Journal club

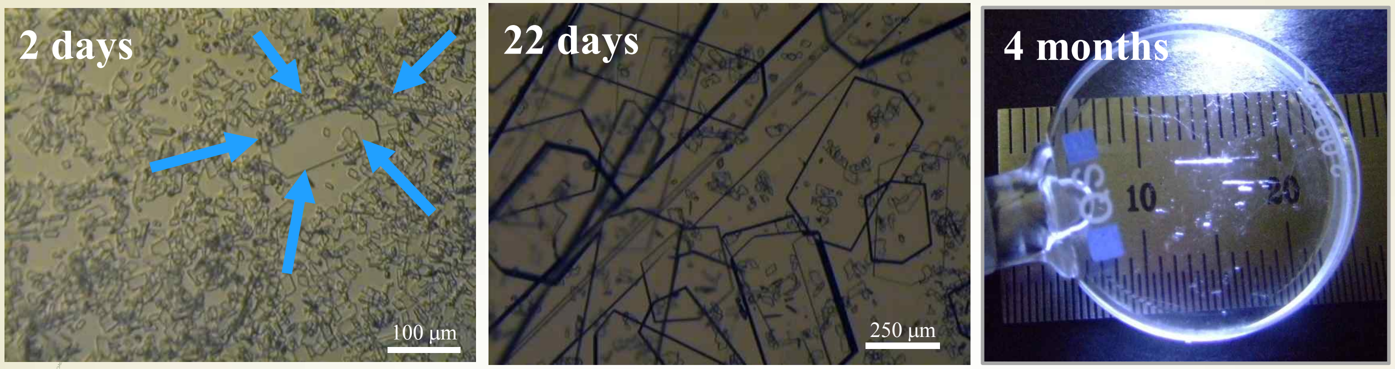
2D assemblies of ionic liquid crystals based on imidazolium moieties: formation of ion-conductive layers

J. Sakuda, M. Yohio, T. Ichikawa, H. Ohno, T. Kato, *New J. Chem*. 2015, **39**, 4471-4477

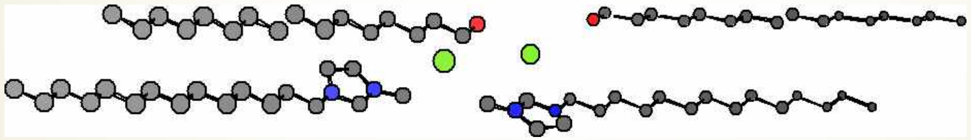
Yoonnam Jeon (2015. 11. 20)

RELATED WORK Molecular designed crystal with self−assembly of IL

Immigration from aggregations to the seed crystals



octanol octane



[C_{14}MIM]Cl

Faced imidazolium rings to reduce the interface between hydrophilic IL rings and hydrophobic alkane solvent

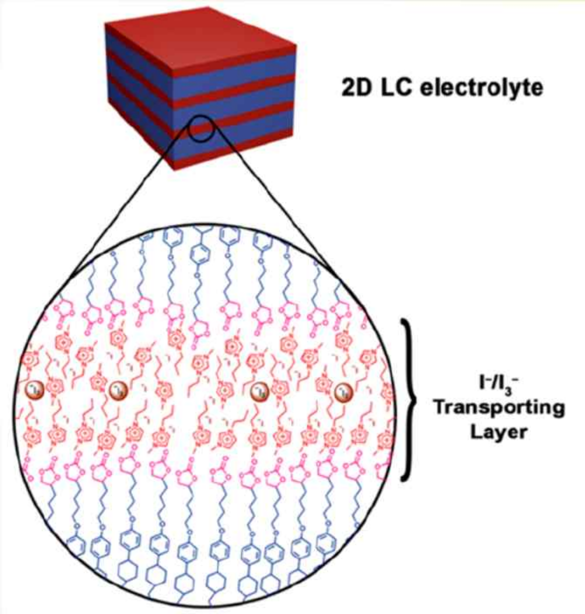
Kang, Kim, Jeon, J. Phys. Chem. C* **117**, 14332 (2013)

INTRODUCTION

Nanostructured liquid crystals
- ion and charge transport
- separation membranes
- catalysis

Ionic liquids (electrolyte materials)
- negligible vapor pressure
- flame retardancy
- high ionic conductivity

→ **Ionic liquid based liquid crystals**
- formation of ion-conductive pathways



Chem. Mater. **26**, 6496 (2014)

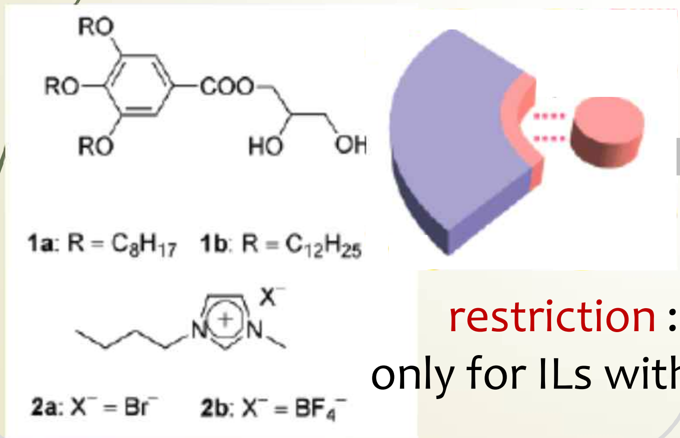
INTRODUCTION

Aim of the present study

- Constructing highly mobile ion-conductive pathways using the self-assembly of ionic liquid crystals and ionic liquids

