

Room-Temperature Zwitterionic Liquid Crystals for Mechanical Actuators

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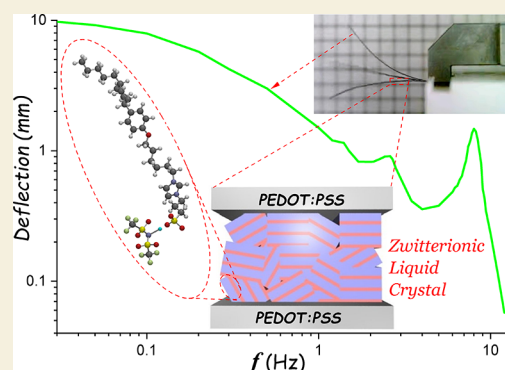


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ABSTRACT: We have developed room-temperature smectic liquid-crystalline (LC) ion conductors by the self-assembly of a zwitterionic mesogenic compound and a series of fluorinated lithium salts. The conductivity of lithium bis(trifluoromethylsulfonyl)imide LC complex reached $4 \times 10^{-3} \text{ S cm}^{-1}$ at ambient conditions. This LC complex sandwiched between two conductive polymer electrodes can be used in low-voltage mechanical actuators with a peak-to-peak bending deflection of ca. 20 mm upon $\pm 1 \text{ V}$, 0.03 Hz excitation.



KEYWORDS: liquid crystal, zwitterion, actuator, ionic conductivity, fluorinated lithium salt, ion channel

Fast ion transport in organic solid and semisolid matrices¹ is a key technological requirement for developing high-performance electrical energy storage and conversion devices such as lithium batteries and fuel cells. The design of ion pathways, such as self-assembled ion channels, has attracted significant interest as biomimicry in electronics. Liquid-crystalline (LC) molecules in self-organized fluid states are highly desirable for constructing ion transport pathways^{2,3} because their orientation can be controlled by external stimuli, and because their self-healable and viscoelastic properties can facilitate ionic transport and reduce the risk of short-circuit in electronic devices.

While supramolecular LC ion transporters were originally developed for battery electrolytes,⁴ new applications have emerged, such as actuators^{5,6} and vibrational electric generators.⁷ To realize these devices, a key issue is to fabricate self-standing and flexible LC polymer membranes exhibiting an ionic conductivity of at least $10^{-5} \text{ S cm}^{-1}$ at room temperature. Although such LC polymer electrolytes were obtained by *in situ* photopolymerization of a nematic LC monomer⁵ or an ionic columnar LC monomer⁶ containing an ionic liquid, the variety of such LC systems is very limited due to a macroscopic phase separation between the ionic liquid and the LC molecules or even a complete dissolution of the system. The design of specific interactions such as hydrogen bonds between the ionic liquids and LC molecules is a key to constructing a nanophase-segregated LC phase. This complication stimulated the development of an alternative design, where the organic ionic liquid is replaced by a solid inorganic salt. This approach is attractive for applications, but it requires highly conductive

room-temperature LC materials, which are challenging to produce. In this work, we report a series of smectic LC complexes comprising a zwitterionic mesogenic compound (ZI) and a fluorinated lithium salt (Figure 1). These LC complexes

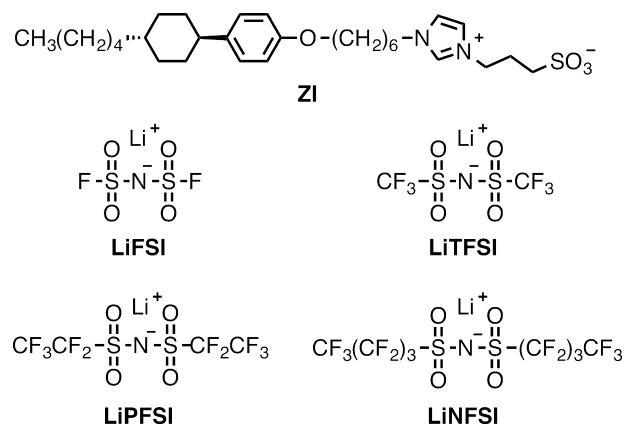


Figure 1. Molecular structures of a zwitterionic mesogenic molecule (ZI) and fluorinated lithium salts.

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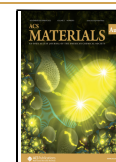


exhibit an electrical conductivity reaching $4 \times 10^{-3} \text{ S cm}^{-1}$ at ambient conditions. Due to the high conductivity, they can act as low-voltage mechanical actuators^{8,9} when sandwiched between two poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) films.

