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Electronic Supplementary Information (ESI)

Zwitterionic liquid crystals as 1D and 3D lithium ion transport media

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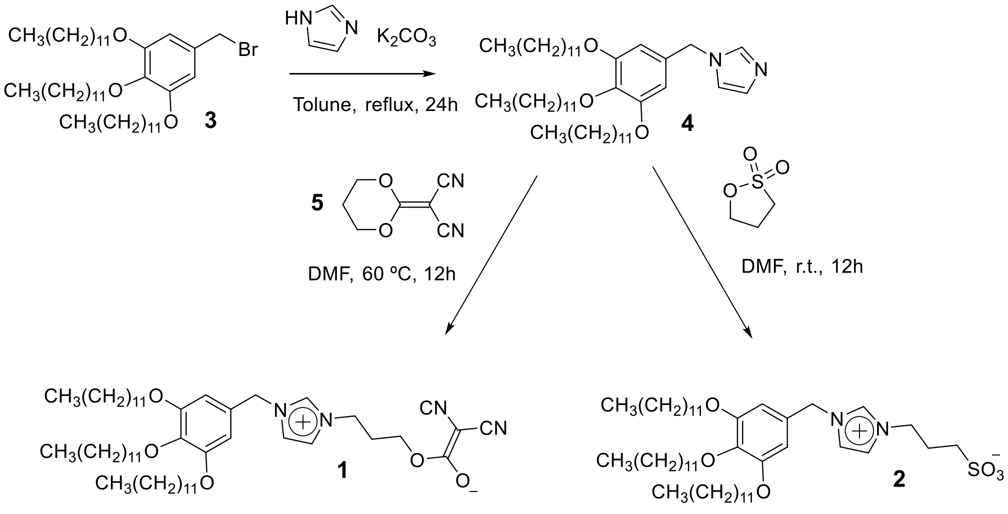
Table of contents:

1. Materials and methods

Liquid-crystalline phases were characterized with an Olympus BH-51 optical polarizing microscope equipped with a Mettler FP82HT hot-stage. Differential scanning calorimetry (DSC) measurements were conducted with a NETZCH DSC 204 Phoenix system at a cooling rate of 10 °C/min. Thermogravimetric analyses were measured with a Rigaku TG-DTA-8120. NMR spectra were recorded using a JEOL JNM-LA400 at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 155 MHz for ^{7}Li NMR. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to internal standard Me_4Si ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.00$) respectively, and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Chemical shifts of ^{7}Li NMR signals were quoted to internal standard LiCl ($\delta = 0.00$) in D_2O. Elemental analyses were carried out on an Exeter Analytical Inc. CE-440 Elemental Analyzer. X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2500 diffractmeter with a heating stage using Ni-filtered CuKα radiation. Mass spectra were obtained with a PerSeptive Biosystems Voyager-DE STR spectrometer. Ionic conductivities as a function of temperature were measured at the heating rate of 2 °C/min by an alternating current impedance method using a HIOKI 3532-80 chemical impedance meter (frequency range: 100 Hz–1 MHz, applied voltage: 0.3 V) and a hot-stage. Ionic conductivity was calculated to be the product of 1/resistance (Ω^{-1}) times cell constant (cm^{-1}). IR spectra were recorded by FT-IR reflection using a JASCO IRT-5000 Intron Infrared Microscope connected to a JASCO FT/IR-6100 Fourier Transform Infrared Spectrometer.

Lithium bis(trifluoromethanesulfonyl)imide with a purity of 99.9 % was purchased from Kishida Chemical and used as received. All the other reagents of the highest quality were purchased from Aldrich, Kanto, Tokyo Kasei, and Wako, and were used as received. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in a dry solvent purchased from Kanto.

2. Synthetic procedures



Scheme S1. Synthetic procedures for compounds **1** and **2.**

Compound **3**[S1] and compound **5**[S2] were synthesized according to the previously described methods.

