

Supplementary Information

Ionic effects on self-assembly, molecular dynamics and conduction properties of 1,2,3-triazole-based amphiphile

Manh Linh Nguyen,^a Ho-Joong Kim,^{*b} and Byoung-Ki Cho^{*a}

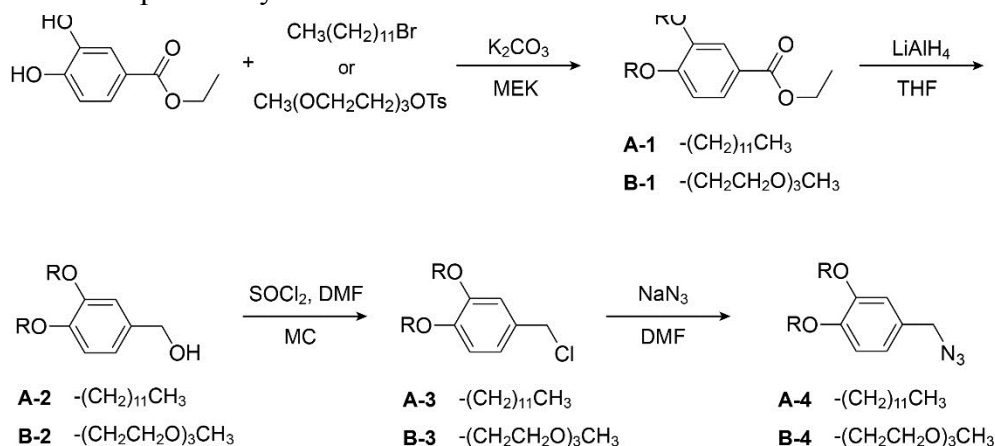
^aDepartment of Chemistry, Dankook University, 119, Dandae-ro, Chungnam, 448-701, Korea; ^bDepartment of Chemistry, Chosun University, Gwangju, 61452, Korea

Experimental Details

Materials and Methods. Tri(ethylene glycol)monomethyl ether (95%), 1-bromododecane, sodium azide (99.5%), lithium aluminum hydride (95%), CuI (98%), 2-methyl-3-butyno-2-ol (98%), (+)-sodium L-ascorbate (NaASC), CDCl₃ (99.8%), lithium bis(trifluoromethane)sulfonimide and CuSO₄·5H₂O were purchased from Sigma-Aldrich Chemical Co. 4-Toluenesulfonyl chloride (98%) was purchased from Junsei Chemical. Sodium hydroxide (min. 93%), anhydrous MgSO₄ (min. 99%), methylene chloride (HPLC grade, MC) and anhydrous potassium carbonate (min. 99%) were purchased from Duksan Pure Chemical, Korea. Bis(triphenylphosphine)palladium(II) dichloride, ethyl 3,4-dihydroxybenzoate, and thionyl chloride were purchased from Tokyo Chemical Industry. Methyl ethyl ketone (MEK) was stored over a type 4 Å molecular sieve. *N,N'*-Dimethylformamide (DMF) was distilled under vacuum, and stored over a type 4 Å molecular sieve. Tetrahydrofuran (THF) was dried by distillation from sodium metal, and stored over a type 4 Å molecular sieve. Triethylamine (TEA) was dried by distillation from calcium hydride, and stored over a type 4 Å molecular sieve. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ solutions using a Bruker AM 400 spectrometer. The purities of the compounds were verified using thin-layer chromatography (TLC; Merck, silica gel 60). Gel permeation chromatography (GPC) measurements were conducted in tetrahydrofuran and *N,N'*-dimethylacetamide (99.9%) (40:1 volume ratio) using a Waters 401 instrument equipped with KF-802, KF-803, AT-G and AT-804S Shodex columns at a flow rate of 1.0 mLmin⁻¹. Differential scanning calorimetry (DSC) measurements were performed using TA Instruments Q2000 thermal analysis equipment at a rate of 10 °C/min. Indium (melting temperature = 429 K and ΔH = 28.45 J/g) was used as a calibration standard. X-ray diffraction (XRD) measurements were performed in transmission mode with synchrotron radiation at the UNIST-PAL 6D beamline of the Pohang Accelerator Laboratory (PAL), Korea. The sample was placed in an aluminum sample holder with polyimide films on both sides. The X-ray spectra were plotted against the *q* value (=4πsinθ/λ). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. A Nikon eclipse LV100 optical polarized microscope equipped with a Linkam TMS 94 heating system was used to observe the thermal transitions and to analyze the anisotropic texture. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer combined with a home-made heating stage. The samples were placed between KBr plates. Dielectric relaxation spectroscopy (DRS) measurements were performed using a Solartron Impedance Analyzer (SI 1260). The sample was measured in an indium tin oxide (ITO) liquid crystal (LC) cell with a thickness of 5 μm (Linkam, United Kingdom). The LC cell was placed on the homemade heating block, which was connected to a Test & Probe Hot Chuck Controller. Impedance experiments were also performed using the