Compound ZI consists of an imidazolium propane sulfonate moieties attached to a cyclohexylbenzene group through a hexamethylene chain spacer to improve the structural rigidity of the molecule. It forms monotropic smectic A LC phases at room temperature after mixing with a series of commercial Li salts (Table 1), such as lithium bis(fluorosulfonyl)imide (LiFSI),

Table 1. Transition Temperature from Smectic A to Isotropic Liquid Phase, $T_{\text{LC-iso}}$; d -Spacing from the (001) Lattice Plane, d_{001} ; and Maximum Ionic Conductivity, σ

compd	$T_{\text{LC-iso}}/^\circ\text{C}^a$	d_{001}/nm	$\sigma/\text{S cm}^{-1}$
ZI	>220	4.5	$<10^{-9}$
ZI/LiFSI	85	4.1	4×10^{-3}
ZI/LiTFSI	83	4.1	4×10^{-3}
ZI/LiPFSI	66	4.1	10^{-6}
ZI/LiNFSI	42	4.1	10^{-7}

^aTransition temperature taken at the peak top determined by DSC on second cooling at a scanning rate of $10^\circ\text{C min}^{-1}$.

lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(pentafluoroethylsulfonyl)imide (LiPFSI), and lithium bis(nonafluorobutanesulfonyl)imide (LiNFSI). The polarized optical microscope images of LC complexes and the DSC thermographs are shown in Figures S1 and S2, respectively. In these series, the transition temperature from the LC phase to isotropic liquid decreases with the increase in anion size, possibly due to the steric hindrance effect. The ionic conductivity also decreases as the anion size increases. For example, the stoichiometric complex of ZI and LiTFSI (ZI/LiTFSI) exhibits a smectic A LC phase below 83°C and a room-temperature conductivity of $4 \times 10^{-3} \text{ S cm}^{-1}$ (Figure S3), whereas the LC ZI/LiNFSI complex is formed below 42°C and has a low conductivity in the order of $10^{-7} \text{ S cm}^{-1}$. This anion dependence of conductivity may be related to the ordering of anions in the layered LC structure.

Zwitterions can enhance ionic conductivity by dissociating an ionic donor.¹⁰ Hence, they have been intensively studied for the design of LC ion transporters; yet reports on room-temperature zwitterionic LCs are scarce, and the achieved conductivities are rather low. For example, Soberats et al. reported columnar and bicontinuous cubic liquid-crystalline imidazolium sulfobetaines doped with LiTFSI,¹¹ but the maximum conductivity was only $\sim 10^{-5} \text{ S cm}^{-1}$, possibly due to the large size of the gallate mesogen with branched alkoxy chains. Rondla et al. employed a much smaller compound, imidazolium sulfobetaine tethering a single alkyl chain doped with LiClO₄.¹² The conductivity of resulting LC complex increased with decreasing size of the zwitterionic molecule, and could further be raised up to $\sim 5 \times 10^{-3} \text{ S cm}^{-1}$ by aligning the LC phase.¹³ This approach appears promising, but unfortunately the authors have not attempted to test their LC phases in potential applications. A lithium conductivity reaching $4.5 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C was also reported for an aqueous zwitterionic bicontinuous cubic liquid crystal phase¹⁴ however, the need for water to maintain the LC phases can be a drawback for solid-state applications including actuators.

Here, we report a bending actuator using a smectic LC complex of ZI/LiTFSI (Figure 2). The ionic LC sample with a

