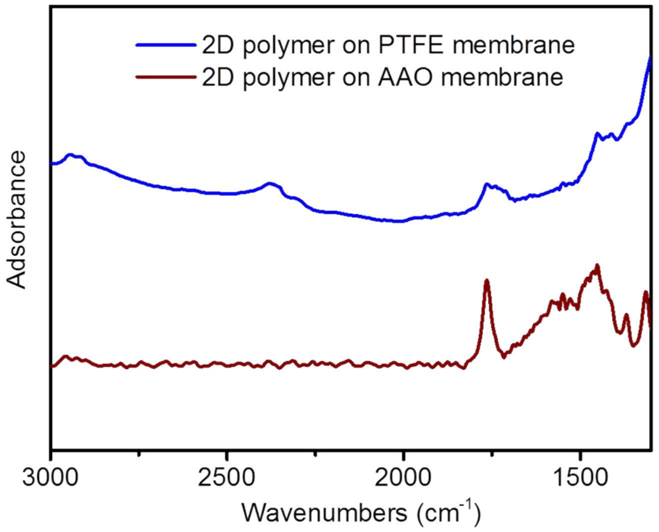
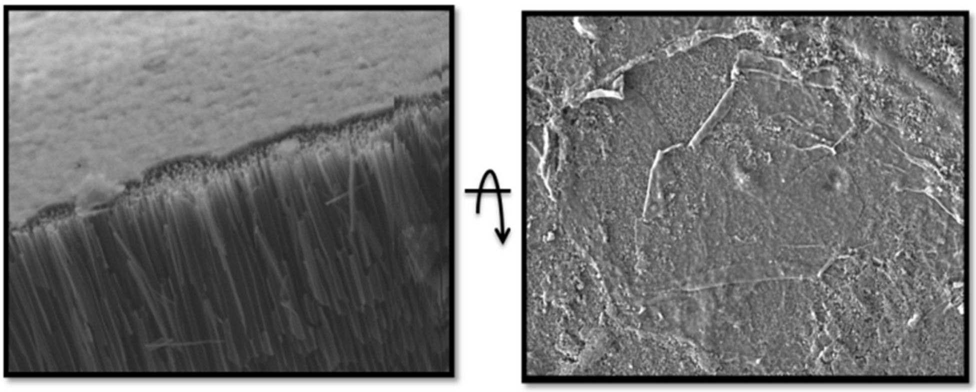


Fig. S1 FT-IR spectra of the CB[6]-based 2D polymer on the PTFE and AAO membranes.



Side view

Surface view

Fig. S2 Deposition of the CB[6]-based 2D polymer on the AAO membrane.

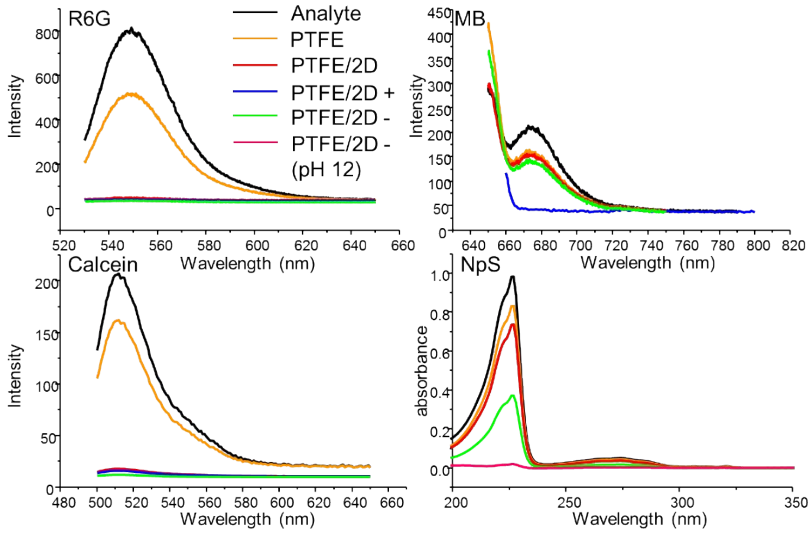


Fig. S3 Fluorescence and UV-Vis spectra of the dye molecules in the filtrate.