Solartron Impedance Analyzer. In this impedance experiment, an in-plane switching (IPS) LC cell with a gap of 12 μm between electrodes was used. Because the effective area (A) of the electrodes is unknown, the cell constant ($= d/A$, d : distance between two electrodes, A : effective area of the electrodes) of the IPS cell was obtained by calibration with a standard solution of KCl (0.0035 M),¹⁻³ and its cell constant (0.27 cm^{-1}) was obtained. In order to analyse the circuit elements, the original data were fitted using a Z-view2 simulation program.

Synthesis. The synthetic procedures of **1** are outlined in Schemes S1 and S2. Tosylated tri(ethylene glycol)monomethyl ether was synthesized by following previous procedure.⁴ 1,3-Dibromo-5-ethynylbenzene was prepared by following a previous procedure.⁵ The ionophobic precursors bearing dodecyl peripheries were synthesized in a similar synthetic procedure described previously.⁶



Scheme S1. Synthesis of azido precursors.

Synthesis of ethyl 3,4-bis(dodecyloxy)benzoate (A-1). Ethyl 3,4-dihydroxybenzoate (8.00 g, 0.04 mol), 1-bromododecane (43.78 g, 0.176 mol), and potassium carbonate (18.21 g, excess) were dissolved in 150 mL of dry MEK. The reaction mixture was heated to reflux for overnight under N_2 atmosphere. After cooling to room temperature, the solvent was removed using a rotary evaporator. Then, the mixture was extracted with MC and deionized water, and dried over MgSO_4 . The organic solvent was removed using a rotary evaporator. The resulting mixture was purified by column chromatography (silica gel) using *n*-hexane:MC = 1:1 as the eluent, to yield 21.69 g (95.2%) of a white solid. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.63 (d, 1H, $J = 4.0$ Hz, Ar- H), 7.53 (s, 1H, Ar- H), 6.86 (d, 1H, $J = 4.0$ Hz, Ar- H), 4.34 (q, 2H, $J = 3.6$ Hz, $\text{COOCH}_2\text{CH}_3$), 4.04 (t, 4H, $J = 6.4$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.85-1.72 (m, 4H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.48 (t, 3H, $J = 3.6$ Hz, $\text{COOCH}_2\text{CH}_3$), 1.48-1.33 (m, 36H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (t, 6H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$).

Synthesis of (3,4-bis(dodecyloxy)phenyl)methanol (A-2). To a stirred solution of compound **A-1** (21.69 g, 0.042 mol) in dry THF 150 mL was added LiAlH_4 (2.38 g, 0.06 mol) at 0 $^\circ\text{C}$. After stirring for 3 h at room temperature, the reaction mixture was quenched with a small amount of methanol and deionized water. The insoluble precipitate was filtered off. The filtrate was concentrated under a reduced pressure, to yield 19.32 g (98.8%) of a white solid. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 6.89 (d, 3H, $J = 13.6$ Hz, Ar- H), 4.60 (d, 2H, $J = 6.2$ Hz, CH_2OH), 3.99 (t, 4H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.81 (t, 4H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.47-1.33 (m, 36H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (t, 6H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$).

Synthesis of 4-(chloromethyl)-1,2-bis(dodecyloxy)benzene (A-3). Compound A-2 (19.32 g, 0.04 mol), thionyl chloride (56.7 mL, 0.057 mol), and 0.5 mL of DMF were dissolved in 100 mL of MC. The mixture was stirred at room temperature under N₂ atmosphere. After 30 min, the resulting mixture was extracted with MC and deionized water, and dried over MgSO₄. After removing MC by a rotary evaporator, the resulting compound was used for the next step without other purification.

