Supplementary Information

Molecular design of a series of gemini-type zwitterionic amphiphiles with various linker lengths: control of their self-organization for developing gyroid nanostructured proton conductive membranes

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1. General Procedures and Materials

General Procedures. ¹H-NMR spectra were obtained on a JEOL JNM-ECX400 at 400 MHz and in CDCl₃ or CD₃OD. Chemical shifts of ¹H signals were quoted to (CH₃)₄Si ($\delta = 0.00$) as internal standard. The thermal properties of the materials were examined with DSC-6000 (Seiko Instruments). The heating and cooling rates were 10 °C min⁻¹. A polarizing optical microscope Olympus BX51 equipped with a Linkam hotstage was used for visual observation. X-ray diffraction measurement was performed using a Rigaku Smart-Lab with CuK α radiation. The ionic conductivities were measured with an impedance analyzer Solartron 1260 (Schlumberger) for **Film-G'** (frequency range: 10 Hz-10 MHz, applied voltage: 0.4 V). Comb-shaped gold electrodes with a glass substrate were used as a cell for the measurements of ionic conductivity. To determine the cell constant of the cell, a 0.01 mol L⁻¹ KCl aqueous solution was employed as a calibration standard.

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under argon atmosphere.

2. Synthesis

The synthetic pathways used to obtain compounds GZ-Ln, SZ, and GZ-Ln-Diene are shown in Scheme S1, Scheme S2, and Scheme S3 respectively.



Scheme S1. Synthetic scheme for GZ-Ln.

Synthesis of S3-Ln

To a solution of 4-pyridinecarboxaldehyde (S1) (5.00 g, 46.7 mmol) in ethanol was added a solution of *n*-alkyldiamine (NH₂(CH₂)_{*n*}NH₂, *n*; carbon number of alkyl chain) (2.05 g, 23.3 mmol). The mixture was refluxed for 3 h. The reaction mixture was cooled to room temperature. To the reaction mixture was added dropwise a solution of NaBH₄ (2.16 g, 57.7 mmol) in ethanol (50ml). The reaction mixture was refluxed for 4 h. To the reaction mixture was added an excess amount of NaOH aq. and CHCl₃. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was washed with diethyl ether repeatedly and collected by filtration. **S3-L***n* was obtained as a white powder in a yield of about 60 %.

Synthesis of S4-Ln

To a solution of **S3-L***n* (0.91 g, 3.35 mmol), triethylamine (1.69 g, 16.8 mmol) and 1-Hydroxybenzotriazole (1.00 g, 7.37 mmol) in CH_2Cl_2 (100 ml) was added myristic acid (1.68 g, 7.37 mmol) at 0 °C. The mixture was stirred for 5 min. To the reaction mixture was added dropwise a solution of EDC/HCl (1.41 g, 7.37 mmol) and stirred for 4 h. The reaction was poured into water and extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by column chromatography (silica gel, eluent: $CHCl_3/methanol = 9.3/0.7$). S4-Ln (n = 4, 8, 10) was obtained as a white powder in a yield of about 53 % while S4-Ln (n = 5, 7) was obtained as a yellow liquid in a yield of about 48 %.

Synthesis of GZ-Ln

To a solution of **S4-L***n* in acetonitrile was added an excess amount of 1,3-propanesultone. The reaction mixture was refluxed for 14-36 h. The crude product was recrystallized from a CHCl₃/CH₃OH/acetone mixed solvent several times. **GZ-L***n* (n = 4, 5, 7, 8, 10) was obtained as a white powder in a yield of about 53%.

GZ-L4:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.67, CH₃OH: δ = 3.34): δ = 9.02-8.91 (m, 4H), 7.91-7.87 (m, 4H), 5.00-4.79 (m, 8H), 4.72 (H₂O), 3.51-3.38 (m, 4H), 2.87-2.81 (m, 4H), 2.58-2.27 (m, 8H), 1.67-1.63 (m, 8H), 1.47-1.20 (m, 40H), 0.89 (t, *J* = 6.5 Hz, 6H). Elemental analysis: Calcd. for C₅₀H₉₄N₄O₁₂S₂ 4H₂O: C, 59.61; H, 9.41; N, 5.56. Found: C, 59.81; H, 9.49; N, 5.53.