How? Interaction design

Diol-based LC + ILs

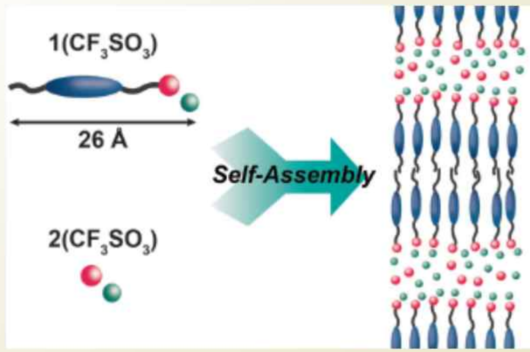


restriction : only for ILs with Br^-

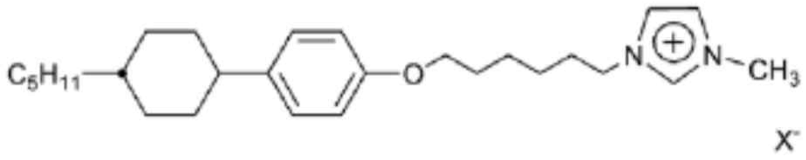
J. Am. Chem. Soc. **130,** 1759 (2008)

Present design

Segregation of the ionic and non-ionic moieties of ionic LCs and ILs

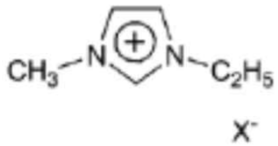


RESULTS & DISCUSSION Molecular design



1(X): X = BF_4, CF_3SO_3, $(CF_3SO_2)_2N$

for the formation of LC layered structures



2(X): X = BF_4, CF_3SO_3, $(CF_3SO_2)_2N$

due to high ionic conductivity

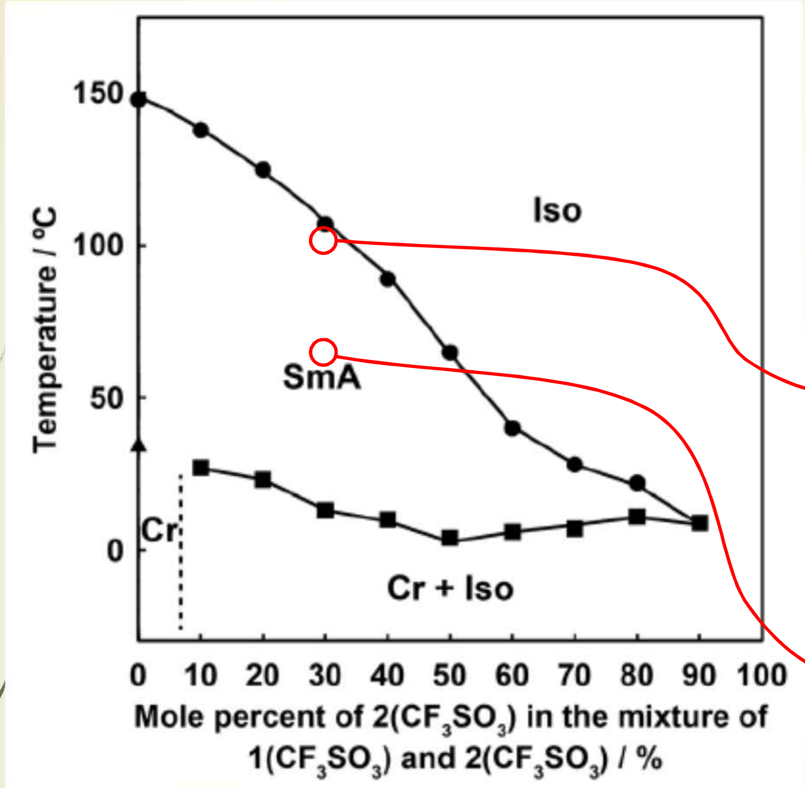
$T_{Iso \rightarrow SmA}$ is high for small counter anion radii → stronger electrostatic interaction

Table 1 Thermal properties of compounds **1(X)**

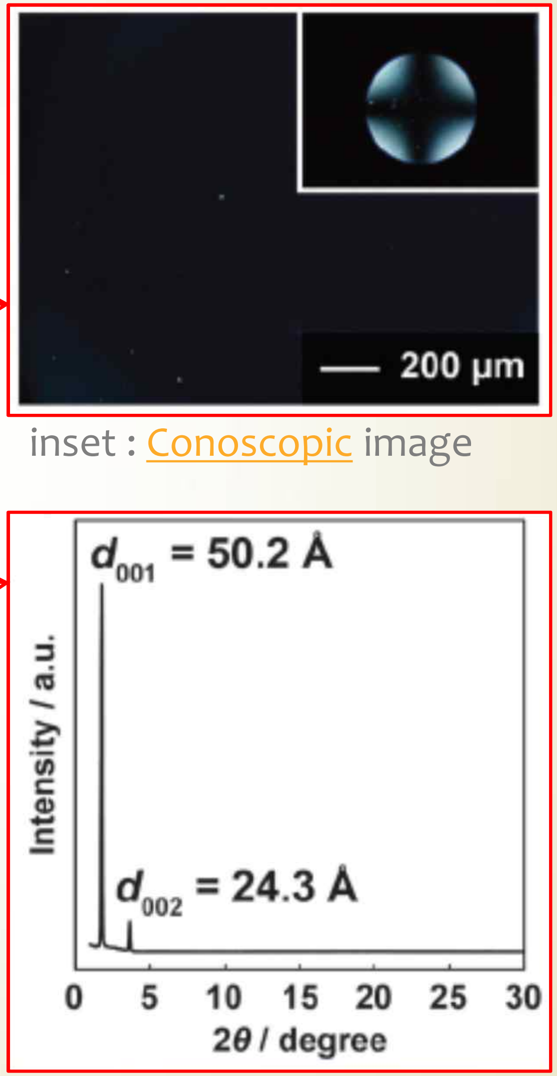
X	Radius of X^{-a} (Å)	Phase transition behavior[b,c]					
BF_4	2.29		250^d	SmA	35^e (10)	Cr
CF_3SO_3	2.70	Iso	148 (1.1)	SmA	35 (22)	Cr
$(CF_3SO_2)_2N$	3.24	Iso	64 (1.6)	SmA		

by DSC cooling process (10K/min)