Compound **4***:* Compound **3** (1.22 g, 1.68 mmol), imidazole (0.45 g, 6.74 mmol) and K_2CO_3 (0.93 g, 6.74 mmol) were suspended in 40 mL of toluene and the mixture was refluxed for a period of 24 h. The solvent was removed by rotatory evaporation. The solid was treated with 100 mL of water and extracted with chloroform (20 mL, 3 times). The organics were collected and dried over $MgSO_4$. After filtration the solvent was evaporated. Recrystallization of the residue from MeOH/EtOAc affords compound **4** as a white solid (0.9 g, 1.26 mmol, 75 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, 1H; ImH), 7.08 (s, 1H; ImH), 6.90 (s, 1H; ImH), 6.30 (s, 2H; ArH), 5.00 (s, 2H; CH_2), 3.90 (m, 6H; CH_2), 1.76 (m, 6H; CH_2), 1.44 (m, 6H; CH_2), 1.28 (m, 48 H; CH_2), 0.89 (t, *J* = 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 137.5, 129.8, 119.4, 105.85, 7.5, 69.3, 51.1, 32.0, 30.4, 29.8, 29.7, 29.5, 26.1, 22.8, 14.2; Elemental analysis calcd. for $C_{46}H_{82}N_2O_3$: C 77.69, H 11.62, N 3.94; found: C 77.81, H 11.93, N 3.81.

Compound 1: Compound **4** (0.20 g, 0.28 mmol) and dicyanoketene propylene acetal **5** (0.07 g, 1.65 mmol) were suspended in 5 mL of DMF. The mixture was stirred at 60 ºC for 12 h. The solvent was removed by rotatory evaporation. The residue was purified by silica gel chromatography with $CHCl_3$/MeOH (9/1) and recrystallization from ethyl acetate to yield compound **1** as a white solid (0.10 g, 0.12 mmol, 42 %). Compound **1** was dried under vacuum at 80 ºC for 12 h before use.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.52 (s, 1H; ImH), 7.17 (s, 1H; ImH), 7.17 (s, 1H; ImH) 6.63 (s, 2H; ArH), 5.39 (s, 2H; CH_2), 4.49 (t, *J* = 5.2 Hz, 4H; CH_2), 4.29 (t, *J* =5.2, 2H; CH_2), 3.94(m, 9H; CH_2), 2.22 (m, 2H; CH_2), 1.74 (m, 6H; CH_2), 1.44 (m, 6H; CH_2), 1.29-1.25 (m, 48 H; CH_2), 0.88 (t, *J*= 6.4 Hz, 9H; CH_3) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 153.9, 139.0, 136.9, 127.6, 123.3, 122.5, 121.6, 121.3, 107.6, 73.5, 69.4, 61.9, 54.1, 49.3, 32.0, 29.8, 29.7, 29.5, 26.2, 22.8, 14.2; Elemental analysis calcd. for $C_{53}H_{88}N_4O_5$: C 73.91, H 10.30, N 6.50; found: C 73.80, H 10.37, N 6.64.

Compound 2: Compound **4** (0.24 g, 0.37 mmol) and propanesultone (0.18 g, 1.48 mmol) were suspended in 5 mL of DMF. The mixture was stirred at room temperature for 12 h. The solvent was removed by rotatory evaporation. The residue was purified by silica gel chromatography with $CHCl_3$/MeOH (9/1) and recrystallization from ethyl acetate to give compound **2** as a white solid (0.10 g, 0.12 mmol, 32 %). Compound **2** was dried under vacuum at 80 ºC for 12 h before use.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H; ImH), 7.25 (s, 1H; ImH), 7.01 (s, 1H; ImH) 6.58 (s, 2H; ArH), 5.33 (s, 2H; CH_2), 4.58 (t, *J* = 6.8 Hz, 4H; CH_2), 3.94(m, 9H; CH_2), 2.91 (t, *J* = 6.4, 2H; CH_2), 2.43 (m, 2H; CH_2), 1.70 (m, 6H; CH_2), 1.44 (m, 6H; CH_2), 1.29-1.25 (m, 48 H; CH_2), 0.88 (t, *J* = 7.2 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0, 139.1, 138.2, 127.3, 121.7, 121.2, 107.7, 73.5, 69.5, 54.2, 48.8, 47.1, 32.0, 30.4, 29.8, 29.8, 29.6, 29.5, 26.4, 26.2, 22.8, 14.2; Elemental analysis calcd. for $C_{49}H_{88}N_2O_6S$: C 70.63, H 10.64, N 3.36; found: C 70.53, H 10.94, N 3.61.