GZ-L5:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.69, CH₃OH: δ = 3.34): δ = 8.95 (dd, *J* = 34.1, 6.6 Hz, 4H), 7.91-7.84 (m, 4H), 4.94-4.67 (H₂O), 3.48 (m, 3H), 2.86 (m, 4H), 2.53-2.25 (m, 8H), 1.73-1.65 (m, 8H), 1.36-1.26 (m, 44H), 0.89 (t, *J* = 6.9 Hz, 6H). Elemental analysis: Calcd. for C₅₁H₉₄N₄O₁₁S₂ 3H₂O: C, 61.05; H, 9.44; N, 5.63. Found: C, 61.02; H, 9.12; N, 5.63.

GZ-L7:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.62, CH₃OH: δ = 3.34): δ = 8.96 (dd, *J* = 35.3, 6.4 Hz, 4H), 7.87 (dd, *J* = 18.5, 6.6 Hz, 4H), 4.93-4.80 (m, 8H), 4.70 (H₂O), 3.46 (t, *J* = 7.8 Hz, 4H), 2.83 (m, 4H), 2.52-2.41 (m, 8H), 1.66 (m, 8H), 1.38-1.28 (m, 51H), 0.89 (t, *J* = 6.9 Hz, 6H). Elemental analysis: Calcd. for C₅₃H₉₄N₄O₉S₂ 1H₂O: C, 63.95; H, 9.52; N, 5.63. Found: C, 63.74; H, 9.56; N, 5.57.

GZ-L8:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.61, CH₃OH: δ = 3.35): δ = 8.98 (dd, *J* = 35.7, 6.9 Hz, 4H), 7.88 (dd, *J* = 19.7, 6.9 Hz, 4H), 4.94-4.79 (m, 8H), 4.72-4.62 (H₂O), 3.48-3.41 (m, 4H), 2.97-2.84 (m, 4H), 2.52-2.20 (m, 8H), 1.69-1.58 (m, 8H), 1.45-1.26 (m, 49H), 0.89 (t, *J* = 6.9 Hz, 6H). Elemental analysis: Calcd. for

C₅₄H₉₉N₄O_{10.5}S₂ 2.5H₂O: C, 62.61; H, 9.57; N, 5.41. Found: C, 62.76; H, 9.64; N, 5.38.

GZ-L10:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.44, CH₃OH: δ = 3.36): δ = 8.99 (dd, *J* = 41.4, 6.6 Hz, 4H), 7.84 (dd, *J* = 24.3, 6.4 Hz, 4H), 4.88-4.75 (m, 8H), 4.28 (H₂O), 3.42 (t, *J* = 7.8 Hz, 4H), 2.85 (t, *J* = 6.4 Hz, 4H), 2.49-2.22 (m, 8H), 1.65 (m, 8H), 1.31-1.14 (m, 53H), 0.88 (t, *J* = 6.9 Hz, 6H). Elemental analysis: Calcd. for C₅₆H₁₀₂N₄O₁₀S₂ 2H₂O: C, 63.72; H, 9.74; N, 5.31. Found: C, 63.68; H, 9.57; N, 5.14.



Scheme S2. Synthetic scheme for SZ.

Synthesis of SZ

To a solution of 4-(ethylamino)pyridine (S5), triethylamine and 1-hydroxybenzotriazole in CH_2Cl_2 was added myristic acid at 0 °C. The mixture was stirred for 5 min. To the reaction mixture was added dropwise a solution of EDC/HCl and stirred for 4 h. The reaction was poured into water and extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by column chromatography (silica gel, eluent: CHCl₃/methanol = 9.3/0.7). S6 was obtained as a white powder in a yield of 64%.