RESULTS & DISCUSSION Liquid–crystalline properties

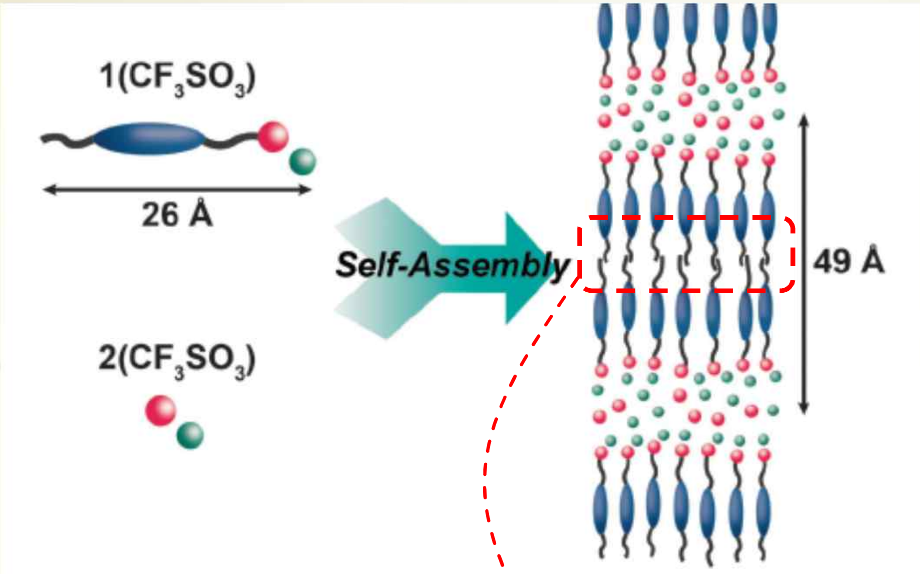


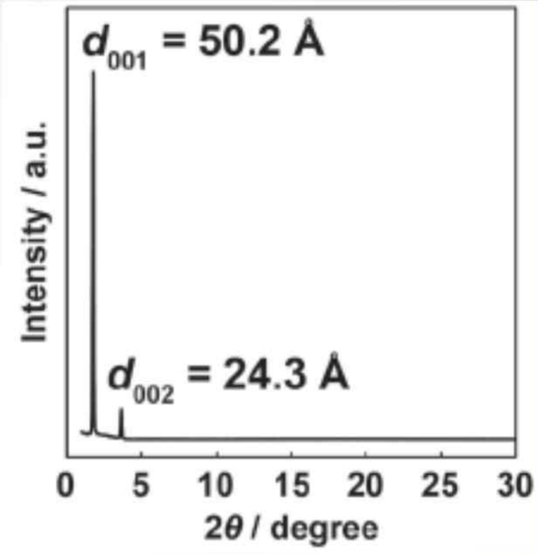
by POM cooling process (1K/min)