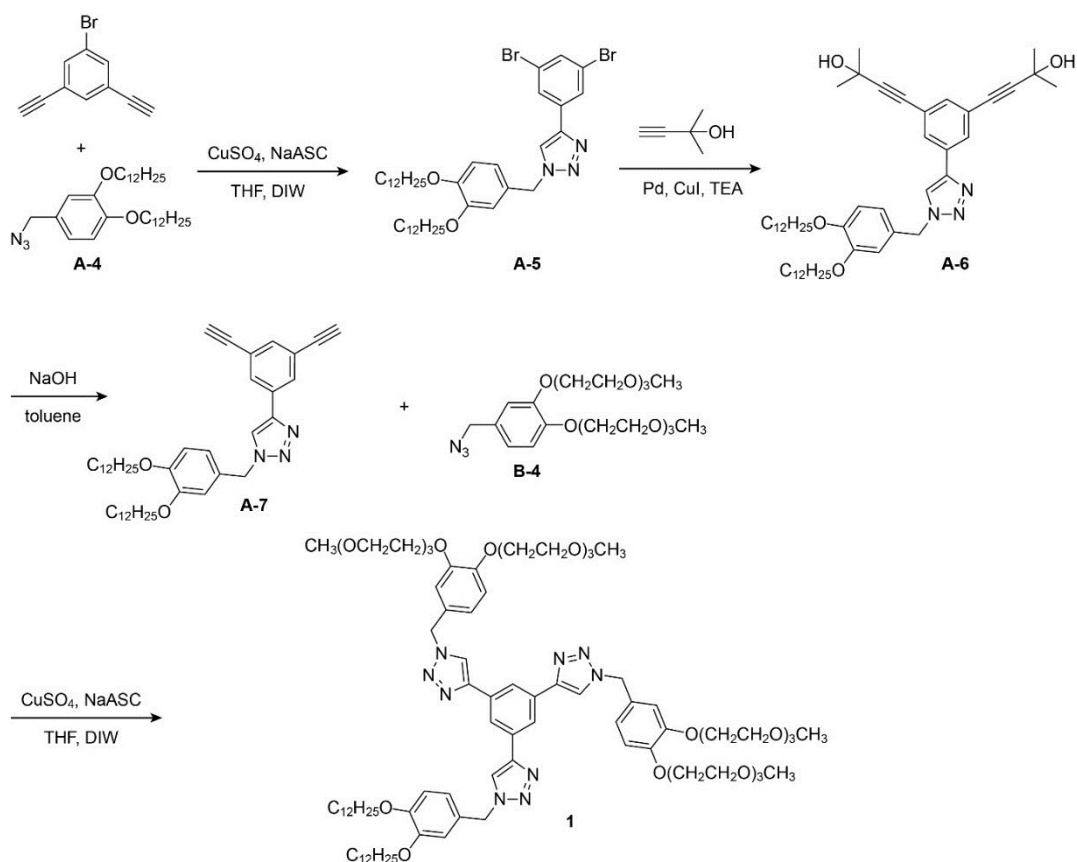
Synthesis of 4-(azidomethyl)-1,2-bis(dodecyloxy)benzene (A-4). Compound A-3 (17.0 g, 0.037 mol) and sodium azide (24.5 g, 0.37 mol) were dissolved in 150 mL of anhydrous DMF. The reaction mixture was heated at 100 °C for overnight under N₂ atmosphere. After cooling to room temperature, the solvent was removed by a rotary evaporator. The reaction mixture was extracted with MC and deionized water three times, and then dried over MgSO₄. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by a silica gel column chromatography using MC as eluent, to yield 17.5 g (92.5%) of a white solid. ¹H-NMR (CDCl₃, δ, ppm): 6.83 (s, 3H, Ar-H), 4.25 (s, 2H, CH₂N₃), 3.99 (t, 4H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₉CH₃), 1.82 (t, 4H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₉CH₃), 1.46-1.26 (m, 36H, OCH₂CH₂(CH₂)₉CH₃), 0.88 (t, 6H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₉CH₃).

