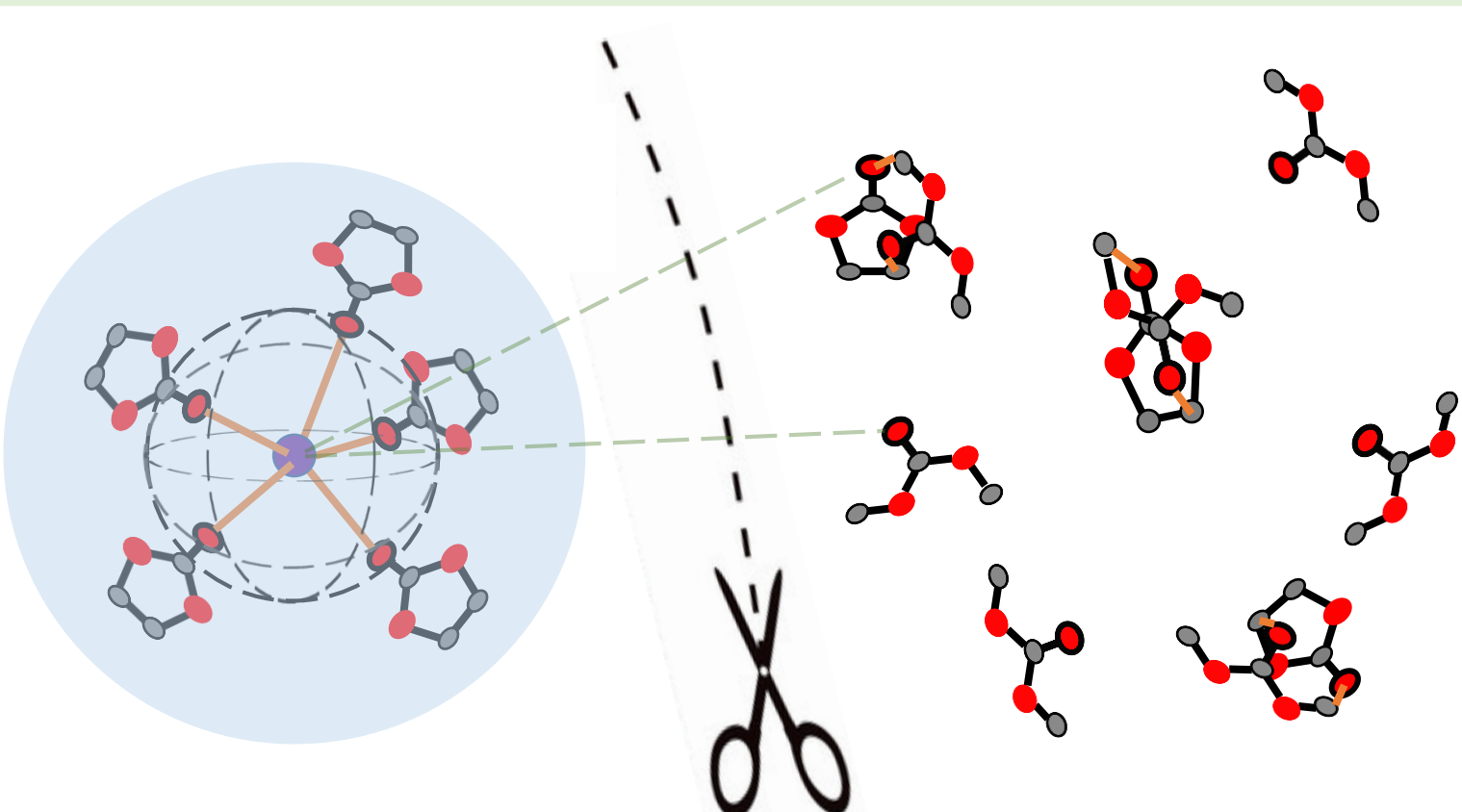


Infrared spectroscopy of Electrolyte System in Lithium-Ion Batteries

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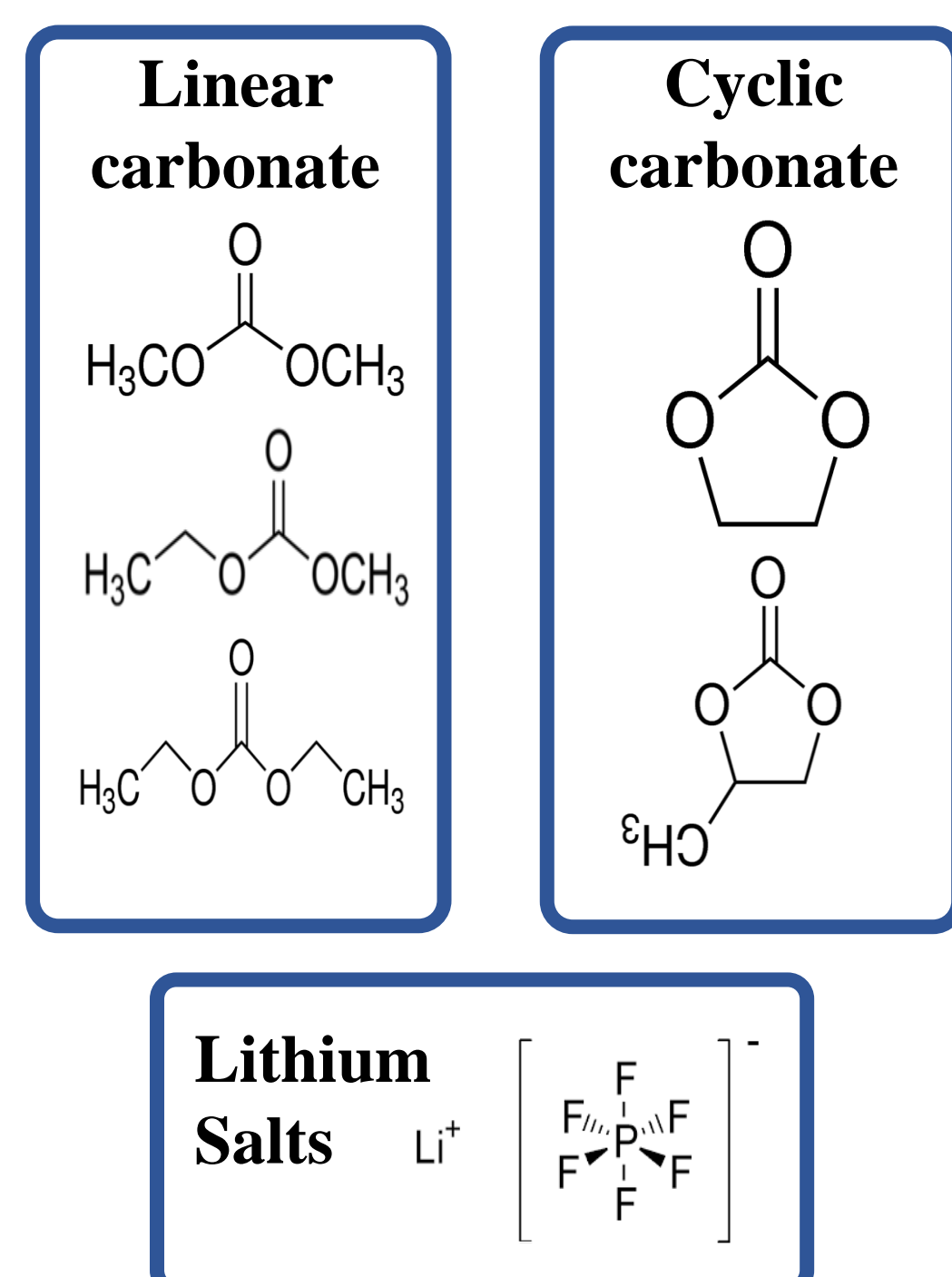
ABSTRACT

Lithium ion battery(LIB) is indispensable material in daily life for the portable energy storage devices. For this reason, various studies of LIB have been steadily done specially to increase the efficiency and stability. According to some researches, small changes in molecular structure seems to affect much to the performance of LIB. To study these phenomena, we observe microscopic interaction of electrolytes, how solvent molecules