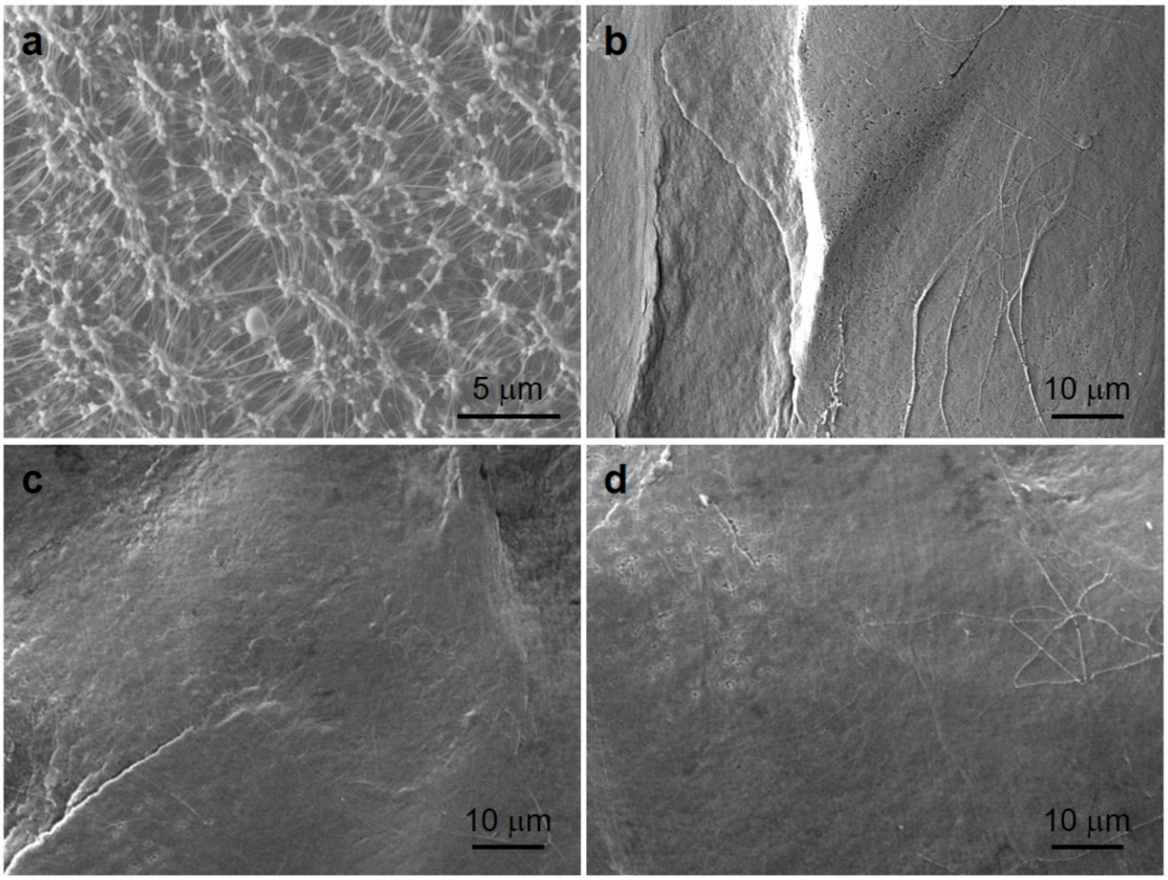


Fig. S4 SEM image of the PTFE membrane (a), and the CB[6]-based 2D polymer deposited membrane before a filtration experiment (b) and after three filtration cycles (c,d). The CB[6]-based 2D polymer coating on the PTFE membrane still remained intact after three filtration cycles.

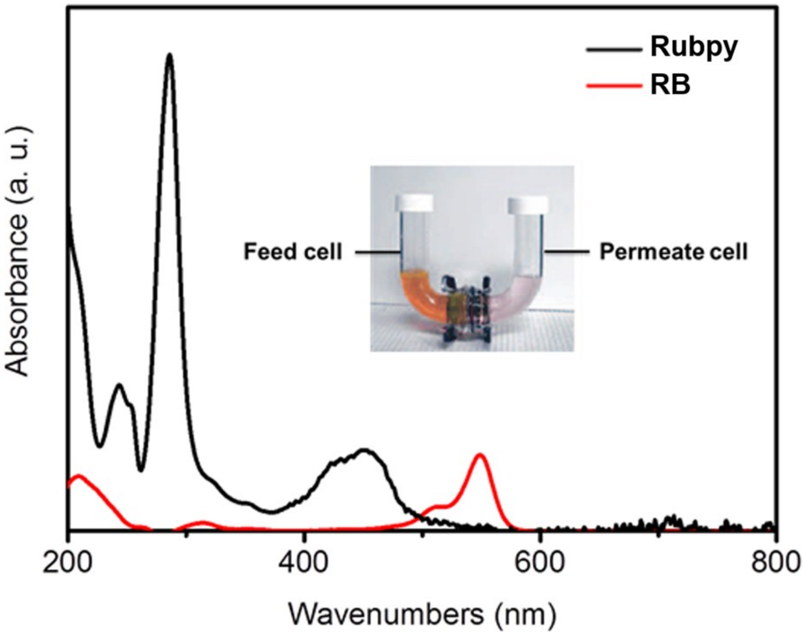


Fig. S5 UV-Vis spectra of Rubpy and RB. Inset shows a hydrophobicity-dependent permeation experimental set-up.

References

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