Supplementary information

Self-assembled nanostructured membranes with an imidazolium-sulfonate betaine group: Ionic columnar liquid crystals on water treatment and CO2 gas separation properties

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Contents

1. Experimental section for synthesis and preparation of membranes

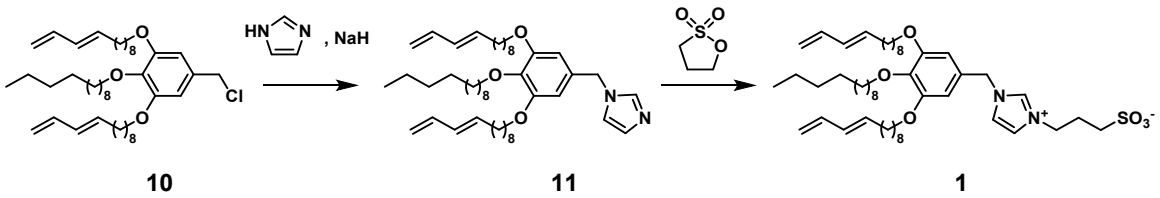
1-1. Materials and general methods

All chemical reagents were purchased from Sigma-Aldrich Japan (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), Tokyo Chemical Industry (Tokyo, Japan), and FUJIFILM Wako Pure Chemical (Osaka, Japan), and were used without further purification. Poly(ethylene terephthalate) (PET) films coated with a poly(vinyl alcohol) (PVA) layer (SO sheet) were provided by AICELLO (Toyohashi, Japan). Flat-sheet polysulfone ultrafiltration membrane CF-30S was obtained from Nitto/Hydranautics (Osaka, Japan). Silica gel column chromatography was carried out using automated flash chromatography systems W-Prep 2XY (Yamazen, Osaka, Japan) with Universal Column (Yamazen) and silica gel 60 (Kanto Chemical, spherical, 40–50 μm). Nuclear magnetic resonance (NMR) spectra of samples in $CDCl_3$ were recorded using a JNM-ECX400 spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The chemical shifts of the ^{1}H and ^{13}C NMR signals were referenced to the internal standards, Me_4Si (δ = 0.00 ppm) and $CDCl_3$ (δ = 77.00 ppm), respectively. NMR results were expressed in terms of chemical shifts (δ, ppm), multiplicity, coupling constant (Hz), and relative intensity. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an AutoflexTM speed spectrometer (Bruker, Billerica, MA, USA) using dithranol as the matrix. Elemental analyses were performed using a CE-440 Elemental Analyzer (Exeter Analytical, North Chelmsford, MA, USA).

Liquid-crystalline (LC) phase transition behavior was examined with a BX-53 optical polarizing microscope (Evident, Tokyo, Japan) equipped with an FP82HT hot-stage (Mettler Toledo, Tokyo, Japan) and an LTS350 hot-stage (Linkam, Redhill, UK). Differential scanning calorimetry (DSC) measurements were conducted with a DSC 3500

Sirius system (NETZSCH, Selb, Germany) at a cooling rate of 10 K min^{-1}. X-ray diffraction (XRD) measurements were performed using a RINT-2500 system (Rigaku, Tokyo, Japan) and a SmartLab system (Rigaku).

*1-2. Synthesis of compound **1***



Scheme S1. Synthesis of compound **1**.

1-(3,5-Bis(dodeca-9,11-dienyloxy)-4-(dodecyloxy)benzyl)-imidazole (**11**)

NaH (60% suspension, 0.113 g, 2.7 mmol) dispersed in *N*,*N*-dimethylformamide (DMF) (10 mL) was added to imidazole (0.176 g, 2.6 mmol)) in DMF (5 mL) and stirred for 30 min at 0 ℃. After that, a DMF solution of compound **10** (1.312 g, 1.97 mmol) synthesized as previously reported[S1] was added to the NaH/imidazole solution. After 1h of stirring, the mixture was heated to 60 ℃ and stirred for 15 h. The mixture was diluted with sat. NH_4Cl aq. and then extracted with ethyl acetate for three times. The organic layer was washed with sat. NH_4Cl aq. and brine and dried over $MgSO_4$. After filtration and concentration in vacuo, the crude product was purified using silica gel column chromatography (eluent, hexane/ethyl acetate, 40/60) to obtain colorless oil (0.753 g, 1.06 mmol, 54%).