To a solution of **S6** in toluene/acetonitrile/2-propanol (10/10/1, v/v/v) was added an excess amount of 1,3-propanesultone. The mixture was refluxed for 8 h. The crude product was recrystallized from a CHCl₃/CH₃OH/acetone mixed solvent several times.

SZ was obtained as a white powder in a yield of 55%.

SZ:

¹H-NMR (400 MHz, CDCl₃ + CD₃OD: solvent peak of CHCl₃: δ = 7.61, CH₃OH: δ = 3.34): δ = 8.96 (dd, *J* = 35.3, 6.9 Hz, 2H), 7.89 (dd, *J* = 18.8, 6.4 Hz, 2H), 4.94-4.75 (m, 4H), 4.73-4.61 (H₂O), 3.58-3.44 (m, 2H), 2.94-2.84 (m, 2H), 2.54-2.20 (m, 4H), 1.71-1.64 (m, 2H), 1.36-1.14 (m, 25H), 0.89 (t, *J* = 6.9 Hz, 3H). Elemental analysis: Calcd. for C₂₅H_{45.4}N₂O_{4.7}S₁ 0.7H₂O: C, 62.42; H, 9.45; N, 5.83. Found: C, 62.20; H, 9.26; N, 5.76.



Scheme S3. Synthetic scheme for GZ-L*n*-Diene (n = 4, 5, 6). GZ-L4-Diene and GZ-L5-Diene were not synthesized due to an undesired thermal polymerization reaction in the reaction step from S4-L*n*-Diene to GZ-L*n*-Diene. GZ-L6-Diene was obtained in a yield of 76% according to the synthesis condition reported in the literature.^[S1]

Synthesis of D4

D4 was synthesized according to the literature.^[S1]

Synthesis of S4-Ln-Diene

To a solution of **S3-L***n* (0.88 g, 3.24 mmol), triethylamine (1.97 g, 19.5 mmol) and 1hydroxybenzotriazole (0.96 g, 7.13 mmol) in CH_2Cl_2 (100 ml) was added **D4** (1.60 g, 7.13 mmol) at 0 °C and stirred for 5 min. To the reaction mixture was added dropwise a solution of EDC/HCl (1.37 g, 7.13 mmol) and stirred for 4 h. The reaction was poured into water and extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by column chromatography (silica gel, eluent: CHCl₃/methanol = 9.3/0.7). **S4-L***n***-Diene** (*n* = 4 and 5) was obtained as a yellow liquid in yields of 52 and 76 %, respectively.

To a solution of **S6** in toluene/acetonitrile/2-propanol (10/10/1, v/v/v) was added an excess amount of 1,3-propanesultone. The mixture was refluxed for 8 h. The crude product was recrystallized from a CHCl₃/CH₃OH/acetone mixed solvent several times. **SZ** was obtained as a white powder in a yield of 55%.

Synthesis of GZ-Ln-Diene

To a solution of a crude compound of S4-L*n*-Diene in acetonitrile was added an excess amount of 1,3-propanesultone. The mixture was refluxed for 14-25 h. In the case of S4-L6-Diene, the crude product was recrystallized from a CHCl₃/CH₃OH/acetone mixed solvent several times. GZ-L6-Diene was obtained as a yellowish powder in a yield of 76%. On the other hand, in the case of S4-L4-Diene and S4-L5-Diene, insoluble products were formed during the reflux process. We assume that they are thermally polymerized compounds of S4-L*n*-Diene and GZ-L*n*-Diene. Therefore, pure compounds of GZ-L4-Diene and GZ-L5-Diene were not obtained (Fig. S1).



Figure S1. The photographs of the product obtained in the quaternisation reaction of S4-L4-Diene with 1,3-propanesultone. The product was insoluble into organic solvents even in the presence of a small amount of HTf_2N , which is an effective additive that increases the solubility of conventional zwitterions into organic solvents.