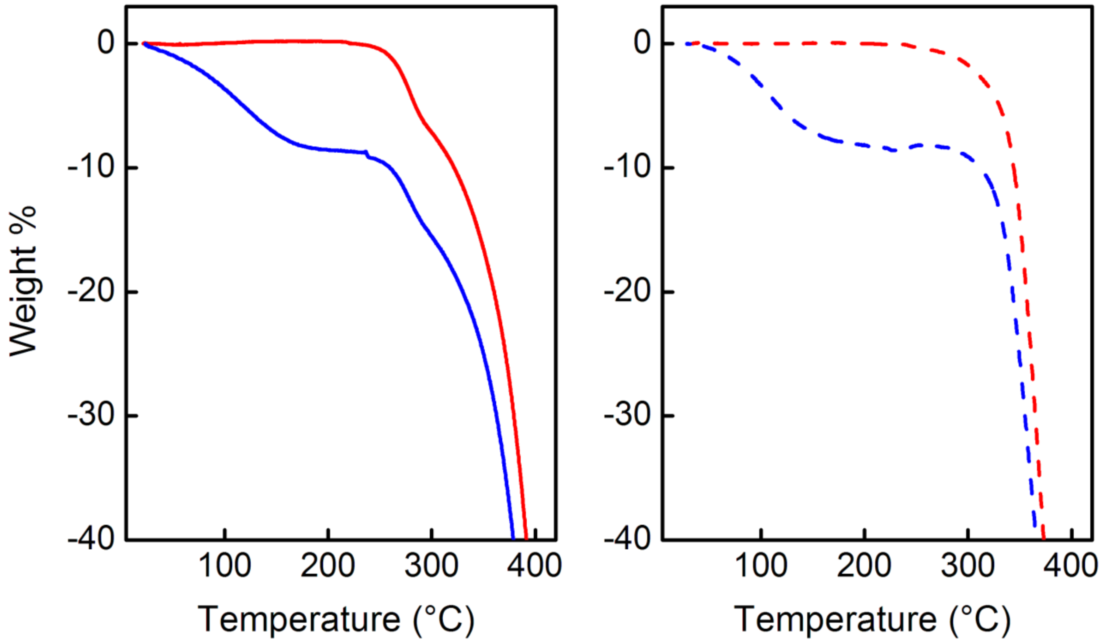


Fig S1. Thermogravimetric analysis charts of **1**/**Li**$^+$(20) (red solid line), **1**/**Li**$^+$(20)**PC**(10) (blue solid line) shown in the left graph and those of **2**/**Li**$^+$(20) (red dashed line) and **2**/**Li**$^+$(20)**PC**(10) (blue dashed line) shown in the right figure. The measurements were recorded with a continuous flow of N_2.

3. Liquid-crystalline properties

Table S1. Liquid-crystalline behaviour of the zwitterions (**1** and **2**) and their mixtures with LiTFSI (**1/Li**$^+$(x) and **2/Li**$^+$(x)).

Sample	mol% of TFSI	Phase transition behavior[a]
1	0	Col$_h$ 190 Decomp.
1/Li$^+$(10)	10	Col$_h$ 190 Decomp.
1/Li$^+$(20)	20	Col$_h$ 190 Decomp.
1/Li$^+$(30)	30	Col$_h$ 190 Decomp.
1/Li$^+$(40)	40	Col$_h$ 190 Decomp.
1/Li$^+$(50)	50	Cub$_{bi}$ (65-88) Col$_h$ 190 Decomp.
2	0	Col$_h$ 200 Decomp.
2/Li$^+$(10)	10	Col$_h$ 200 Decomp.
2/Li$^+$(20)	20	Col$_h$ 200 Decomp.
2/Li$^+$(30)	30	Col$_h$ 200 Decomp.
2/Li$^+$(40)	40	Col$_h$ 200 Decomp.
2/Li$^+$(50)	50	Col$_h$ 200 Decomp.

[a] Examined by polarizing optical microscope and X-ray diffraction. The phase transition temperatures were determined on heating processes (5 °C min^{-1}) from 25 °C to decomposition or isotropization temperature of the sample. The transition temperatures were taken at the starting points where the phase transitions occur. In the case of slow phase transition, a temperature range is given. Mixtures containing more than 50 mol% of LiTFSI show no homogeneous LC phases. Col$_h$: columnar hexagonal, Cub$_{bi}$: bicontinuous cubic, Iso: isotropic phases, Decomp.: decomposition.

