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

Bartolome Soberats, a,b Masafumi Yoshio, * a Takahiro Ichikawa, † Hiroyuki Ohno, ‡ and Takashi Kato* a,b

We describe the development of self-assembled one- and three-dimensional lithium ion conductors composed of zwitterionic liquid crystals, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and propylene carbonate (PC). Two types of wedge-shaped zwitterions based on imidazolium dicyanoethenolate and sulfonate were synthesized. These compounds alone show liquid-crystalline (LC) columnar hexagonal (Col h) phases and low ionic conductivities (10−6−10−7 S cm−1). The increase in the ionic conductivities was achieved by the addition of LiTFSI (10−5 S cm−1) followed by that of PC (10−4 S cm−1). Moreover, LC bicontinuous cubic (Cub b) phases are induced by tuning the ionic nature of the zwitterionic liquid crystal with the ratio of LiTFSI and PC. The dissociation of LiTFSI in the zwitterions and the ion-dipole interaction between the lithium ion and PC are shown to be significant keys for the enhancement of the conductivities and stabilization of the nanosegregated LC structures.

Introduction

Construction of supramolecular nanostructures with diverse functionalities using molecular self-assembly is of increasing interest for emerging nanotechnologies.1−19 An important challenge is to build nanochannels capable of ion transport.21−44 The use of liquid-crystalline (LC) self-assembly is a promising approach for the development of nanochannels with various dimensions and enhanced ion transport function.30−46 Recently, LC ion-conductive materials has been applied to energy devices, such as lithium ion batteries and dye-sensitized solar cells.27−50 Among the LC organizations, thermotropic LC bicontinuous cubic (Cub b) assemblies attracted considerable attention because they form three-dimensionally interconnected ionic channels suitable for ion transport.34,38,44−46 However, the design of three-dimensional (3D) ion-conductive thermotropic LC materials is still challenging because the formation of Cub b phases requires a delicate balance of volume and interactions between the polar and the non-polar parts in the material.44 One of the approaches for induction of functional thermotropic Cub b phases is the use of two-component assemblies.31−54 For example, we achieved 3D proton transport in the Cub b phases formed by complexation of zwitterionic molecules and organic acids.52,53 The acid dissociates in the presence of zwitterions, which enables the proton transport. Interestingly, the proton conductivity and LC behavior are tuned by the amount of acid and also by the further addition of water.53 LC Cub b phases were also induced for the complexes of a pyridinium-based zwitterions and lithium salts, although their ionic conductivities were not examined.54 Anhydrous 3D lithium ion transport was previously achieved in LC materials by mixing lithium salts and ionic molecules.31,55 For example, we developed nanostructured polymer electrolytes upon photo-crosslinking of thermotropic LC Cub b assemblies composed of wedge-shaped ammonium salt and a lithium salt.55 Gin and co-workers also reported LC Cub b polymer electrolytes based on the lyotropic LC assemblies of a polymerizable lithium sulfonate and a dilute LiClO4 solution in propylene carbonate (PC).51 These approaches are based on the solubilization of lithium ions in nanostructured channels. However, we consider that the dissociation of lithium salts in zwitterionic LC media is a promising strategy for the development of lithium ion transport materials with induced Cub b phases.

Herein we report on the development of one-dimensional (1D) and 3D lithium ion transport channels (Fig. 1). We designed and prepared imidazolium-type zwitterions 1 and 2 (Fig. 2) to co-assemble with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and PC forming well-defined ionic pathways capable of the lithium ion transport. Zwitterionic liquid crystals tethering charge-delocalized anions are expected to form well-defined ionic channels, but have no transportable ions (Fig. 1, left). After addition of a lithium salt, the salt may be dissociated by the interactions with zwitterionic moieties, which allows lithium to move along the ionic pathways (Fig. 1 middle). At the same time, our intention is to increase the lithium ion mobility by the incorporation of PC as a polar additive (Fig. 1, right).31 It is expected that the optimization of the ratio of additives, lithium salt and PC, can induce Cub b phases and enhance the ionic conductivities (Fig. 1).
Results and discussion