RESULTS & DISCUSSION Formation of layered structure

T = 58°C

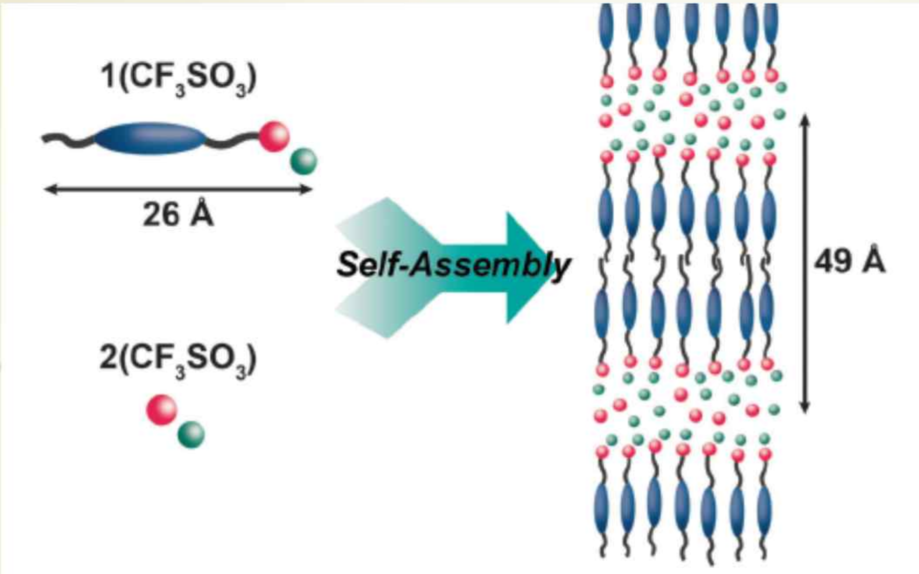


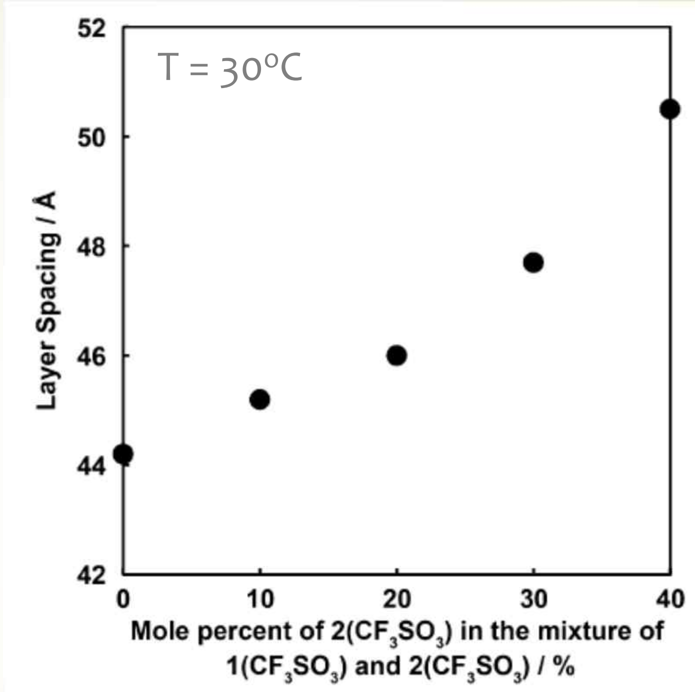


※ 26Å x 2 = 52Å

※ interdigitated layer : 4Å

RESULTS & DISCUSSION Formation of layered structure



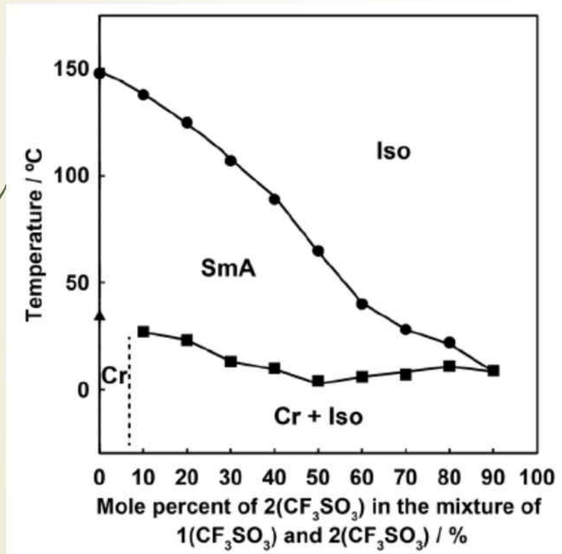


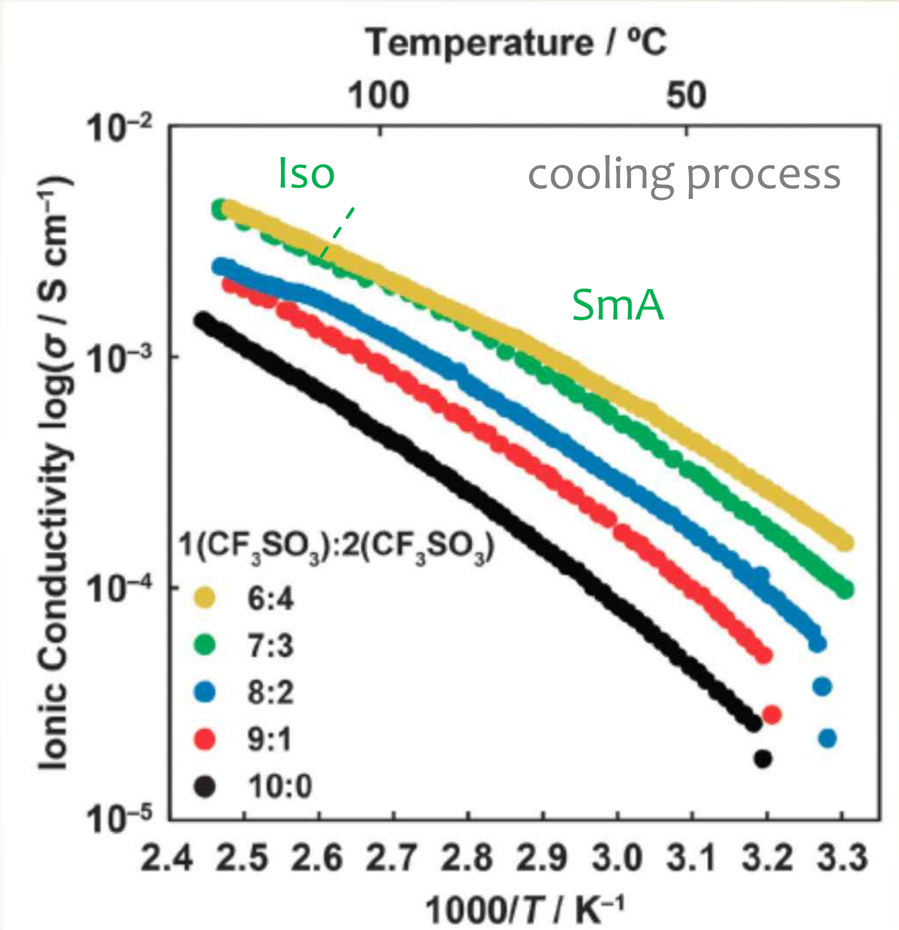
Increasing $2(CF_3SO_3)$ concentration : increasing layer spacing

IL : organized into ion-conductive layers formed by the imidazolium moiety in $1(CF_3SO_3)$

RESULTS & DISCUSSION Ion−conductive properties

electrodes : comb-shaped gold electrodes deposited on a glass substrate





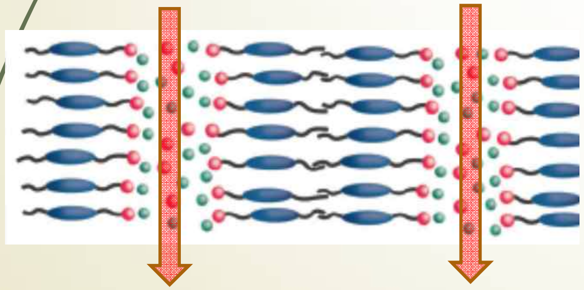
(Relation between conductivity & phase transition : not discussed)