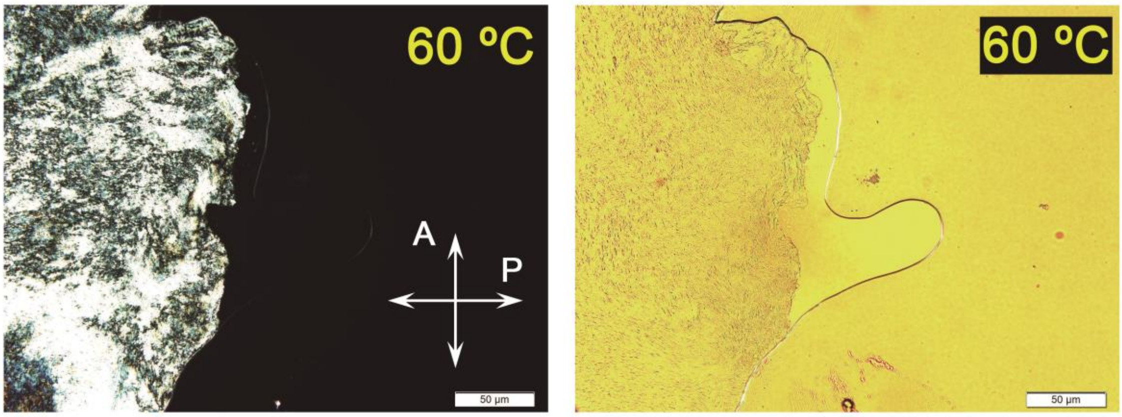


Fig. S2. Polarizing optical microscope (left) and optical microscope (right) images of **1/Li**$^+$(20)**PC**(15) at 60 °C. The mixture shows biphasic behavior.

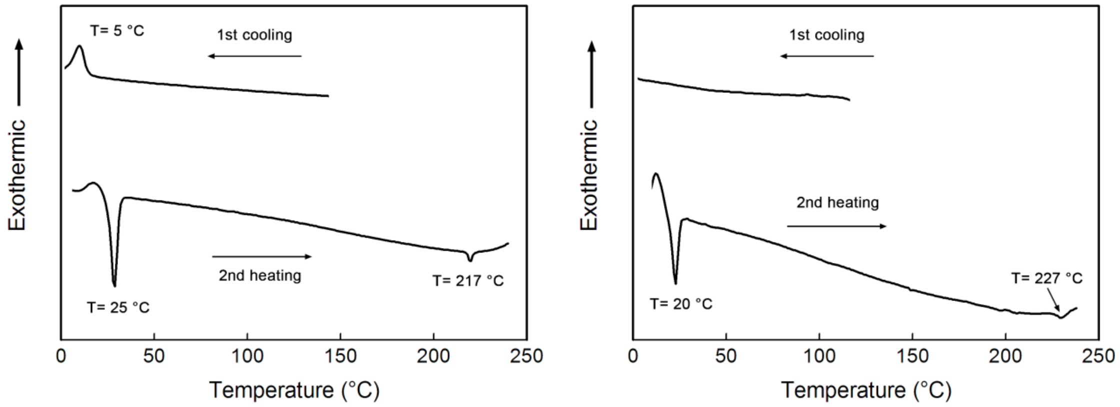


Fig. S3. Differential scanning calorimetry traces of compound **1** (left) and **1/Li**$^+$(50) (right).

The XRD analysis (Fig. 4 in the main text) and POM observation (Fig. 5 in the main text) of **1/Li**$^+$(50) confirmed the formation of a Cub$_{bi}$ phase from RT to 65 ºC at which the transition to Col$_h$ phase starts. However, no transition peak showing the Col$_h$-Cub$_{bi}$ transition for **1/Li**$^+$(50) is detected in the DSC chart (Fig S3 right).

Compound **1** and the mixture **1/Li**$^+$(50) show small DSC peaks at 217 and 227 °C on the heating process (Fig. S3), which are probably due to the decomposition of samples. The POM observations reveal that the thermal decompositions of **1** and **2** take place around at 190 and 200 °C respectively, accompanied by the color change from colorless to yellow.