Synthesis of ethyl 3,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (B-1). Ethyl 3,4-dihydroxybenzoate (4.00 g, 0.027 mol), tosylated tri(ethylene glycol)monomethyl ether (20.97 g, 0.066 mol), and potassium carbonate (9.50 g, excess) were dissolved in 40 mL of dry MEK. The reaction mixture was heated to reflux for overnight under N₂ atmosphere. After cooling to room temperature, the solvent was removed using a rotary evaporator. Then, the mixture was extracted with MC and brine, and dried over MgSO₄. The organic solvent was removed using a rotary evaporator. The resulting mixture was purified by sequential column chromatographies (silica gel) from MC:ethyl acetate (EA) = 1:1 solvent mixture to EA to MC:methanol = 30:1 solvent mixture as the eluents, to yield 7.2 g (70.0%) of a colourless liquid. ¹H-NMR (CDCl₃, δ, ppm): 7.65 (d, 1H, *J* = 6.8 Hz, Ar-H), 7.57 (s, 1H, Ar-H), 6.86 (d, 1H, *J* = 4.0 Hz, Ar-H), 4.33 (q, 2H, *J* = 7.2 Hz, COOCH₂CH₃), 4.21 (t, 4H, *J* = 4.0 Hz, OCH₂CH₂), 3.91-3.37 (m, 20H, OCH₂CH₂(OCH₂CH₂)₂OCH₃), 3.30 (s, 6H, (OCH₂CH₂)₃OCH₃), 1.38 (t, 3H, *J* = 7.2 Hz, COOCH₂CH₃).

Synthesis of (3,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)methanol (B-2). To a stirred solution of compound B-1 (7.13 g, 0.015 mol) in dry THF 40 mL was added LiAlH₄ (0.86 g, 0.022 mol) at 0 °C. After stirring for 2 h at room temperature, the reaction mixture was quenched with a small amount of methanol and deionized water. The insoluble precipitate was filtered off. The filtrate was concentrated under a reduced pressure, to yield 5.90 g (91.0%) of a colourless liquid. ¹H-NMR (CDCl₃, δ, ppm): 6.98 (s, 1H, Ar-H), 6.87 (2H, Ar-H), 4.59 (d, 2H, *J* = 5.8 Hz, CH₂OH), 4.18 (t, 4H, *J* = 5.2 Hz, OCH₂CH₂), 3.88-3.37 (m, 20H, OCH₂CH₂(OCH₂CH₂)₂OCH₃), 3.30 (s, 6H, (OCH₂CH₂)₃OCH₃), 1.82 (t, 1H, *J* = 5.8 Hz, CH₂OH).

Synthesis of 4-(chloromethyl)-1,2-bis(dodecyloxy)benzene (B-3). Compound B-2 (5.86 g, 0.014 mol), thionyl chloride (18.9 mL, 0.019 mol), and 0.2 mL of DMF were dissolved in 25 mL of MC. The mixture was stirred at room temperature under N₂ atmosphere. After 60 min, the resulting mixture was extracted with MC and deionized water, and dried over MgSO₄. After removing MC by a rotary evaporator, the resulting compound was used for the next step without other purification.

Synthesis of 4-(azidomethyl)-1,2-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (B-4). Compound **B-3** (6.0 g, 0.013 mol) and sodium azide (8.64 g, 0.13 mol) were dissolved in 25 mL of anhydrous DMF. The reaction mixture was heated at 100 °C for overnight under N₂ atmosphere. After cooling to room temperature, the solvent was removed by a rotary evaporator. The reaction mixture was extracted with MC and brine three times, and then dried over MgSO₄. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by sequential silica gel column chromatographies (silica gel) from MC to EA to MC:methanol = 30:1 solvent mixture as the eluents, to yield 5.5 g (92.4%) of a colourless liquid. ¹H-NMR (CDCl₃, δ, ppm): 6.92-6.82 (m, 3H, Ar-H), 4.24 (s, 2H, CH₂N₃), 4.17 (t, 4H, *J* = 5.2 Hz, OCH₂CH₂), 3.89-3.53 (m, 20H, OCH₂CH₂(OCH₂CH₂)₂OCH₃), 3.38 (s, 6H, (OCH₂CH₂)₃OCH₃).



Scheme S2. Synthesis of amphiphile **1**.