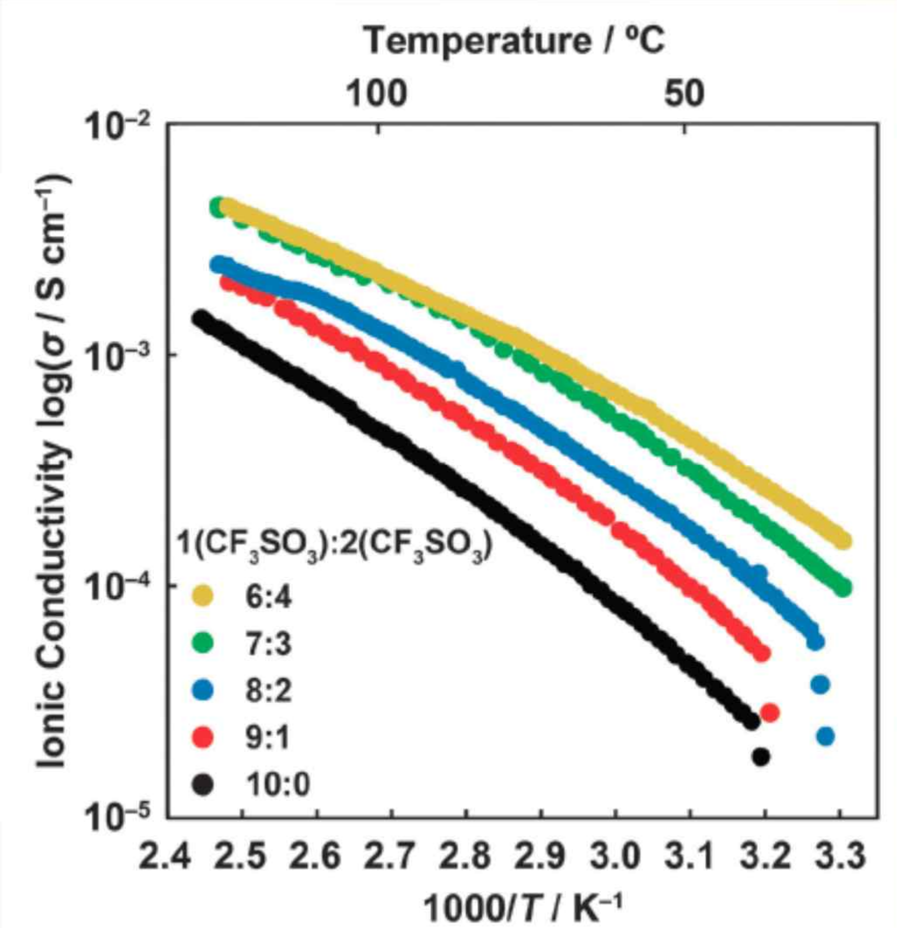
RESULTS & DISCUSSION Ion−conductive properties

Homeotropically aligned monodomain is spontaneously formed

enable

Measurement of conductivities parallel to the ion-conductive pathways

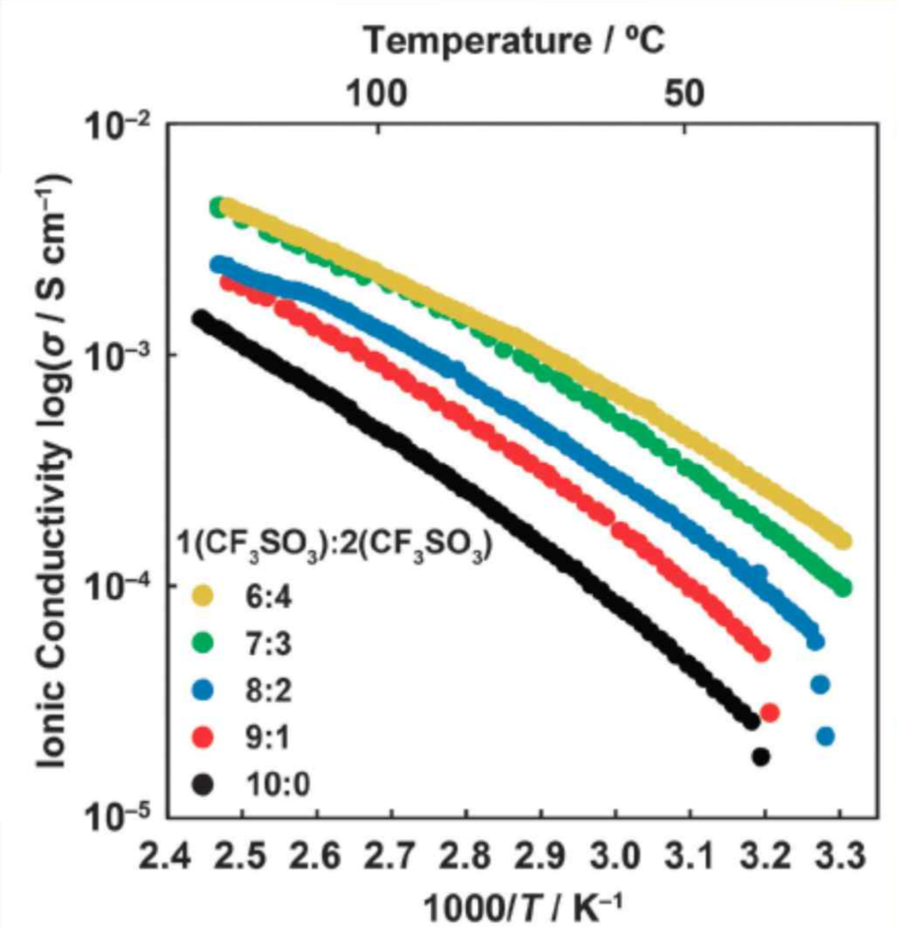




RESULTS & DISCUSSION Ion−conductive properties

Increasing 2(CF_3SO_3) concentration (increasing layer spacing)