Material design

Wedge-shaped zwitterions 1 and 2 (Fig. 2) are designed to act as LC ion transport media. The ionic parts of 1 and 2 consist of an imidazolium moiety tethering a dicyanoethenolate anion or sulfonate anion through a propylene spacer. We expected that compounds 1 and 2 would show different LC phase transition behavior and ion transport properties due to the differences in size of the anions and in the distribution of negative charges. LiTFSI (Fig. 2) is chosen as a lithium ion source because of its thermal stability and high delocalization of negative charge.\(^{35,54,61}\) Ohno and coworkers previously reported that the equimolar mixtures of an imidazolium-based sulfobetaine whose melting point is over 100 °C and lithium salts (LiTFSI, LiOSO\(_2\)CF\(_3\), LiBF\(_4\), and LiClO\(_4\)) become room temperature ionic liquids.\(^{62}\) Among them, the LiTFSI complex gives the lowest glass transition temperature and exhibits the highest ionic conductivity.\(^{62}\) Lin and coworkers reported that the mixtures of imidazolium-type carboxylates or sulfonates and LiTFSI form smectic A phases exhibiting ionic conductivities.\(^{63,64}\) In addition, the employment of bulky LiTFSI as an additive for zwitterionic liquid crystals, can induce the structural change of LC phases because of the change of the molecular shapes and volume balance between the polar and nonpolar parts.\(^{35,54}\) Thus we considered that the complexation of 1 or 2 and LiTFSI would lead to the development of 3D lithium ion conductive materials exhibiting Cubi LC phases. Furthermore, to enhance the dissociation of lithium ion in the zwitterionic transport media, PC (Fig. 2) is used as a polar additive because the carbonyl group of PC has the ability to coordinate to lithium ions.\(^{31,40,48,65}\)

Supramolecular interactions between components

In order to examine the interactions between lithium ion, zwitterion, and PC, \(^{7}\)Li NMR measurements of LiTFSI, the mixture of 1 and LiTFSI and tertiary mixture of LiTFSI, 1 and PC were conducted in the CDCl\(_3\)/THF-d\(_6\) solutions using LiCl in D\(_2\)O as an internal standard (Fig. 3). The results for 2 are shown in the ESI† (Fig. S10). The \(^{7}\)Li chemical shift of LiTFSI shows a downfield shift of 0.06 ppm in the presence of 1 (Fig. 3, middle). This result suggests the formation of a complex between 1 and LiTFSI, where the lithium ion may interact with the dicyanoethenolate anion (Fig. 1 top middle and Fig. S9).\(^{65,66}\) The addition of PC to the mixture of 1 and LiTFSI induces a further downfield shift of 0.03 ppm (Fig. 3,
top) compared to the chemical shift for the mixture of 1 and LiTFSI (Fig. 3, middle). This shift may be attributed to the ion-dipole interactions between lithium ions and PC. It should be mentioned that the stepwise downshifts of $^{7}$Li signal are detected by the addition of zwitterions followed by PC, in spite of the presence of THF which is a competitive solvent.

The interactions between 1, LiTFSI and PC were also confirmed by IR measurements in the bulk state. The IR spectra of 1, the mixture of 1 and LiTFSI and tertiary mixture of 1, LiTFSI and PC were recorded at room temperature (Fig. S11). Single compound 1 shows two absorption bands at 2193 and 2165 cm$^{-1}$ which are characteristic of the C$\equiv$N vibrations of the dicyanoethenolate moiety.52 These bands are shifted to 2202 and 2173 cm$^{-1}$, respectively, after the addition of 50 mol% of LiTFSI. Further addition of 10 wt% of PC resulted in the high wavenumber shift of CN bands to 2206 and 2179 cm$^{-1}$, respectively. These results suggest the existence of interactions between zwitterionic molecule, LiTFSI and PC.