3. Characterization of Thermotropic Liquid-Crystalline Properties

<u>Thermotropic liquid-crystalline property of GZ-L4/HTf₂N</u> GZ-L4

(a)



Figure S2. (a) POM image of **GZ-L4** in the Sm phase at 150 °C. (b) XRD pattern of **GZ-L4** in the Sm phase at 150 °C. (c) DSC thermograms of **GZ-L4**.



Figure S3. (a) POM image of the GZ-L4/0.5HTf₂N mixture in the Sm phase at 150 °C. (b) XRD pattern of the GZ-L4/0.5HTf₂N mixture in the Sm phase at 30 °C. (c) DSC thermograms of the GZ-L4/0.5HTf₂N mixture.

GZ-L4/1.0HTf₂N



Figure S4. (a) POM image of the GZ-L4/1.0HTf₂N mixture in the Sm phase at 25 °C. (b) XRD pattern of the GZ-L4/1.0HTf₂N mixture in the Sm phase at 30 °C.

GZ-L4/1.5HTf₂N



Figure S5. (a) POM image of the GZ-L4/1.5HTf₂N mixture on the phase transition from the Col to Cub_{bi} phases at 105 °C on cooling. (b) XRD pattern of the GZ-L4/1.5HTf₂N mixture in the Cub_{bi} phase at 30 °C. (c) DSC thermograms of the GZ-L4/1.5HTf₂N mixture.



Figure S6. POM images of the GZ-L4/1.5HTf₂N mixture on phase transition from the Cub_{bi} to Col phases at 114°C on heating.

GZ-L4/2.0HTf₂N



Figure S7. (a) POM image of the GZ-L4/2.0HTf₂N mixture in the Col phase at 135 °C. (b) XRD pattern of the GZ-L4/2.0HTf₂N mixture in the Col phase at 30°C. (c) DSC thermograms of the GZ-L4/2.0HTf₂N mixture.

<u>Thermotropic liquid-crystalline property of GZ-L5/HTf₂N</u> GZ-L5



Figure S8. (a) POM image of **GZ-L5** in the Sm phase at 145 °C. (b) XRD pattern of **GZ-L5** in the Sm phase at 150°C on cooling. (c) DSC thermograms of **GZ-L5**.



Figure S9. (a) POM image of the GZ-L5/0.5HTf₂N mixture in the Sm phase at 150 °C. (b) DSC thermograms of the GZ-L5/0.5HTf₂N mixture.



Figure S10. (a) POM image of the GZ-L5/1.0HTf₂N mixture in the Sm phase at 140 °C. (b) XRD pattern of the GZ-L5/1.0HTf₂N mixture in the Sm phase at 30°C. (c) DSC thermograms of the GZ-L5/1.0HTf₂N mixture.

GZ-L5/1.5HTf₂N



Figure S11. POM image of the GZ-L5/1.5HTf₂N mixture in the Col phase at 70 °C.

GZ-L5/2.0HTf₂N



Figure S12. POM image of the GZ-L5/2.0HTf₂N mixture in the Col phase at 95 °C.

<u>Thermotropic liquid-crystalline property of GZ-L6/HTf₂N</u> GZ-L6



Figure S13. (a) POM image of **GZ-L6** in the Sm phase at 150 °C. (b) XRD pattern of **GZ-L6** in the Sm phase at 150°C. (c) DSC thermograms of **GZ-L6**.



Figure S14. (a) POM image of the GZ-L6/0.5HTf₂N mixture in the Sm phase at 25 °C.
(b) XRD pattern of the GZ-L6/0.5HTf₂N mixture in the Sm phase at 30°C.



Figure S15. (a) POM image of the GZ-L6/1.0HTf₂N mixture in the Cub_{bi} phase at 25 °C. (b) XRD pattern of the GZ-L6/1.0HTf₂N mixture in the Cub_{bi} phase at 30°C. (c) DSC thermograms of the GZ-L6/1.0HTf₂N mixture.