Increasing conductivity



RESULTS & DISCUSSION Ion−conductive properties

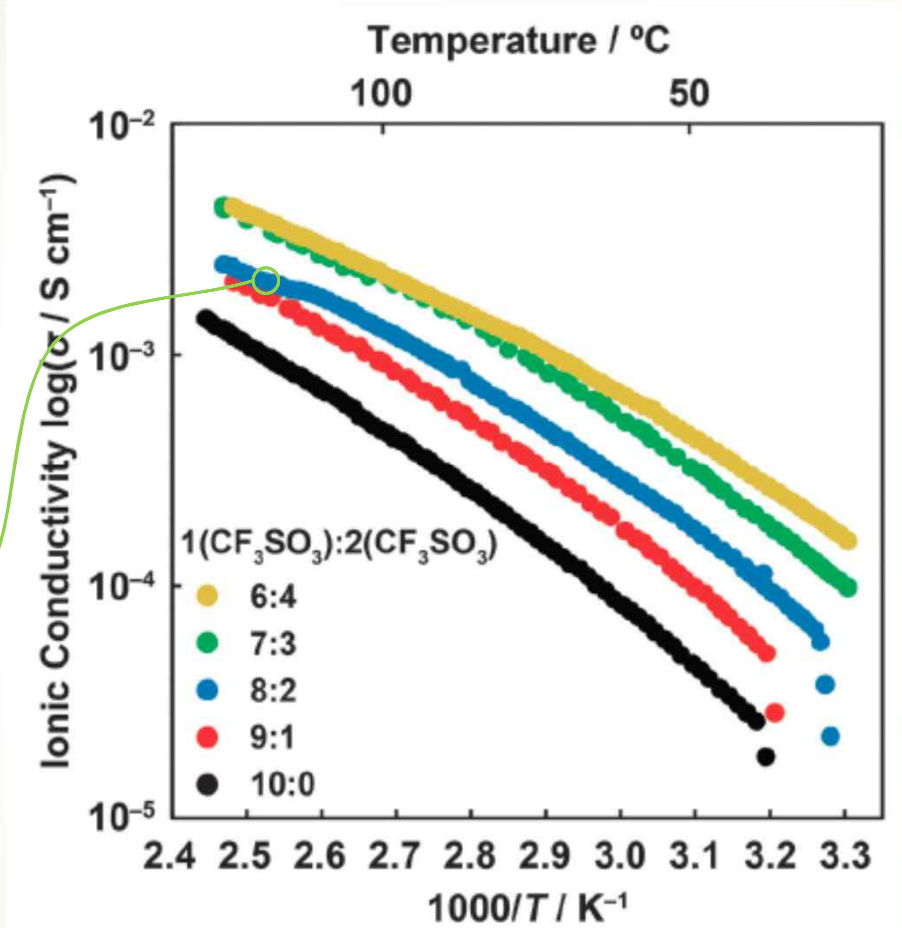
Non-covalent systems based on diol LC molecules with the same mesogenic moiety as $1(CF_3SO_3)$ with LC:IL = 8:2

σ = 4.8 x 10^{-4} S/cm at T = 122°C

Mol. Crys. Liq. Cryst. **413**, 2235 (2004)