Liquid-crystalline properties

Compounds 1 and 2 show LC columnar hexagonal (Col$\alpha$) phases from room temperature to around 200 °C at which decomposition occurs (Table 1 and Table S1). Mixtures of the zwitterions with LiTFSI [1/Li$^{+}(x)$ and 2/Li$^{+}(x)$, x denotes the mol% of LiTFSI] were prepared by mixing the THF solutions of LiTFSI and the zwitterions, followed by the evaporation of the solvent to yield the anhydrous mixtures as white solids. The liquid crystallinity of the 1/Li$^{+}(x)$ and 2/Li$^{+}(x)$ mixtures was examined by a polarizing optical microscope (POM), X-ray diffraction (XRD) and differential scanning calorimetry. The mixtures 1/Li$^{+}(x)$ with 10-40 mol% of LiTFSI and all the mixtures 2/Li$^{+}(x)$ exhibit only Col$\alpha$ phases (Table 1 and Table S1).7 As for 1/Li$^{+}(50)$, the Cub$\alpha$ phase is induced in addition to the formation of Col$\alpha$ phase. The Cub$\alpha$ phase is observed from room temperature to 65 °C and slowly changed to the Col$\alpha$ phase between 65 and 88 °C under POM observation on the heating rate of 5 °C min$^{-1}$. The formation of ionic pairs composed of ionic liquid-like imidazolium TFSI and lithium dicyanoethenate, which is bulkier than lithium sulfonate, may disturb the columnar packing.7,55 The change in the volume fraction of the polar and nonpolar parts may also contribute to the induction of the Cub$\alpha$ phase.7,55 Figures 4 and 5 show the XRD patterns and POM images of 1/Li$^{+}(50)$ in the Cub$\alpha$ and Col$\alpha$ phases. The small-angle XRD pattern of 1/Li$^{+}(50)$ at 55 °C (Fig. 4a) shows two strong and three weak peaks at 39.2, 34.0, 25.7, 21.4 and 20.4 Å corresponding to the (211), (220), (321), (420) and (332) reflections, respectively. The reciprocal d-spacing ratio of these peaks is $\upsilon_{6}:\upsilon_{8}:\upsilon_{14}:\upsilon_{20}:\upsilon_{22}$, which corresponds to a Cub$\alpha$ phase with an Ia3d symmetry. In contrast, the wide-angle XRD pattern of 1/Li$^{+}(50)$ at 120 °C (Fig. 4b) shows the (100), (110) and (200) reflections, which are characteristic of a Col$\alpha$ phase. The POM image of 1/Li$^{+}(50)$ at 58 °C shows no birefringence (Fig. 5a), indicating the formation of a Cub$\alpha$ phase. On heating the sample to 90 °C (Fig. 5b), a birefringence upon the formation of the Col$\alpha$ phase with polydomain organization is observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase transition behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Col$\alpha$ 217 Decomp.</td>
</tr>
<tr>
<td>1/Li$^{+}(20)$</td>
<td>Col$\alpha$ 190 Decomp.</td>
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<tr>
<td>1/Li$^{+}(50)$, Col$\alpha$ 65-88</td>
<td>Col$\alpha$ 190 Decomp.</td>
</tr>
<tr>
<td>1/Li$^{+}(20)$PC(5)</td>
<td>Col$\alpha$ 50-68, Col$\alpha$ 120°</td>
</tr>
<tr>
<td>1/Li$^{+}(20)$PC(10)</td>
<td>Col$\alpha$ 50-75, Col$\alpha$ 120°</td>
</tr>
<tr>
<td>1/Li$^{+}(50)$PC(5)</td>
<td>Col$\alpha$ 81-92, Iso</td>
</tr>
<tr>
<td>1/Li$^{+}(50)$PC(10)</td>
<td>Col$\alpha$ 74-86, Iso</td>
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</tbody>
</table>

<table>
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<th>Sample</th>
<th>Phase transition behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Col$\alpha$ 207 Decomp.</td>
</tr>
<tr>
<td>2/Li$^{+}(20)$</td>
<td>Col$\alpha$ 200 Decomp.</td>
</tr>
<tr>
<td>2/Li$^{+}(50)$</td>
<td>Col$\alpha$ 200 Decomp.</td>
</tr>
<tr>
<td>2/Li$^{+}(20)$PC(5)</td>
<td>Col$\alpha$ 120°</td>
</tr>
<tr>
<td>2/Li$^{+}(20)$PC(10)</td>
<td>Col$\alpha$ 120°</td>
</tr>
<tr>
<td>2/Li$^{+}(50)$PC(5)</td>
<td>Col$\alpha$ 120°</td>
</tr>
<tr>
<td>2/Li$^{+}(50)$PC(10)</td>
<td>Col$\alpha$ 120°</td>
</tr>
</tbody>
</table>