^{1}H NMR (400 MHz): δ = 7.53 (s, 1H), 7.09 (s, 1H), 6.90 (s, 1H), 6.31 (s, 2H), 6.30 (dt, *J* = 16.8, 10.8 Hz, 2H), 6.04 (dd, *J* = 16.0, 10.8 Hz, 2H), 5.70 (dt, *J* = 15.6, 7.2 Hz, 2H),

5.08 (d, *J* = 16.8, 2H), 5.01 (s, 2H), 4.95 (d, *J* = 10.8 Hz, 2H), 3.94–3.87 (m, 6H), 2.07 (q, *J* = 7.1 Hz, 4H), 1.80–1.70 (m, 6H), 1.50–1.20 (m, 38H), 0.88 (t, *J* = 6.8 Hz, 3H).

3-(1-(3,5-Bis((dodeca-9,11-dien-1-yl)oxy)-4-(dodecyloxy)benzyl)-imidazolium-3-yl)propane-1-sulfonate (**1**)

To a solution of **11** (731 mg, 1.03 mmol) in dry toluene (15 mL), 1,3-propanesultone (201 mg, 4.41 mmol) was added and stirred at r.t. After stirring for 1 day, the organic solution was concentrated in vacuo. The crude product was purified using silica gel column chromatography twice (eluent for the first column chromatography, CH_2Cl_2/MeOH, gradient from 90/10 to 80/20, eluent for the second column chromatography, CH_2Cl_2/MeOH, gradient from 95/5 to 85/15). Compound **1** was obtained as white solid (470 mg, 0.57 mmol, 55 %).

^{1}H NMR (400 MHz): δ = 9.01 (s, 1H), 7.17 (s, 1H), 7.01 (s, 1H), 6.57 (s, 2H), 6.29 (dt, J = 17.6, 10.4 Hz, 2H), 6.03 (dd, J = 15.6, 10.4 Hz, 2H), 5.68 (dt, J = 15.2, 7.2 Hz, 2H), 5.32 (s, 2H), 5.06 (d, 16.8 Hz, 2H), 4.93 (d, 10.0 Hz, 2H), 4.59 (t, 6.0 Hz, 2H), 3.94 (m ,6H), 2.90 (t, J = 5.6 Hz, 2H), 2.42 (m, 2H), 2.06 (q, 7.1 Hz, 4H), 1.80-1.65 (m, 6H), 1.50-1.20 (m, 38H), 0.87 (t, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz): δ = 153.88, 138.95, 137.59, 137.42, 135.58, 130.95, 127.66, 122.13, 121.37, 114.67, 107.67, 73.53, 69.45, 53.96, 48.75, 47.40, 32.64, 32.01, 30.43, 29.84, 29.77, 29.70, 29.56, 29.48, 29.28, 26.41, 26.22, 22.77, 14.20.

MS (MALDI-TOF): Calcd for $[M + H]^+$, 825.58; found 824.85; Calcd for $[M + Na]^+$, 847.56; found 847.33; Calcd for $[M + K]^+$, 863.54; found 863.39; Calcd for $[M – H]^–$, 823.57; found 824.07.

Elemental analysis (%) calculated for $C_{49}H_{80}N_2O_6S$: C 71.32, H 9.77, N 3.39, found: C 70.82 H 9.49, N 3.59.

1-3. Preparation of nanostructured membranes

The water permeable membranes for salt rejection and virus filtration were fabricated by the photo-polymerization method previously reported.[S1] In CH_2Cl_2, monomer **1** (1 wt%) and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (0.01 wt%) were dissolved. A film composed of **1** and the photoinitiator was prepared by spin-coating of the solution on a PVA-coated PET substrate. The LC film was transferred onto the polysulfone support membrane. The sandwiched layers were heated to 80 °C and cooled to 30 °C. UV-irradiation (365 nm, 30 mW/cm^2) was performed with a UV-light emitting diode (UV-LED) system, HLDL100U (CCS, Kyoto, Japan) for 10 min at 30 °C under an ambient condition. After the UV-irradiation, the PVA layer was removed by immersing the resulting membranes in deionized water.

1-4. Virus filtration

The virus rejection performance of the composite membrane was tested using 25 mm membrane filtration units with agitation UHP-25K (Advantec, Tokyo, Japan) connected to a reservoir RP-2 (Advantec) containing a feed solution.[S2] The membranes were activated by immersing them into 2-propanol (17 vol.%) aq. solution and then submerged in Milli-Q water for 15 min prior to the filtration of viruses. A prepared virus stock was inoculated into the feed solution and mixed to obtain a concentration of approximately 10^7 copies mL^{-1}. Pure air gas containing less than 0.1ppm CO_2 was used to provide a pressure of 0.3 MPa for the feed solution entering into the stirred cell. Filtrate samples

were collected over the time periods from 0–1 h, 1–2 h, 2–4 h, and 4–6 h.