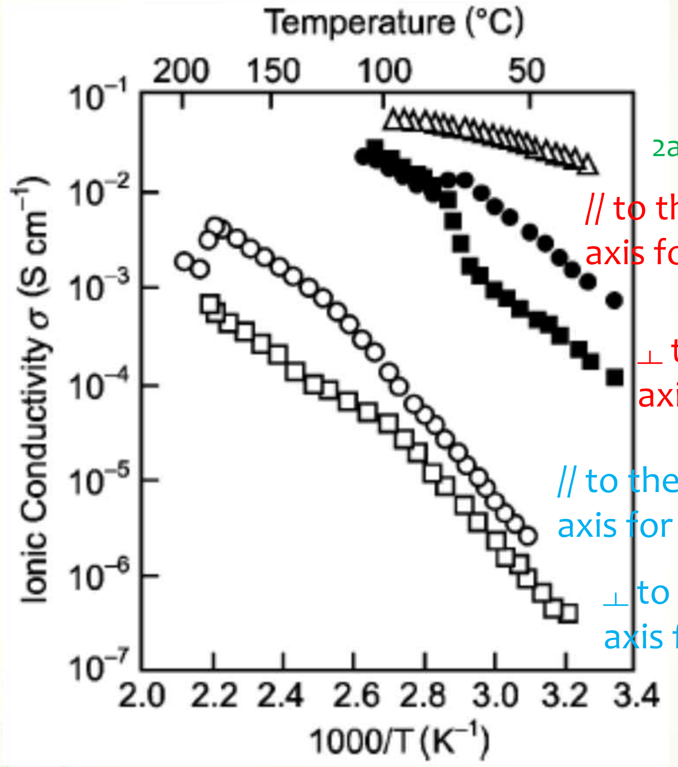
σ = 2.0 x 10^{-3} S/cm at T = 122°C

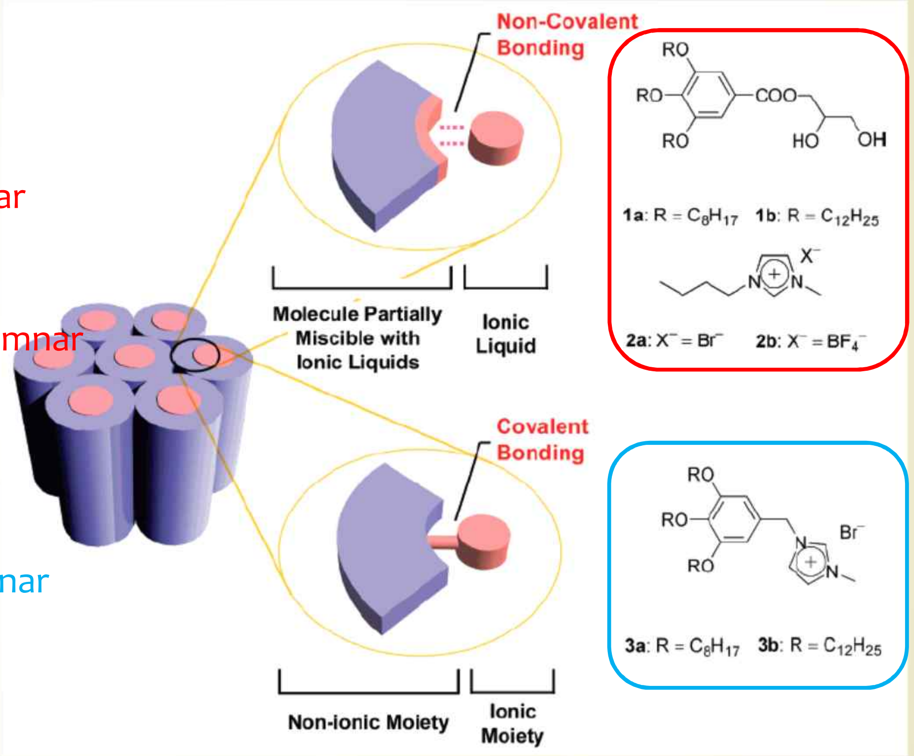
one order of magnitude higher



RESULTS & DISCUSSION Ion−conductive properties

J. Am. Chem. Soc. **130,** 1759 (2008)





※ σ = 2.0 x 10^{-2} S/cm at T ~ 100°C

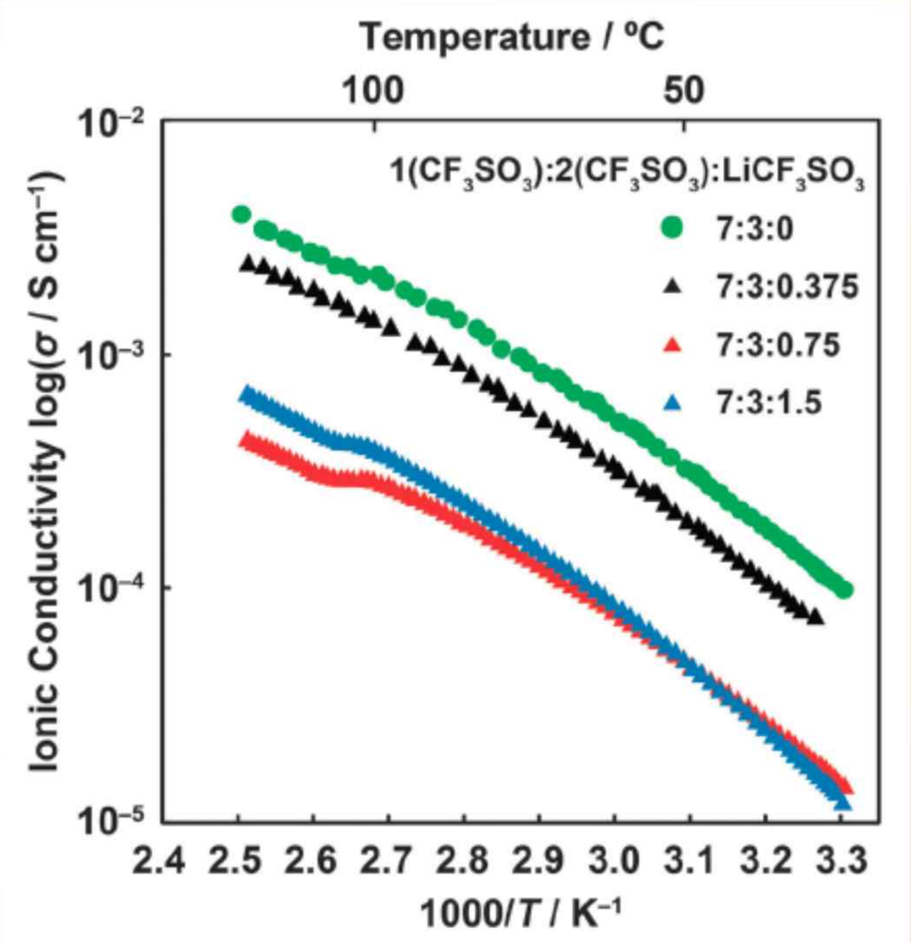
RESULTS & DISCUSSION Ion–conductivities with Li salts