* Ratio of LiTFSI and PC is indicated as follows: 1/Li$^{+}(x)$, 2/Li$^{+}(x)$, 1/Li$^{+}(x)$PC(y) and 2/Li$^{+}(x)$PC(y), where x is the mol% of LiTFSI and y indicates the wt% of PC. Determined by polarizing optical microscope observation. The LC behavior was examined on heating processes (5 °C min$^{-1}$) from 25 °C to decomposition or isotropization temperature of the sample. The given transition temperatures correspond to the starting of the phase transitions. 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. Mixtures with 15 wt% or more of PC showed biphasic behavior. For PC containing samples, the microscopic observation was conducted up to 120 °C. All the mixtures showed decomposition at around 200 °C. Col$\alpha$: columnar hexagonal, Cub$\alpha$: bicontinuous cubic, Iso: isotropic, Decomp.: decomposition.
Compounds 1, 2 and the mixtures 1/Li\textsuperscript{+}(20), 1/Li\textsuperscript{+}(50), 2/Li\textsuperscript{+}(20) and 2/Li\textsuperscript{+}(50) were selected to study the effects of addition of PC. Compounds 1 and 2 show biphasic behavior after addition of 5 and 10 wt% of PC.\textsuperscript{2} In contrast, the mixtures 1/Li\textsuperscript{+}(x) and 2/Li\textsuperscript{+}(x) form homogenous LC mixtures upon the addition of 5 or 10 wt% of PC [1/Li\textsuperscript{+}(x)PC(y) and 2/Li\textsuperscript{+}(x)PC(y), y indicates the wt% of PC] (Table 1).\textsuperscript{4} These results suggest that LiTFSI is essential for the stabilization of the LC phases in the mixtures containing zwitterions 1 or 2 and PC. The mixtures of 2/Li\textsuperscript{+}(x)PC(y) show only Col\textsubscript{h} phases, but the mixtures based on 1/Li\textsuperscript{+}(x)PC(y) exhibit Cub\textsubscript{h}n LC phases (Table 1). This behavior also indicates that the interactions of dicyanoethenolate anion, lithium ion and PC play key roles in the induction of cubic phases. For example, 1/Li\textsuperscript{+}(20) shows only a Col\textsubscript{h} phase, but Cub\textsubscript{h}n phases are formed after addition of 5 or 10 wt% of PC (Table 1). Moreover, the cubic phase observed for 1/Li\textsuperscript{+}(50) is thermally stabilized up to 80 °C by adding PC (Table 1). Remarkably, as far as we know the use of PC for the induction or stabilization of Cub\textsubscript{h}n phases has not yet been reported.

In order to know more details about the structural organization of these complexes, we studied the XRD parameters of the LC phases of 1, 2, and the selected mixtures with LiTFSI and LiTFSI/PC. Table 2 displays the unit cell distances for the Cub\textsubscript{h}n phases and the intercolumnar distances for the Col\textsubscript{h} phases of the selected mixtures. Compounds 1 and 2 in the Col\textsubscript{h} phases show intercolumnar distances of 40 Å. The molecular lengths of 1 and 2 in the extended conformation are estimated to be 33 and 30 Å, respectively. Thus, these results suggest that these zwitterionic molecules self-assemble into well-packed Col\textsubscript{h} structures, where aliphatic chains and zwitterionic moieties are interdigitated (Fig. 1 and Fig. S9).\textsuperscript{51-54,60,63,64} The addition of 50 mol% of LiTFSI to 1 and 2 produces an increase in the intercolumnar distances (Table 2). In the case of 2/Li\textsuperscript{+}(50), the intercolumnar distance also increases upon the addition of 10 wt% of PC. Similar swelling is observed in the Cub\textsubscript{h}n phases of 1/Li\textsuperscript{+}(50) after the addition of 10 wt% of PC, where the unit cell distance increases 2.6 Å (Table 2). These results imply that the LiTFSI and PC are incorporated within the ionic channels by interacting with the zwitterionic moieties (Fig. 1, Fig. S8, Fig. S9 and Fig. S11).

![X-ray diffraction (XRD) patterns of 1/Li\textsuperscript{+}(50) at a) 55 °C and b) 120 °C. The mark * corresponds to the diffraction of the Kapton film.](image)

**Fig. 4** X-ray diffraction (XRD) patterns of 1/Li\textsuperscript{+}(50) at a) 55 °C and b) 120 °C. The mark * corresponds to the diffraction of the Kapton film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters (Å)</th>
<th>LC phase\textsuperscript{a}</th>
<th>Temperature (°C)</th>
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<tr>
<td>1</td>
<td>40.8</td>
<td>Col\textsubscript{h}</td>
<td>120</td>
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<tr>
<td>1/Li\textsuperscript{+}(50)</td>
<td>43.4</td>
<td>Col\textsubscript{h}</td>
<td>120</td>
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<tr>
<td>1/Li\textsuperscript{+}(50)</td>
<td>96.1</td>
<td>Cub\textsubscript{h}</td>
<td>55</td>
</tr>
<tr>
<td>1/Li\textsuperscript{+}(50)PC(10)</td>
<td>98.7</td>
<td>Cub\textsubscript{h}</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>40.4</td>
<td>Col\textsubscript{h}</td>
<td>100</td>
</tr>
<tr>
<td>2/Li\textsuperscript{+}(50)</td>
<td>41.3</td>
<td>Col\textsubscript{h}</td>
<td>100</td>
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<td>2/Li\textsuperscript{+}(50)PC(10)</td>
<td>42.2</td>
<td>Col\textsubscript{h}</td>
<td>100</td>
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</tbody>
</table>

\textsuperscript{a} Col\textsubscript{h}: columnar hexagonal; Cub\textsubscript{h}: bicontinuous cubic.