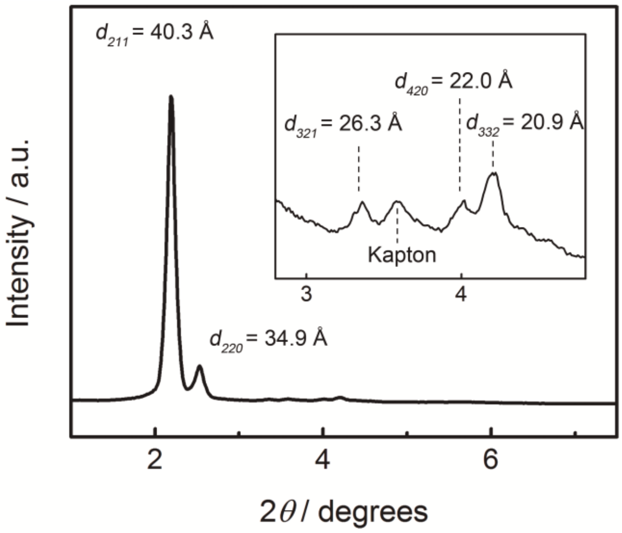


Fig. S4. X-ray diffraction pattern of **1/Li**$^+$(50)**PC**(10) at 60 ºC, which can be assigned to the LC Cub$_{bi}$ phase.

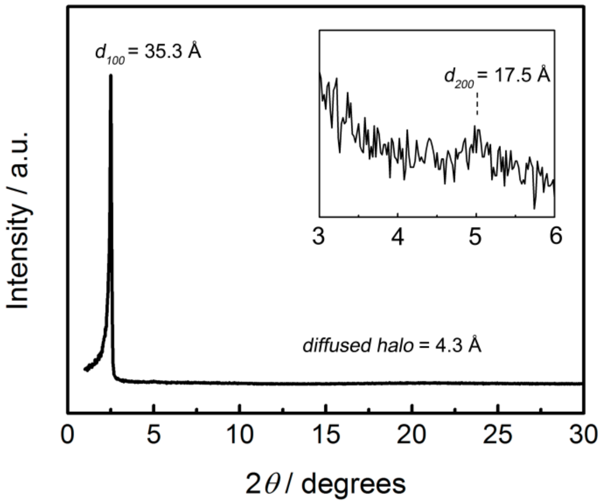


Fig. S5. X-ray diffraction pattern of **2** at 100 ºC, which can be assigned to the LC Col$_h$ phase.

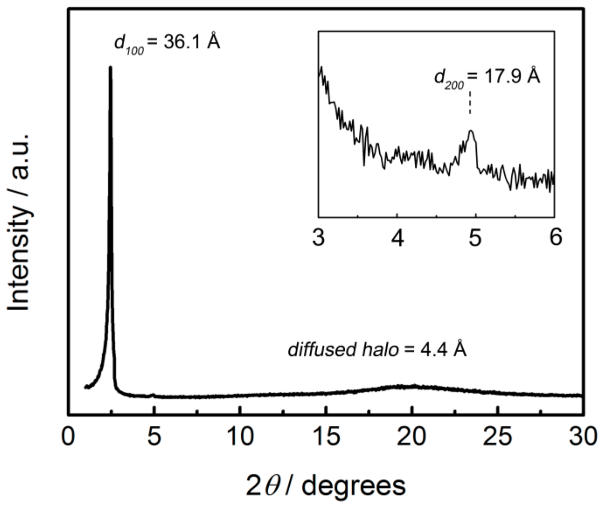


Fig. S6. X-ray diffraction pattern of **2/Li**$^+$(50) in the columnar phase at 100 ºC.