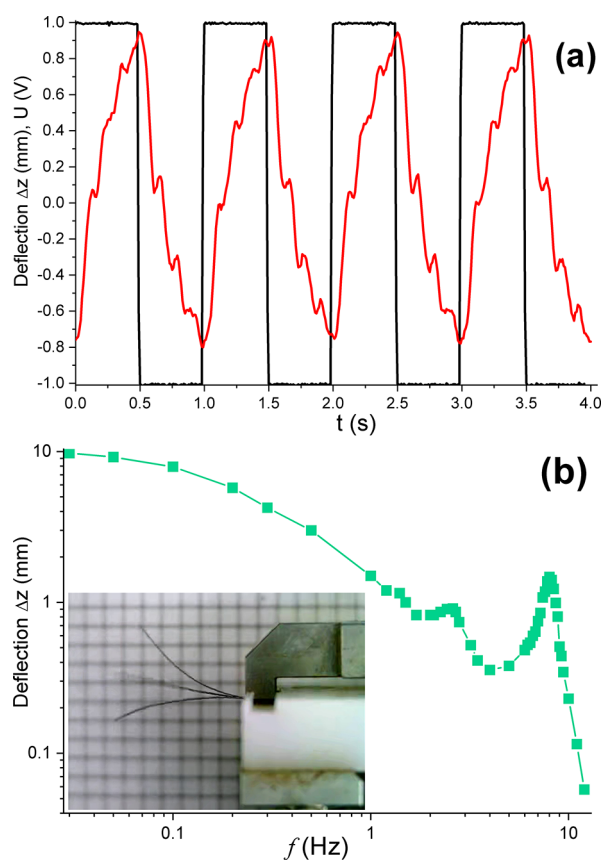


Figure 2. (a) Deflection of an actuator (Δz) comprising a smectic LC complex of ZI/LiTFSI sandwiched between PEDOT:PSS electrodes, excited by square $\pm 1 \text{ V}$ pulses (U), and (b) the frequency response of the deflection. The inset in (b) shows an overlay of three photographs of the actuator, at maximum (top and bottom) and zero deflection (center); grid size is $2 \times 2 \text{ mm}$. The bending deflection was measured by using a laser displacement meter near the end of the actuator strip (ca. 12 mm from the clamp).

thickness of $30 \mu\text{m}$ was sandwiched between two flexible PEDOT:PSS electrodes with a thickness of ca. $20 \mu\text{m}$ each. The good adhesion between the ionic LC material and electrodes resulted in stable free-standing actuator strips. The actuator exhibited a large and persistent deflection of $\sim 1 \text{ mm}$ when excited by square voltage pulses with a 0.2 V peak-to-peak amplitude. The actuator stripe shows a bending motion to the direction of positive electrode. The deflection increased linearly with applied voltage in the range $0.1\text{--}2 \text{ V}$, followed by sublinear increase in the $2\text{--}4 \text{ V}$ range and degradation at a higher bias.

Figure 2a reveals that, when excited with a bipolar square voltage pulse, the studied actuator responds with a resonance frequency f superimposed on a slow rise. When excited by a square voltage pulse with $+1.0 \text{ V}$, deflection peaks appear at ca. 0.12, 0.25, and 0.37 s. In such a case, maximum deflection should be observed when the pulse length, that is half of its period, matches $n/(2f)$, where $n = 1, 3, 5$, etc. Indeed, the frequency dependence of deflection Δz plotted in Figure 2b reveals a primary peak at $f = 8 \text{ Hz}$ and minor peaks at $f/3 \sim 2.6 \text{ Hz}$ and $f/5 \sim 1.6 \text{ Hz}$. The value of f could be tuned by changing the thickness and length of the actuator, and this tunability is useful for potential applications. Note that the entire frequency

response in Figure 2b is reflected in a single-pulse experiment presented in Figure 2a and this simple approach can be applied for evaluating LC mechanical actuators. In contrast, our attempts to make actuators based on ZI/LiPFSI and ZI/LiNFSI failed, possibly due to the relatively low conductivity of these LCs.

We have employed a combination of polarization-resolved Fourier transform infrared (FTIR) absorption, X-ray diffraction (XRD), and density-functional theory (DFT) to characterize the microscopic structure of ionic LC complexes. DFT predicts that, in the ZI/LiNFSI complex, ZI slightly bends and LiNFSI aligns almost parallel to the ZI backbone, with the Li⁺ cation facing the SO₃⁻ anion, as shown in the top part of Figure 3. This

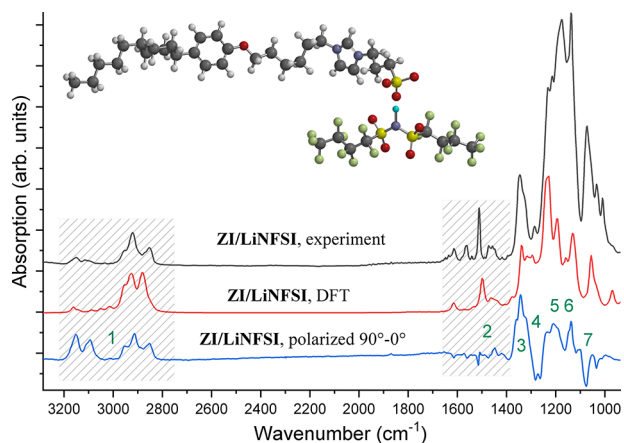


Figure 3. Top inset: geometry of the ZI/LiNFSI molecule predicted by DFT. Curves, from top to bottom: experimental and simulated absorption FTIR spectra of ZI/LiNFSI and the difference between experimental spectra recorded with polarizers oriented perpendicular and parallel to the molecular chains. Numbers mark characteristic IR modes identified by DFT in the text. Spectra are vertically offset for clarity.

prediction is confirmed by the polarized FTIR spectrum represented by the bottom curve in Figure 3. To measure this spectrum, we have partially aligned the LC sample of ZI/LiNFSI on a Si substrate by mechanical shearing (Figure S4), recorded FTIR absorption spectra with a polarizer oriented perpendicular and parallel to the alignment direction (Figure S5), and plotted their difference in Figure 3. We then identified the characteristic absorption peaks using DFT as follows: 1, C–H stretching in ZI; 2 and 4, C–H bending in ZI; 3, S=O stretching in LiNFSI; 5 and 6, C–F stretching in LiNFSI; 7, C–C backbone stretching in ZI. Considering this assignment, the polarized FTIR spectrum of Figure 3 is consistent with the DFT prediction that the LiNFSI molecule aligns parallel to ZI in the ZI/LiNFSI complex. The same conclusion was reached for the LC samples of ZI/LiTFSI (Figure S6) and ZI/LiFSI (Figure S7).