1-5. Salt rejection

Rejection/permeation performances of the composite membrane for NaCl and $MgSO_4$ were studied as follows[S1]: a membrane disc of 7 cm in diameter was set into a cross-flow filtration cell of Spin-flow Cell (Iwai Pharma Tech, Tokyo, Japan). An aqueous solution of each solute was supplied to the membranes under an operating pressure of 0.75 MPa to perform membrane filtration. The temperature was controlled at 25 °C. The salt rejection rate was calculated based on the electrical conductivity of the feed and permeate water, which was measured using Seven2Go with an InLab 738-ISM probe (Mettler-Toledo, Tokyo, Japan).

2. Assembled structures of the liquid-crystalline (LC) compounds

The intercolumnar distance and average number of molecules per cross-section layer of the columns were calculated based on the results of XRD measurements. The approximate calculation was done according to an established method in previous papers.[S2,S3]

Table S1. Comparison of assembled structures of compounds **1**–**4** in their LC states.

Compound	Molecular weight	Lattice size of Col_h (nm)	Number of molecules
1	825.25	3.96	4.5
2[S4]	833.31	4.04	4.6
3[S1]	804.95	3.86	4.3
4[S1]	810.01	3.70	4.0

3. Infrared (IR) study of monomer 1 and photopolymerized 1 in their bulk states

Attenuated total reflection (ATR) Fourier transformed infrared (FTIR) spectra (**Fig. S1**) were obtained using an FT/IR-6100 spectrometer (JASCO, Tokyo, Japan) equipped with a diamond prism system PKS-D1 (JASCO).

The film of compound **1** for the ATR-FTIR analyses was fabricated from a mixture of the monomer and the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (1 wt.%) sandwiched between PVA-coated glass plates. The film was heated to 80 °C and then cooled to 30 °C, followed by irradiation with UV light (365 nm, 30 mW/cm^2) for 10 min at 30 °C. A self-standing film for the IR measurement was obtained by immersing the photo-irradiated film in water, thereby removing the PVA layer. For the LC monomer and polymer on the porous substrate (**Fig. S2**), it is difficult to examine the ATR spectra due to the very small thickness of the LC layers.

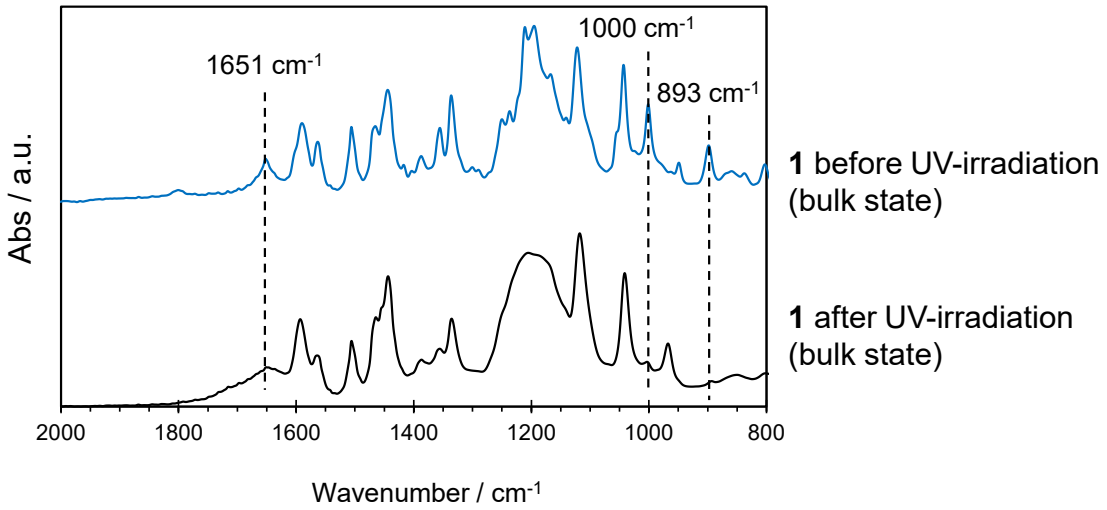


Fig. S1 ATR-IR spectra of **1** before and after UV-irradiation.