![Polarizing optical microscope (POM) images of 1/Li\textsuperscript{+}(50) at a) 58 °C and b) 90 °C. A: analyzer; P: polarizer.](image)

**Fig. 5** Polarizing optical microscope (POM) images of 1/Li\textsuperscript{+}(50) at a) 58 °C and b) 90 °C. A: analyzer; P: polarizer.
Ionic conductivities

The ionic conductivities of the zwitterions 1 and 2, and the mixtures 1/Li\(^{+}\)(x), 2/Li\(^{+}\)(x), 1/Li\(^{+}\)(x)PC(y) and 2/Li\(^{+}\)(x)PC(y) were measured as a function of temperature (Fig. 6, Fig. 7 and Fig. S12) by the alternating current impedance method.\(^{33}\) All the conductivities were measured on heating processes. Fig. 6 shows the ionic conductivities of the mixtures based on 1 (Fig. 6a) and 2 (Fig. 6b) containing 0 to 50 mol\% of LiTFSI. All samples are not aligned. The samples exhibiting the Col\(_h\) phases show polydomain textures under POM observation (Fig. 5b). The addition of LiTFSI to 1 and 2 significantly increase the ionic conductivities. This observation suggests that the presence of mobile species enhances the ionic conductivities in the systems. The ionic conductivities for 1/Li\(^{+}\)(x) and 2/Li\(^{+}\)(x) increase with increasing amount of LiTFSI. This enhancement is more significant for the 2/Li\(^{+}\)(x) mixtures than that for the 1/Li\(^{+}\)(x) mixtures. For example, the value of the ionic conductivity of 2 at 100 °C is 5 \times 10^{-8} S cm\(^{-1}\) while 2/Li\(^{+}\)(50) mixture shows the value of 6 \times 10^{-8} S cm\(^{-1}\). On the other hand, the addition of 50 mol\% of LiTFSI to 1 increases the conductivity from 1 \times 10^{-8} S cm\(^{-1}\) to 4 \times 10^{-7} S cm\(^{-1}\) at 100 °C. All the mixtures show a gradual increase in the ionic conductivity with the increase of temperature. Compound 1/Li\(^{+}\)(50) shows a change in the increasing trend of the ionic conductivities between 65 and 80 °C on heating (Fig. 6a), probably due to the slow Cub\(_{h}-\)Col\(_h\) phase transition.\(^{34,32}\)

It is noteworthy that the highest conductivities in the 1/Li\(^{+}\)(x) and 2/Li\(^{+}\)(x) series are obtained in the 1:1 mixtures (Fig. 6). Previous works on LC lithium ion transport materials used lower amounts of lithium salts.\(^{51,55,63,64}\) Generally, low lithium ion concentration in the electrolytes gives better ionic conductivities.\(^{67,68}\) For example, McFarlane and coworkers reported that for the binary mixtures of N-alkylmethylpyrrolidinium TFSI and LiTFSI the conductivity continued to increase by doping less than 30 mol\% of LiTFSI and further doping up to 50 mol\% of LiTFSI resulted in the decrease in the conductivity.\(^{68}\) It is assumed that in the present system the 1:1 mixtures form ionic liquid-like structures within the ionic channels, resulting in the increase of the ionic mobility.

Interestingly, the addition of PC to 1/Li\(^{+}\)(x) and 2/Li\(^{+}\)(x) leads to the enhancement of ionic conductivities (Fig. 7 and Fig. S12). The ionic conductivity of 1/Li\(^{+}\)(50) increases four times after the addition of 5 or 10 wt\% of PC (Fig. 7a). On the other hand, the stepwise increase in conductivities for 2/Li\(^{+}\)(50) is seen by adding 5 and 10 wt\% of PC (Fig. 7b). The highest ionic conductivities in the series are observed for 2/Li\(^{+}\)(50)PC(10). The value reaches 10^{-7} S cm\(^{-1}\) at around 100 °C.\(^{31}\)