Having outlined the geometry of individual molecules, we have employed XRD to probe their arrangement in the LC phases (Figure 4). XRD patterns of the studied LCs were dominated by a broad halo at $\sim 20^\circ$ and a 001 peak at $\sim 2^\circ$, accompanied by its 002, 003, and 004 harmonics. Such a simple pattern indicates a layered structure with the constituent mesogens aligned approximately perpendicular to the layers (Figure S8). Remarkably, the 001 lattice spacing of ZI (d_{001}) remained unchanged with the addition of LiFSI; it decreased from 4.5 to 4.1 upon doping with LiTFSI, LiPFSI, or LiNFSI, but d_{001} was independent of either the doping salt or its

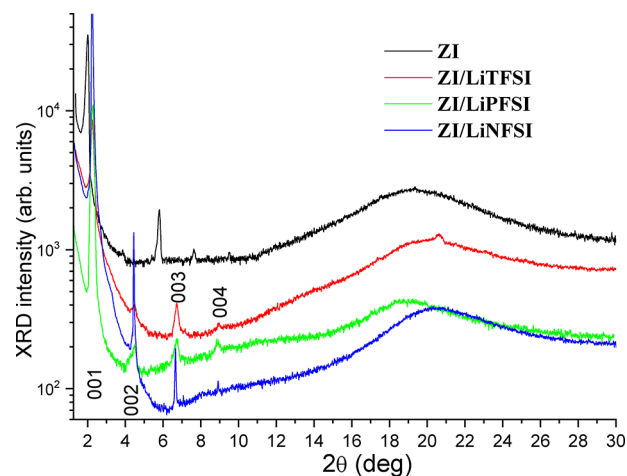


Figure 4. XRD patterns of ZI at 80 °C and the lithium salt complexes at room temperature. Spectra are vertically offset for clarity.

concentration. This result differs from previous reports on zwitterionic LCs;^{11,12} it suggests that the unit cell size is similar in the LC phases of ZI/LiTFSI, ZI/LiPFSI, and ZI/LiNFSI, and thus the free volume should decrease in this sequence, due to the increase in molecular size from LiTFSI to LiNFSI. As a consequence, the ionic mobility should decrease, as observed in Table 1.

We have further simulated the relative intensities of the 001, 002, 003, and 004 XRD peaks, as outlined in Figure S9 and its description. The simulation agrees with the experiment and suggests that the molecule responsible for XRD has a length of 2.25, 2.25, 2.33, and 2.50 nm for ZI, ZI/LiTFSI, ZI/LiPFSI, and ZI/LiNFSI, respectively. Considering that the ideal straight ZI molecule should be ~ 2.9 nm long, this result agrees with the DFT predictions that ZI bends in the studied LC complexes and that the doped LiTFSI, LiPFSI, and LiNFSI should be aligned in the direction of the long axis of ZI molecule, thereby effectively increasing its length (see top inset of Figure 3).

In summary, we have designed and synthesized a zwitterionic molecule ZI that forms ionically conductive smectic A LC phases upon mixing with an appropriate ionic donor, such as LiTFSI. We have confirmed that the resulting LC complexes are stable at ambient conditions and can be used in mechanical actuators. A combination of DFT simulations and polarization-resolved FTIR and XRD measurements suggests that the ZI molecule is bent and that the doping salt aligns to the ZI backbone in the corresponding LC phase.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialsau.2c00053>.

Preparation of a zwitterionic compound and its complexes with lithium salts and their polarized optical microscope images, differential scanning calorimetry thermograms, FTIR spectra, and XRD patterns (PDF)

Bending actuation of ZI/LiTFSI-based actuator excited by ± 1 V, 1 Hz square pulses (MP4)

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Author Contributions

M.Y. designed the experiment and synthesized compound ZI. K.I. performed the measurements, modeling, and analysis. Both authors wrote the manuscript. CRediT: **Konstantin V. Iakoubovskii** data curation (lead), formal analysis (lead), writing-original draft (equal); **Masafumi Yoshio** conceptualization (lead), data curation (lead), funding acquisition (lead), project administration (lead), resources (lead), software (lead), supervision (lead), validation (equal), writing-original draft (equal), writing-review & editing (lead).

Notes

The authors declare no competing financial interest.

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