Figure S16. (a) POM image of the **GZ-L6/1.5HTf**₂**N** mixture in the Col phase at 60 °C. (b) XRD pattern of the **GZ-L6/1.5HTf**₂**N** mixture in the Col phase at 30°C.



Figure S17. (a) POM image of the GZ-L6/2.0HTf₂N mixture in the Col phase at 58 °C. (b) DSC thermograms of the GZ-L6/2.0HTf₂N mixture.

<u>Thermotropic liquid-crystalline property of GZ-L7/HTf₂N</u> GZ-L7



Figure S18. (a) POM image of **GZ-L7** in the Sm phase at 200 °C. (b) XRD pattern of **GZ-L7** in the Sm phase at 150 °C. (c) DSC thermograms of **GZ-L7**.



Figure S19. (a) POM image of the $GZ-L7/0.5HTf_2N$ mixture in an unidentified mesophase at 25 °C. XRD patterns of the $GZ-L7/0.5HTf_2N$ mixture (b) in an unidentified mesophase at 30 °C and (c) in Sm phase at 140°C. (d) DSC thermograms of the $GZ-L7/0.5HTf_2N$ mixture.



Figure S20. (a) POM image of the **GZ-L7/1.0HTf₂N** mixture in the Iso phase at 25 °C. (b) XRD pattern of the **GZ-L7/1.0HTf₂N** mixture in the Iso phase at 30 °C. (c) DSC thermograms of the **GZ-L7/1.0HTf₂N** mixture.



Figure S21. (a) POM image of the **GZ-L7/1.5HTf**₂**N** mixture in the Iso phase at 25 °C. (b) XRD pattern of the **GZ-L7/1.5HTf**₂**N** mixture in the Iso phase at 30 °C.

GZ-L7/2.0HTf₂N



Figure S22. POM image of the GZ-L7/2.0HTf₂N mixture in the Iso phase at 25 °C.

<u>Thermotropic liquid-crystalline property of GZ-L8/HTf₂N</u> GZ-L8



Figure S23. (a) POM image of **GZ-L8** in the Sm phase at 140 °C. (b) XRD pattern of **GZ-L8** in the Sm phase at 150 °C. (c) DSC thermograms of **GZ-L8**.



Figure S24. (a) POM image of the GZ-L8/0.5HTf₂N mixture in the Sm phase at 25 °C. (b) XRD pattern of the GZ-L8/0.5HTf₂N mixture in the Sm phase at 30 °C. (c) DSC thermograms of the GZ-L8/0.5HTf₂N mixture.

GZ-L8/1.0HTf₂N



Figure S25. (a) POM image of the GZ-L8/1.0HTf₂N mixture in the Iso phase at 25 °C. (b) XRD pattern of the GZ-L8/1.0HTf₂N mixture in the Iso phase at 30 °C. (c) DSC thermograms of the GZ-L8/1.0HTf₂N mixture.

GZ-L8/1.5HTf₂N



Figure S26. POM image of the GZ-L8/1.5HTf₂N mixture in the Iso phase at 25 °C.

GZ-L8/2.0HTf₂N



Figure S27. POM image of the GZ-L8/2.0HTf₂N mixture in the Iso phase at 25 °C.

<u>Thermotropic liquid-crystalline property of GZ-L10/HTf₂N</u> GZ-L10



Figure S28. (a) POM image of **GZ-L10** in the Sm phase at 150 °C. (b) XRD pattern of **GZ-L10** in the Sm phase at 150 °C. (c) DSC thermograms of **GZ-L10**.

GZ-L10/0.5HTf₂N



Figure S29. (a) POM image of the GZ-L10/0.5HTf₂N mixture in the Sm phase at 30 °C. (b) XRD pattern of the GZ-L10/0.5HTf₂N mixture in the Sm phase at 30 °C. (c) DSC thermograms of the GZ-L10/0.5HTf₂N mixture.