The activation energies (E\(_a\)) of the ion conduction were estimated for 1/Li\(^{+}\)(50) and 1/Li\(^{+}\)(50)PC(10) in the Cub\(_{h}\) phases and for 2/Li\(^{+}\)(50) and 2/Li\(^{+}\)(50)PC(10) in the Col\(_h\) phases (ESI†). It was found that the E\(_a\) significantly decreased after the addition of PC to 1/Li\(^{+}\)(x) and 2/Li\(^{+}\)(x). For example, the value of E\(_a\) of 1/Li\(^{+}\)(50) in the Cub\(_{h}\) phase was 64 kJ mol\(^{-1}\), while that for 1/Li\(^{+}\)(50)PC(10) was 41 kJ mol\(^{-1}\). In the case of 2/Li\(^{+}\)(50) and 2/Li\(^{+}\)(50)PC(10) in the Col\(_h\) phase, the values are 38 kJ mol\(^{-1}\) and 23 kJ mol\(^{-1}\), respectively. These reductions in the E\(_a\) by the addition of PC were attributed to the weakening of the interactions between zwitterions and lithium ion upon the formation of ion-dipole interactions among the PC (Fig. 3). The formation of more mobile ionic channels would facilitate the transport of lithium ions.

Conclusions

We successfully developed 1D and 3D lithium ion transport LC materials by the co-assembly of a wedge-shaped zwitterion (1 or 2), LiTFSI and PC. LC zwitterions provide stable nanostructured media for the lithium ion transport and exhibit LC phases with up to 50 mol\% of LiTFSI and up to 10 wt\% of PC. The LC phases and ionic conductivities are tuned by the appropriate molecular design and changing the ratio of LiTFSI and PC. Remarkably, the supramolecular interactions between zwitterions, LiTFSI and PC are the key for the stabilization of LC phases and for the enhancement of conductivities. It is expected that the ionic conductivities may be further enhanced by increasing the PC fraction of the electrolyte materials. The system described here introduces important advances in the development of nanostructured lithium ion-conductive materials, and open new pathways for the
development of LC electrolytes that can be applied in energy devices.

Experimental

Synthesis and characterization of compounds 1 and 2 are described in the Electronic Supporting Information (ESI†)

Preparation of the mixtures

Compounds 1 and 2 were dried under vacuum at 80 °C for 12 h before their use. They showed no hygroscopic behavior in a period of days at ambient conditions. All the materials and solvents for the preparation of the mixtures were dried before use.

Mixtures 1/LiTFSI(x) and 2/LiTFSI(x) were prepared by adding the appropriate volume of a THF solution of LiTFSI (0.026 M) to a weighted amount of zwitterion 1 and 2 (10-30 mg) in a microtube. The solution was homogenised by sonication and then the solvent was slowly removed by rotatory evaporation. The samples were dried under vacuum at 80 °C for 12 h before their study. The presence of no volatiles was confirmed by thermogravimetric analyses (Fig. S1).

The mixtures 1/LiTFSI(x)PC(y) and 2/LiTFSI(x)PC(y) were prepared by adding the appropriate amount of PC to 1/LiTFSI(x), and 2/LiTFSI(x) respectively. The solid blend was homogenised by using a spatula and then heated to 50 °C for 5 min. These mixtures were prepared at ambient conditions in the laboratary (Humidity: 40-60 %). The presence of volatiles was monitored by thermogravimetric analyses (Fig. S1). The thermograms indicate no inclusion of volatile in the sample, but the loss of less than 1 wt% of the added PC during the sample preparation (Fig. S1).

Acknowledgements

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Notes and references

† Mixtures containing more than 50 mol% of LiTFSI show no homogeneous LC phases.
‡ The wt% of PC is given to the respect to the mass of zwitterion. 5 and 10 wt% of PC is roughly equivalent to 22 and 45 mol% of PC to the respect of zwitterion.
§ Mixtures 1/LiTFSI(x) and 2/LiTFSI(x) show biphasic behaviour after addition of 15 wt% or more of PC. Microscope images of a mixture exhibiting biphasic behavior are shown in Fig. S2.

¶ Thermogravimetric analyses of PC-containing mixtures indicate that the evaporation of PC under N2 flow starts below 100 °C. (Fig. S1). This evaporation is lower when the samples are sandwiched.

Electronic Supplementary Information (ESI) available: [Materials and methods, synthetic procedures, characterization of compounds, thermogravimetric analyses of the materials, liquid crystalline characterization experiments including XRD patterns and POM images, 1H NMR studies, IR spectra and supplementary ion conduction measurements. See DOI: 10.1039/b0060000xs/]