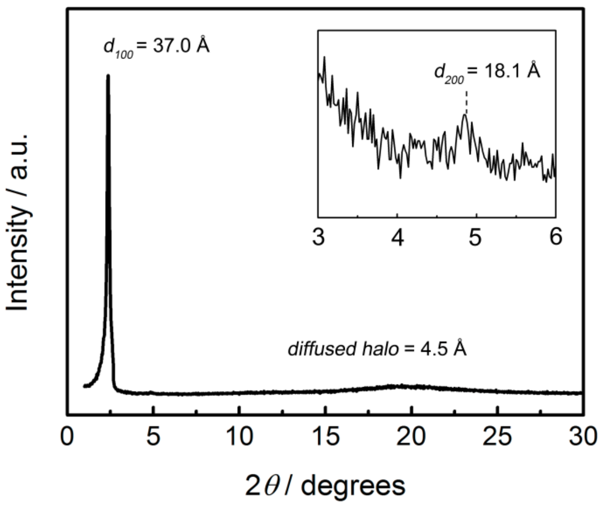


Fig. S7. X-ray diffraction pattern of **2/Li**$^+$(50) **PC**(10) in the columnar phase at 100 ºC.

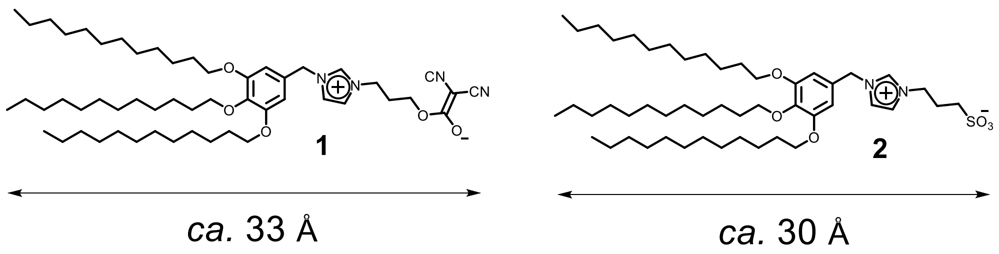


Fig. S8. Molecular structures of compounds **1** and **2** and their molecular length in the extended conformation estimated by MM2 calculations.

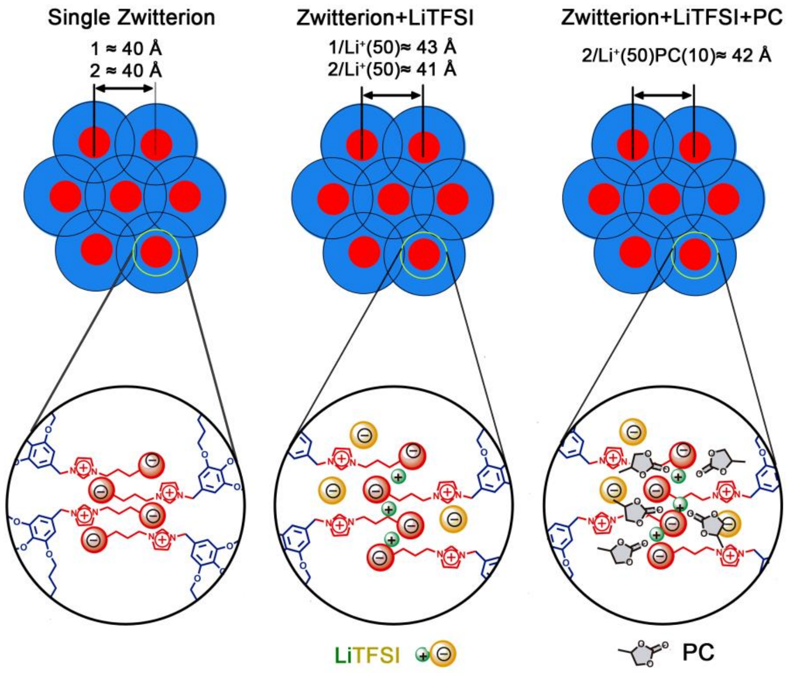


Fig. S9. Schematic representation of the self-assembled structures in the $\mathrm{Col_h}$ phases for zwitterionic compounds (**1** and **2**), their mixtures with LiTFSI and tertiary mixtures of zwitterions/LiTFSI/PC.