Synthesis of 1-(3,4-bis(dodecyloxy)benzyl)-4-(3,5-dibromophenyl)-1H-1,2,3-triazole (A-5). 1,3-Dibromo-5-ethynylbenzene (1.41 g, 0.0054 mol), compound **A-4** (3.0 g, 0.0059 mol), NaASC (3.23 g, 0.016 mol), and CuSO₄·5H₂O (2.0 g, 0.008 mol) were dissolved in the mixture of 40 mL of THF and 4 mL of deionized water. The reaction mixture was stirred for 12 hours at room temperature. The solvent was removed by a rotary evaporator. The resulting mixture was extracted with chloroform and brine three times, and then dried over MgSO₄. After removing chloroform by a rotary evaporator, and the resulting mixture was purified by a silica gel column chromatography (silica gel) using MC:*n*-hexane = 1:10 solvent mixture as the eluent, to yield 3.12 g (75.2 %) of a white solid. ¹H-NMR (CDCl₃, δ, ppm): 7.88 (s, 2H, Ar-H), 7.62 (s, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 6.87-6.81 (3H, Ar-H), 5.47 (s, 2H, benzyl-H), 3.96

(m, 4H, OCH₂CH₂), 1.82 (m, 4H, OCH₂CH₂), 1.50–1.20 (m, 36H, OCH₂CH₂(CH₂)₉CH₃), 0.87 (t, 6H, *J* = 6.2 Hz, OCH₂CH₂(CH₂)₉CH₃).

Synthesis of 4,4'-(5-(1-(3,4-bis(dodecyloxy)benzyl)-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)bis(2-methylbut-3-yn-2-ol) (A-6). Compound A-5 (3.12 g, 0.004 mol), butynol (3.45 g, 0.041 mol), Pd(PPh₃)₂Cl₂ (0.16 g) and CuI (0.08 g) were dissolved in 20 mL of dry TEA. The mixture was heated for 12 hours with stirring under N₂ atmosphere. After cooled to room temperature, the solvent was removed by a rotary evaporator. And then the mixture was extracted with MC and brine three times. The MC layer was washed with deionized water several times, and dried over MgSO₄. The solvent was removed by a rotary evaporator, and the crude product was then purified by sequential silica gel column chromatographies from MC to MC:EA = 9:1 as the eluents, to yield 1.25 g (40.0%). ¹H-NMR (CDCl₃, δ, ppm): 7.78 (s, 2H, Ar-*H*), 7.60 (s, 1H, Ar-*H*), 7.40 (s, 1H, Ar-*H*), 6.86-6.82 (3H, Ar-*H*), 5.47 (s, 2H, benzyl-*H*), 3.96 (m, 4H, OCH₂CH₂), 1.80 (m, 4H, OCH₂CH₂), 1.50–1.20 (m, 48H, OCH₂CH₂(CH₂)₉CH₃ and C(CH₃)₂OH), 0.87 (t, 6H, *J* = 6.2 Hz, OCH₂CH₂(CH₂)₉CH₃). M_w/M_n = 1.01 (GPC).

Synthesis of 1-(3,4-bis(dodecyloxy)benzyl)-4-(3,5-diethynylphenyl)-1*H*-1,2,3-triazole (A-7). Compound A-6 (1.23 g, 0.0016 mol) and NaOH (0.64 g, 0.016 mol) were dissolved in 20 mL of toluene. The mixture was heated to reflux for 12 hours, and then cooled to room temperature. The solvent was removed by a rotary evaporator. The mixture was extracted with MC and brine three times. The MC layer was washed with deionized water several times, and dried over MgSO₄. The solvent was removed by a rotary evaporator, and the crude product was then purified by silica gel column chromatography using MC as the eluent, to yield 0.72 g (69.0%). ¹H-NMR (CDCl₃, δ, ppm): 7.89 (s, 2H, Ar-*H*), 7.63 (s, 1H, Ar-*H*), 7.54 (s, 1H, Ar-*H*), 6.86-6.81 (3H, Ar-*H*), 5.47 (s, 2H, benzyl-*H*), 3.96 (m, 4H, OCH₂CH₂), 3.10 (s, 2H, C≡C-*H*), 1.80 (m, 4H, OCH₂CH₂), 1.40–1.20 (m, 36H, OCH₂CH₂(CH₂)₉CH₃), 0.87 (t, 6H, *J* = 6.2 Hz, OCH₂CH₂(CH₂)₉CH₃). M_w/M_n = 1.01 (GPC).