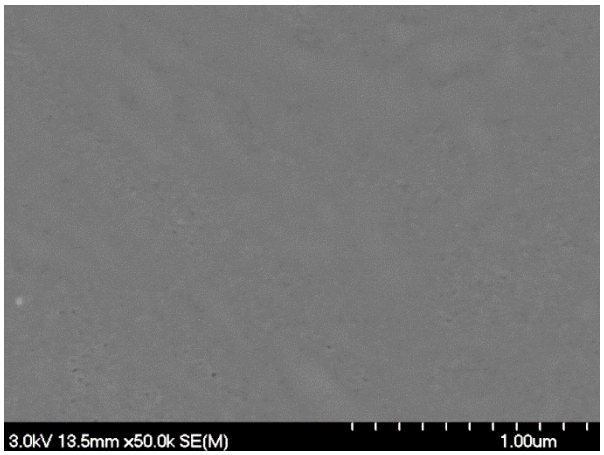
Supplementary note:

The peak at 1651 cm^{-1} corresponds to the C=C stretching vibration of the diene moieties while the peaks at 1000 cm^{-1} and 893 cm^{-1} correspond to the C-H out-of-plane bending vibration of the diene moieties (**Fig. S1**). The disappearance of these IR absorption peaks after the UV-irradiation indicates the consumption of the polymerizable diene moieties via the crosslinking reaction.

4. Scanning electron microscope (SEM) observation and water contact angles of the nanostructured membranes

Scanning electron microscope (SEM) observations of **P1** were conducted with a S-4700 (Hitachi, Tokyo, Japan) operated at 3 kV (**Fig. S2**). SEM samples were platinum coated with a Hitachi E-1030 ion sputter in advance.

(a)



(b)

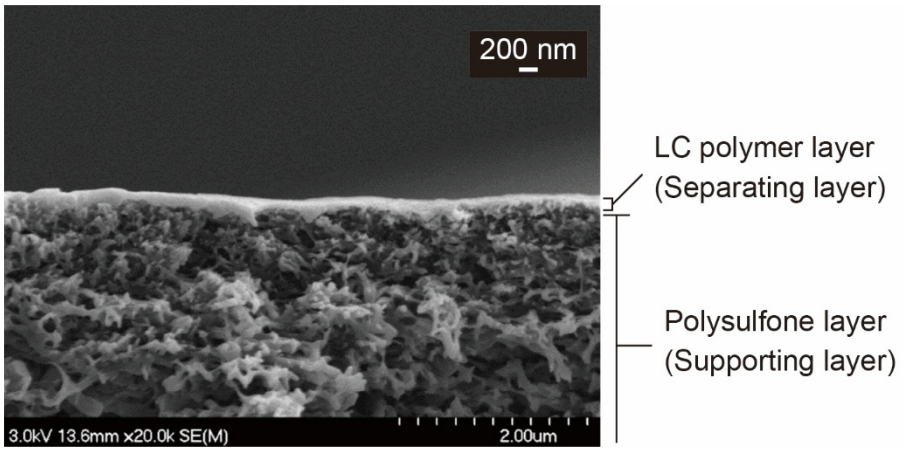


Fig. S2 SEM images for surface of membrane **P1**. (a) Top view, (b) cross-sectional view.

Water contact angles of membranes **P1** and **P3** (**Fig. S3**) were recorded with KYOWA DropMaster DMF-301 (Kyowa Interface Science, Saitama, Japan).

(a) (b)

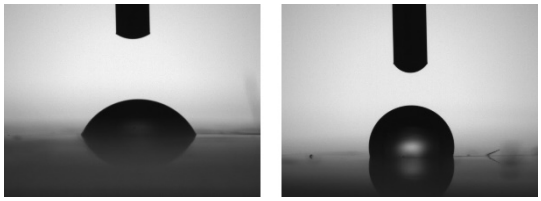


Fig. S3 Photographs of water droplets on membranes (a) **P1** and (b) **P3**.

5. Gas permeation

The gas-separation properties of the membranes were evaluated under isobaric conditions.[S5] The membranes (diameter = 25 mm) were placed in a flat sheet membrane cell with an effective membrane area of 1.77×10^{-4} m^2. Mixtures of CO_2 and N_2 (flow rates of CO_2 and N_2 were 10 and 90 mL(STP)/min, respectively) was humidified by passing through a temperature-controlled water bath and supplied into the membrane cell. On the permeate side, helium was fed as a sweep gas (flow rate: 50 mL(STP)/min). Mass flow controllers (MFC; HEMMI Slide Rule, Tokyo, Japan) were used to regulate the gas flow rates. The relative humidity (RH) on both sides was controlled by adjusting the water bath temperature. A GC-3200 gas chromatograph (GL Science, Tokyo, Japan) equipped with a thermal conductivity detector (TCD) was used to analyze the gas composition in the permeate streams. The TCD was calibrated using standard gases (Air Liquide Japan, Tokyo) for CO_2 and N_2, and water vapor was measured with a temperature/humidity transmitter (HF535-WBA3D1XX; Rotronic, Bassersdorf, Switzerland) equipped with a high-temperature zone probe (HC2-IC102; Rotronic).

6. References

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