Addition of $LiCF_3SO_3$

Decrease in the conductivity

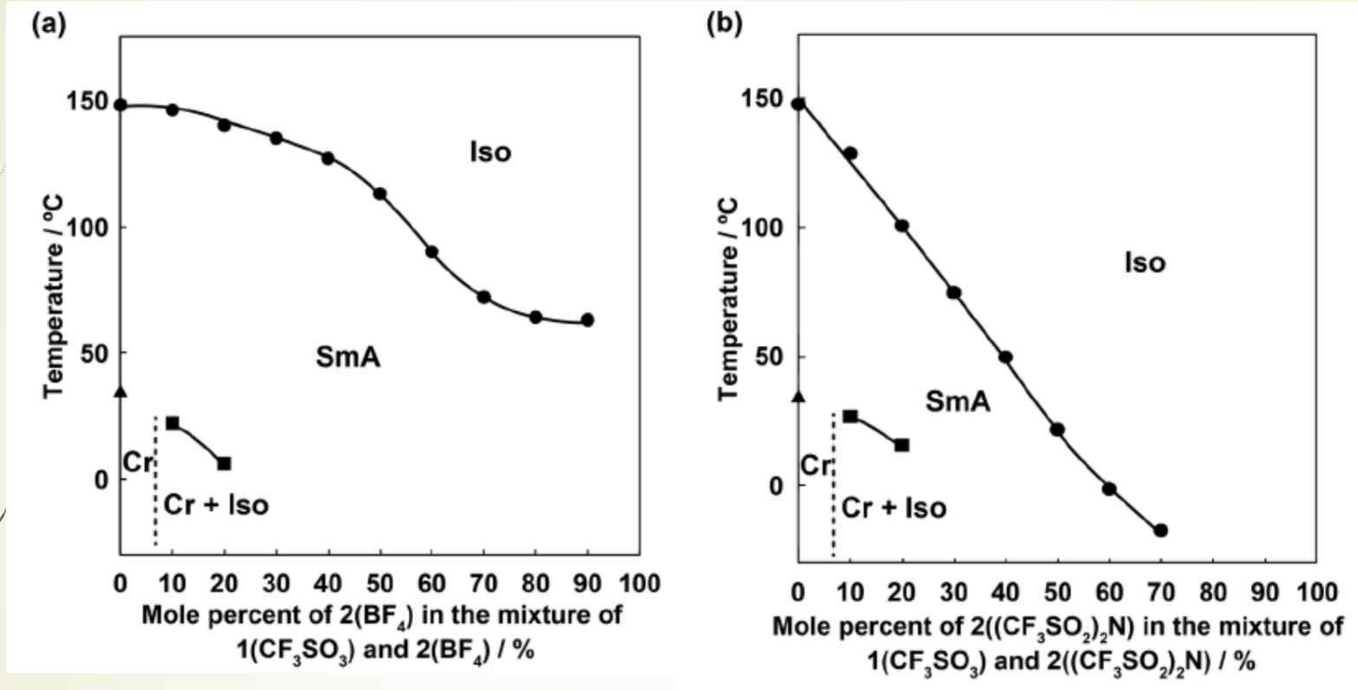
attributed to the lower mobility from the formation of aggregated species through the coordination of the anion to the lithium cations

J. Phys. Chem. B **112**, 2991 (2008)



RESULTS & DISCUSSION For different counter anions

cooling process

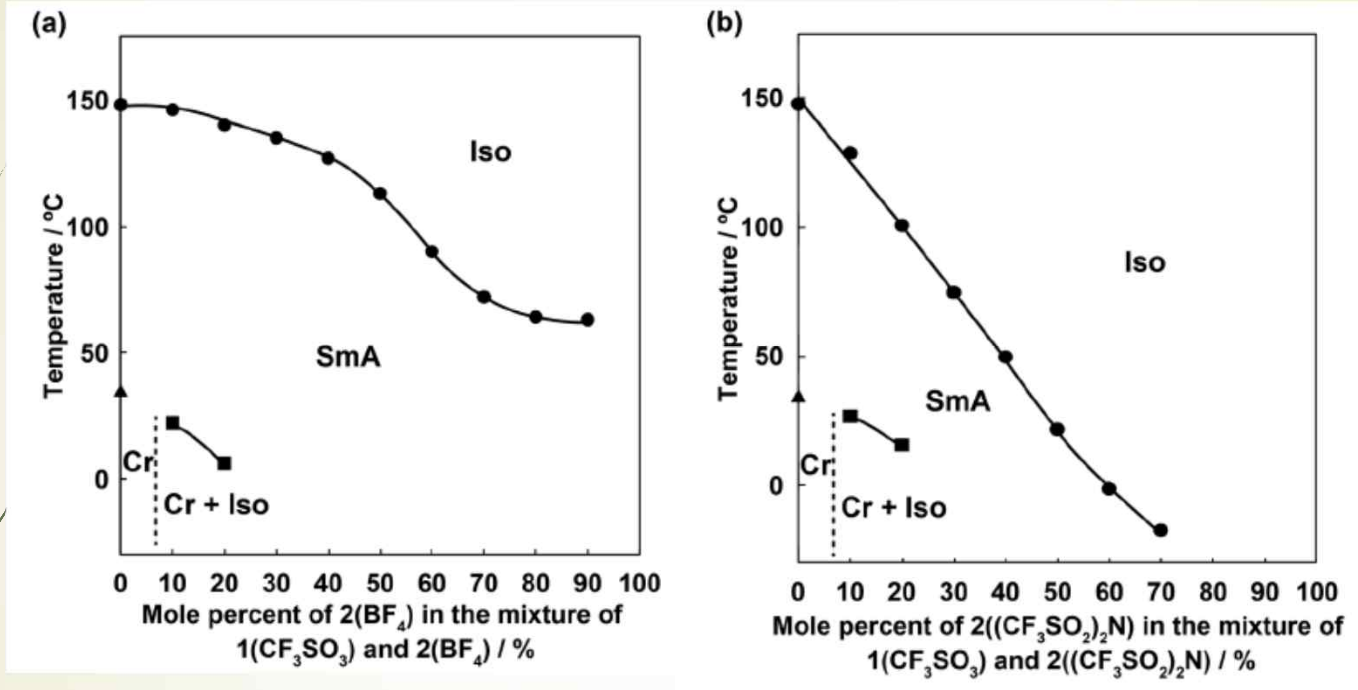


LC states over the entire composition range

→ 1(CF_3SO_3) has high compatibility with 2(X)

RESULTS & DISCUSSION For different counter anions

cooling process



- 2(X) > 30% : 1(CF_3SO_3) does not crystallize on cooling to -30°C
  (except 1(CF_3SO_3) + 2(CF_3SO_3))
- $T_{Iso \rightarrow SmA}$ decreases with an increasing radius of 2(X)

➡ Addition of 2(X) with larger counter anions : destabilizes the LC phase