Synthesis of 4,4'-(5-(1-(3,4-bis(dodecyloxy)benzyl)-1*H*-1,2,3-triazol-4-yl)-1,3-phenylene)bis(1-(3,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyl)-1*H*-1,2,3-triazole) (1). Compound A-7 (0.68 g, 0.001 mol), B-4 (0.57 g, 0.0012 mol), NaASC (0.83 g, 0.0042 mol), and CuSO₄·5H₂O (0.52 g, 0.0021 mol) were dissolved in the mixture of 15 mL of THF and 1.5 mL of deionized water. The reaction mixture was stirred for 12 hours at room temperature. The solvent was removed by a rotary evaporator. The resulting mixture was extracted with chloroform and brine three times, and then dried over MgSO₄. After removing chloroform by a rotary evaporator, and the resulting mixture was purified by sequential silica gel column chromatographies (silica gel) from MC to MC:methanol = 20:1 solvent mixture as the eluents. A further purification using a HPLC yielded 1.02 g (65.0%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.19 (s, 3H, Ar-*H*), 7.82 (s, 3H, Ar-*H*), 6.94-6.84 (m, 9H, Ar-*H*), 5.47 (s, 6H, benzyl-*H*), 4.18-4.01 (m, 8H, OCH₂CH₂O), 4.01-3.90 (m, 4H, OCH₂CH₂CH₂), 3.90-3.45 (m, 40H, OCH₂CH₂(OCH₂CH₂)₂OCH₃), 3.34 (s, 12H, (OCH₂CH₂)₂OCH₃), 1.78 (m, 4H, OCH₂CH₂CH₂), 1.50-1.20 (m, 36H, OCH₂CH₂(CH₂)₉CH₃), 0.86 (t, 6H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₉CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 149.86, 149.69, 147.51, 131.81, 127.49, 126.72, 122.28, 121.82, 121.28, 120.20, 114.94, 114.07, 113.91, 72.04-69.0 (OCH₂), 59.10 (OCH₃), 54.47 (N-CH₂-Ph), 32.04, 29.82, 29.76, 29.57, 29.49, 26.17, 22.81, 14.24. M_w/M_n = 1.01 (GPC). Anal. Calcd for C₈₅H₁₃₁N₉O₁₈: C, 65.15; H, 8.43; N, 8.04. Found: C, 65.12; H, 8.44; N, 8.07.

Preparation of ionic samples (1-0.1 and 1-0.2). The ionic samples were prepared by mixing 0.2 g of amphiphile (1) with an appropriate volume of lithium

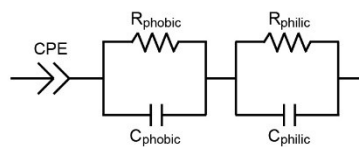
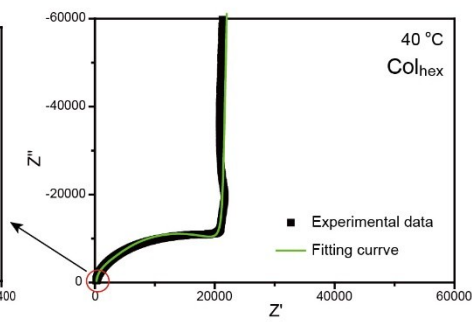
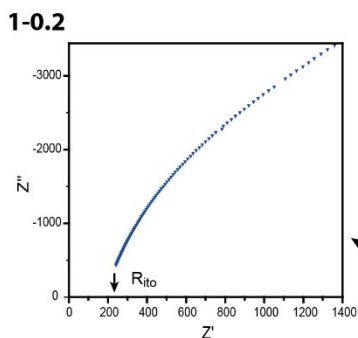
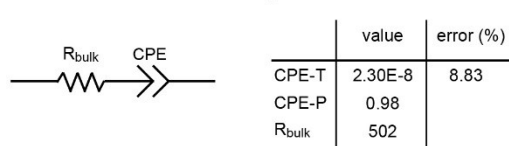
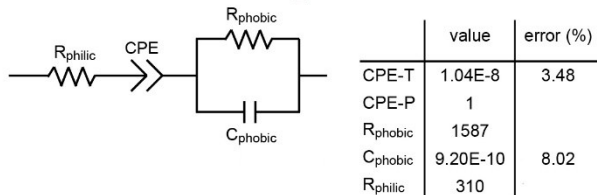
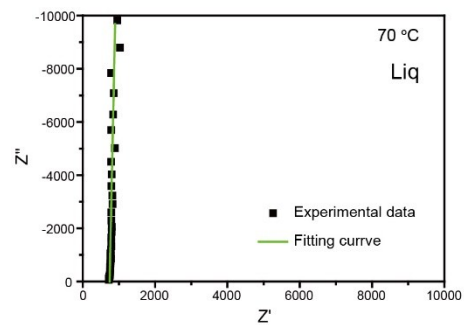
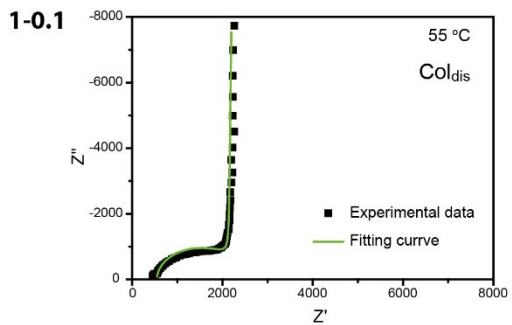
bis(trifluoromethane)sulfonimide (LiTFSI) solution (0.035 M in dry THF), followed by slow evaporation of the solvent under reduced pressure at room temperature. The samples were then dried in a vacuum oven at 110 °C for 24 hours to maintain constant mass.