Intercolumnar distance "a" of the $\mathrm{Col_h}$ phases was calculated from the following equation: $a = 2\langle d_{100}\rangle/\sqrt{3}$, where $\langle d_{100}\rangle = (d_{100}+\sqrt{3}\ d_{110}+2\ d_{200})/3$. The number of molecules per columnar slice (n) was estimated to be 4.6 for **1** and 4.3 for **2** in the $\mathrm{Col_h}$ phases from the calculation using the following equation: $n = \sqrt{3}N_A a2h\rho/2M$, where N_A is Avogadro's number (6.02×10^{23} mol^{-1}), a is the intercolumnar distance, h is the layer thickness, and M is molecular weight. The density (ρ) of the material is approximated to be1.0 g cm^{-3}. The value of h has been taken from the halo of XRD pattern.[S3]

The unit cell distance "a" of the $\mathrm{Cub_{bi}}$ phases was calculated from the d_{211} and d_{220} lattices by using the following equation: $a = d_{hkl}\ \sqrt{h^2+k^2+l^2}$. The average value of a is given in the table 2.

4. NMR experiments

All the ^{7}Li NMR experiments were recorded by using LiCl in D_2O (0.05 M) as internal standard in a coaxial tube. The lithium signal of this solution was used as reference and set at 0 ppm. ^{7}Li NMR spectra of LiTFSI (0.013 M, 450 μL) and LiTFSI/Zwitterion (0.013 M of LiTFSI/0.020 M of **1** or **2**, the total volume 450 μL) were recorded in $CDCl_3$:THF 6:1 v:v solution. The effect of PC was examined after the addition of the appropriate amount of PC to the LiTFSI/zwitterion solutions by using a micropipette. All the experiments were conducted at RT.

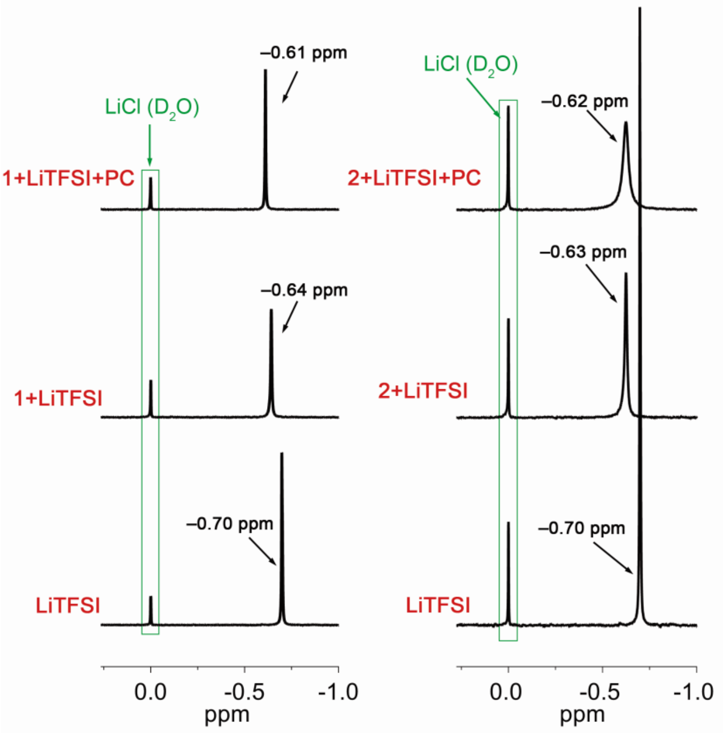


Fig. S10 ^{7}Li NMR stacked spectra of LiTFSI (0.013 M, 450 μL) (left and right bottom), **1**/LiTFSI (0.020 M/0.013 M, 450 μL) (left middle), **2**/LiTFSI (0.020 M/0.013 M, 450 μL) (right middle), **1**/LiTFSI/PC (0.020 M/0.013 M/0.13 M, 450 μL) (top left) and **2**/LiTFSI/PC (0.020 M/0.013 M/0.13 M, 450 μL) (top right). All the spectra were recorded in $CDCl_3$:THF 6:1 solution using LiCl in D_2O (0.05 M) as internal standard in a coaxial tube. Green box indicates the LiCl signal in D_2O which was set at 0 ppm.