GZ-L10/1.0HTf₂N



Figure S30. (a) POM image of the GZ-L10/1.0HTf₂N mixture in the Iso phase at 40 °C. (b) XRD pattern of the GZ-L10/1.0HTf₂N mixture in the Iso phase at 30 °C. (c) DSC thermograms of the GZ-L10/1.0HTf₂N mixture.

$GZ-L10/1.5HTf_2N$



Figure S31. POM image of the GZ-L10/1.5HTf₂N mixture in the Iso phase at 25 °C.

$GZ-L10/2.0HTf_2N$



Figure S32. POM image of the GZ-L10/2.0HTf₂N mixture in the Iso phase at 25 $^{\circ}$ C.

<u>Thermotropic liquid-crystalline property of SZ/HTf₂N</u> SZ



Figure S33. (a) POM image of **SZ** in the Sm phase at 140 °C. (b) XRD pattern of **SZ** in the Sm phase at 150 °C. (c) DSC thermograms of **SZ**.



Figure S34. (a) POM image of the SZ/0.25HTf₂N mixture in the Meso phase at 25 °C. (b) XRD pattern of the SZ/0.25HTf₂N mixture in an unidentified mesophase at 40 °C. (c) DSC thermograms of the SZ/0.25HTf₂N mixture.



Figure S35. (a) POM image of the SZ/0.5HTf₂N mixture in the Meso phase at 71 °C. (b) XRD pattern of the SZ/0.5HTf₂N mixture in an unidentified mesophase at 30 °C.



Figure S36. (a) POM image of the **SZ/0.75HTf**₂**N** mixture in the Iso phase at 30 °C. (b) XRD pattern of the **SZ/0.75HTf**₂**N** mixture in the Iso phase at 30 °C.



Figure S37. (a) POM image of the SZ/1.0HTf₂N mixture in the Iso phase at 25 °C. (b) XRD pattern of the SZ/1.0HTf₂N mixture in the Iso phase at 30 °C.



Figure S38. DSC thermograms of GZ-Ln and SZ on heating.

4. Characterization of phase transition behavior of the GZ-Ln/HTf₂N mixtures upon water absorption



Figure S39. XRD patterns of the GZ-L4/1.0HTf₂N mixture after exposure to humidified air with various RH. (a) RH = 50 %, (b) RH = 80 % and (c) RH = 95 %.



Figure S40. XRD patterns of the GZ-L5/1.0HTf₂N mixture after exposure to humidified air with various RH. (a) RH = 50 %, (b) RH = 80 % and (c) RH = 95 %.



Figure S41. XRD patterns of the GZ-L6/1.0HTf₂N mixture after exposure to humidified air with various RH. (a) RH = 50 %, (b) RH = 80 %, and (c) RH = 95 %.

Table S1. The calculated water content of the $GZ-Ln/1.0HTf_2N$ mixtures and the $SZ/0.5HTf_2N$ mixtures in the driest state and after exposure to humidified air with various RH (RH = 50, 60, 70, 80, and 90) are shown. The samples of the mixtures in the driest state were prepared by vacuuming for at least 2 h at 40 °C.

	The driest state	RH = 50	RH = 60	RH = 70	RH = 80	RH = 90	
GZ-L4/1.0HTf ₂ N	3.3	8.9	9.7	10.2	11.0	12.9	
GZ-L5/1.0HTf ₂ N	3.7	8.1	10.2	12.4	15.8	20.7	
GZ-L6/1.0HTf2N	4.7	7.3	9.1	11.6	14.9	20.4	
GZ-L7/1.0HTf ₂ N	-	9.8	11.1	12.7	15.8	20.8	
GZ-L8/1.0HTf2N	4.9	8.9	10.5	13.3	16.5	22.3	
GZ-L10/1.0HTf ₂ N	4.7	7.7	9.5	11.4	14.6	19.2	
SZ/0.5HTf2N	5.2	_	16.4	18.7	22.0	28.0	

Calculated water content of the mixtures (wt%)

Table S2. The estimated number of water molecules per zwitterionic part of the **GZ**- $Ln/1.0HTf_2N$ mixtures and the **SZ/0.5HTf_2N** mixtures in dry states and after exposure to humidified air with various RH (RH = 50, 60, 70, 80 and 90) are shown. The samples of the mixtures in the driest states were prepared by vacuuming for at least 2 h at 40 °C.