Table S1. Preparation of ionic samples

	Amphiphile (1)	mol. of [EO]	LiTFSI solution (0.035 M)	[LiTFSI]/[EO]
1-0.1	0.2 g (0.13 mmol)	1.53 mmol	4.4 mL	0.1
1-0.2	0.2 g (0.13 mmol)	1.53 mmol	8.8 mL	0.2

Reference

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- (4) I. Kim, N.-E. Lee, Y.-J. Jeong, Y.-H. Chung, B.-K. Cho and E. Lee, *Chem. Commun.*, 2014, **50**, 14006-14009.
- (5) J.-W. Choi, M.-H. Ryu, E. Lee and B.-K. Cho, *Chem. Eur. J.*, 2010, **16**, 9006-9009.
- (6) S. Park, M.-H. Ryu, T. J. Shin and B.-K. Cho, *Soft Matter*, 2014, **10**, 5804-5809.



	value	error (%)
CPE-T	9.32E-9	2.37
CPE-P	0.99	0.30
R _{phobic}	17584	0.46
C _{phobic}	8.04E-10	1.13
R _{philic}	3525	2.25
C _{philic}	6.96E-10	0.94

In this magnified graph, the Z' at zero Z'' is the resistance value (R_{ito}) of the ITO cell. To simplify the equivalent circuit the R_{ito} is omitted in the simulation.

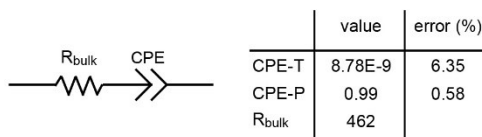
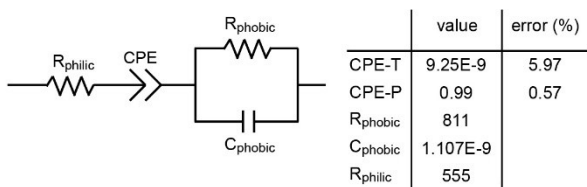
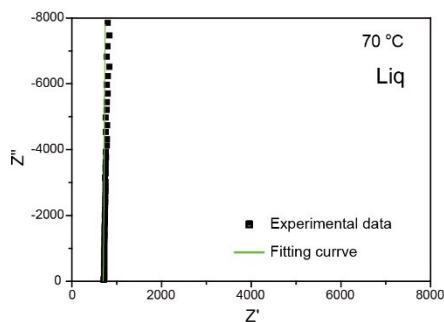
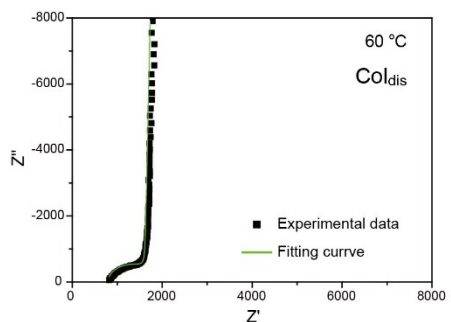


Fig. S1 Fitted impedance data using the Z-view2 simulation program.