5. IR experiments

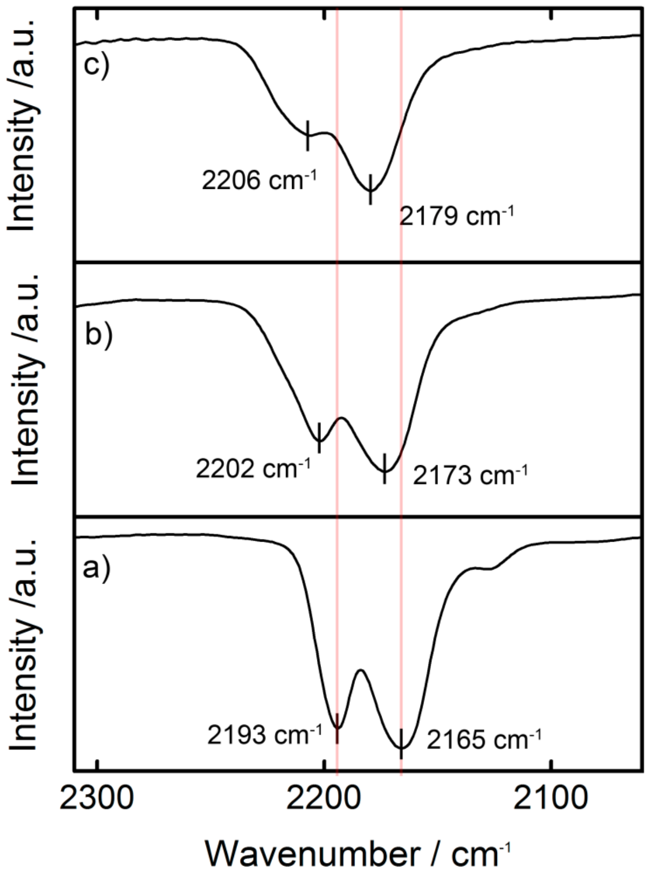


Fig. S11 Infrared stacked spectra of a) **1**, b) **1/Li**$^+$(50) and c) **1/Li**$^+$(50)**PC**(10). Red lines indicate the positions of the IR vibrations of the two nitrile groups for compound **1**.

6. Ionic conductivities measurements

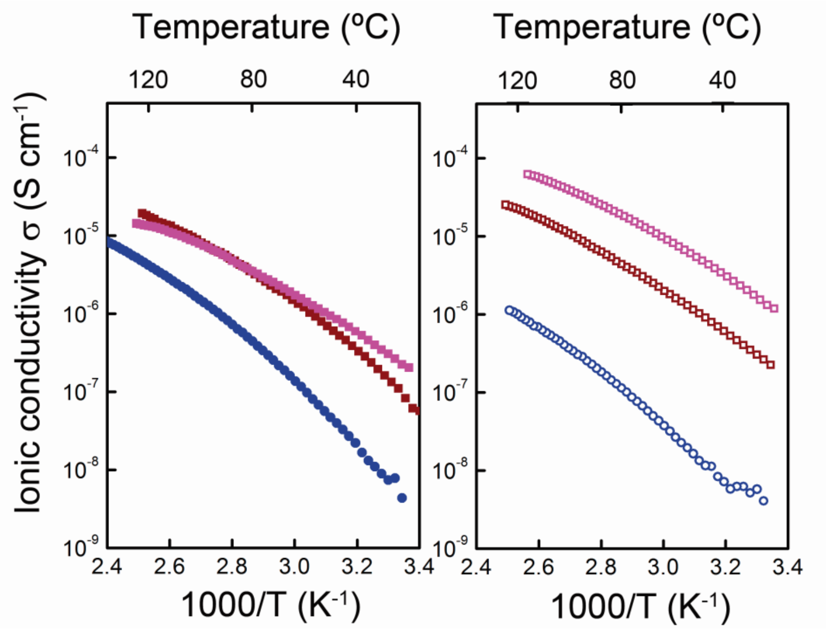


Fig. S12 Ionic conductivities as a function of the temperature of **1/Li**$^+$(20) (left, filled symbols) and **2/Li**$^+$(20) (right, empty symbols) with 0 (blue) 5 (brown) and 10 (pink) wt% of PC.

The activation energies of the ionic conductivity (*Ea*) were calculated from the slope of the ionic conductivities as function of temperature by using the Arrhenius equation: $k = Ae^{(-Ea/RT)}$ where *A* is the prefactor, *k* is the ionic conductivity, *R* is the gas constant and *T* is temperature.

7. References

S1 K. Tanabe, T. Yasuda, M. Yoshio and T. Kato, *Org. Lett.*, 2007, **9**, 4271–4274.
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S3 V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2001, **123**, 1302–1315.