	The driest state	RH = 50	RH = 60	RH = 70	RH = 80	RH = 90
GZ-L4/1.0HTf ₂ N	1.2	3.3	3.6	3.8	4.2	5.0
GZ-L5/1.0HTf2N	1.3	3.0	3.9	4.8	6.4	8.9
GZ-L6/1.0HTf2N	1.6	2.7	3.5	4.5	6.1	8.8
GZ-L7/1.0HTf2N	_	3.8	4.4	5.1	6.6	9.2
GZ-L8/1.0HTf2N	1.8	3.5	4.2	5.4	7.0	10.1
GZ-L10/1.0HTf2N	1.8	3.0	3.8	4.6	6.2	8.6
SZ/0.5HTf ₂ N	2.3	_	6.6	7.8	9.5	13.1

The number of water molecules per zwitterionic part

5. Characterization of Film-G'

Experimental procedures of polymerization

We prepared the **GZ-L6-Diene/0.5HTf**₂**N** mixture. It exhibits a Sm phase. 1 wt% of DMPA was added to it as a photo-polymerization initiator. In order to induce the **GZ-L6-iene/0.5HTf**₂**N** mixture to form a Cub_{bi} phase, we placed it under relative humidity (RH) controlled conditions (RH = 80%) at 30 °C for 2 h. UV irradiation was performed for the **GZ-L6-Diene/0.5HTf**₂**N** mixture in the Cub_{bi} phase for 1 h at 30 °C and RH = 80% using a xenon lamp as a light source, which yielded a gyroid-nanostructure polymer film (**Film-G'**).



Figure S42. POM images of the GZ-L6-Diene/0.5HTf₂N mixture on a glass substrate equipping gold electrodes. (a) The initial sample, (b) after the exposure to humidified air with RH = 80% for 4 h and (c) after polymerization (Film-G').



Figure S43. XRD patterns at 30 °C of the GZ_6 -Diene/0.5HTf₂N mixture: (a) in the initial state (the driest state), (b) after the exposure to humidified air with RH = 80% for 2 h and (c) after polymerization (Film-G'). The initial sample was prepared by vacuuming for at least 2 h at 40 °C.

We confirmed the success of the *in situ* polymerization process based on the change of the states of materials from highly-viscous liquid-crystalline state to a self-standing polymer films. The change of the states of materials can be confirmed by the change of the solubility into various organic solvents. Namely, before polymerization, these materials are soluble into methanol and chloroform while those after polymerization are insoluble into these conventional organic solvents. The preservation of the nanostructure has been performed by POM and XRD measurements (Figure S43, 44).

Table S3. The estimated water content of **Film-G'** and **Film-G** when exposed to various RH conditions (RH = 60, 70, 80 and 90) are shown. The water contents in the equilibrium state at various RH values were calculated by evaluating the weight change of the films. **Film-G'** shows the lower water content than **Film-G** in the equilibrium state at the same RH values.

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	RH = 60	RH = 70	RH = 80	RH = 90
Film-G'	3.5	_a	9.6	13.3
Film-G	8.5	10.8	13.1	15.6

Estimated water content (wt%) of Film-G' and Film-G

^{*a*}Not examined.



Figure S44. Cole–Cole plots obtained by using alternating current impedance measurements for **Film-G'(X)** at 30 °C after the exposure to humidified air with various RH conditions for 12 h. (a) RH = 60 %, (b) RH = 70 %, (c) RH = 80 %, and (d) RH = 90 %.

6. Reference

[S1] T. Kobayashi, Y. X. Li, A. Ono, X. B. Zeng and T. Ichikawa, *Chem. Sci.*, 2019, **10**, 6245.