interact with lithium ion and how they transfer it, and how these results influence on the conductivity of battery therefore.

For this study, we use infrared spectroscopy because infrared absorption is highly sensitive to the change of environment around Li^+ ion. With salt concentration dependence, mixing ratio between main and co-solvent, and investigation low frequency mode, we can investigate the effect of salt exchange and solvent exchange. This will provide molecular information about the electrolytes for new advanced battery system.

INTRODUCTION

Component of Electrolyte

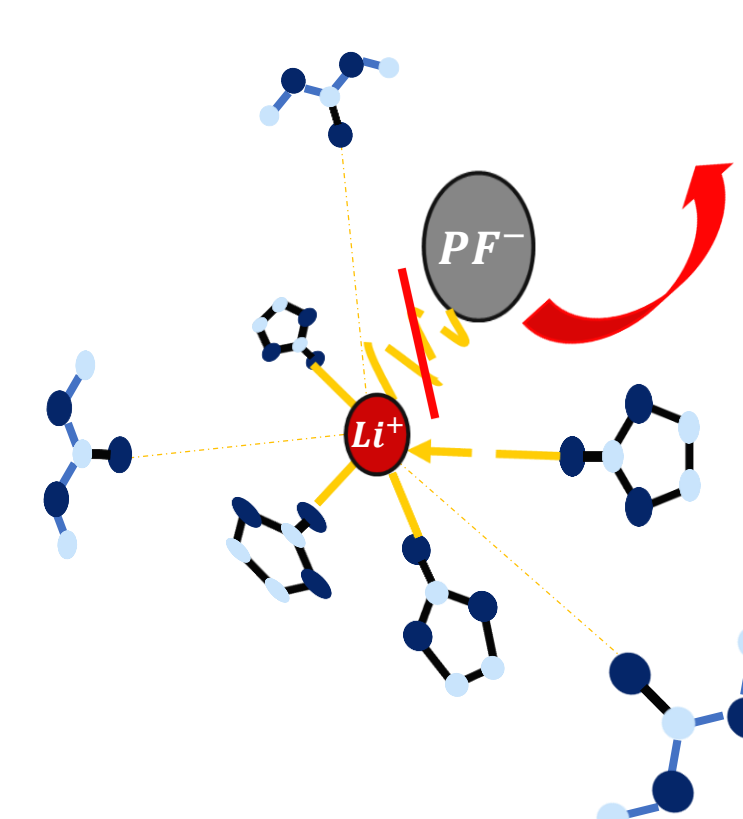


Property of Carbonate

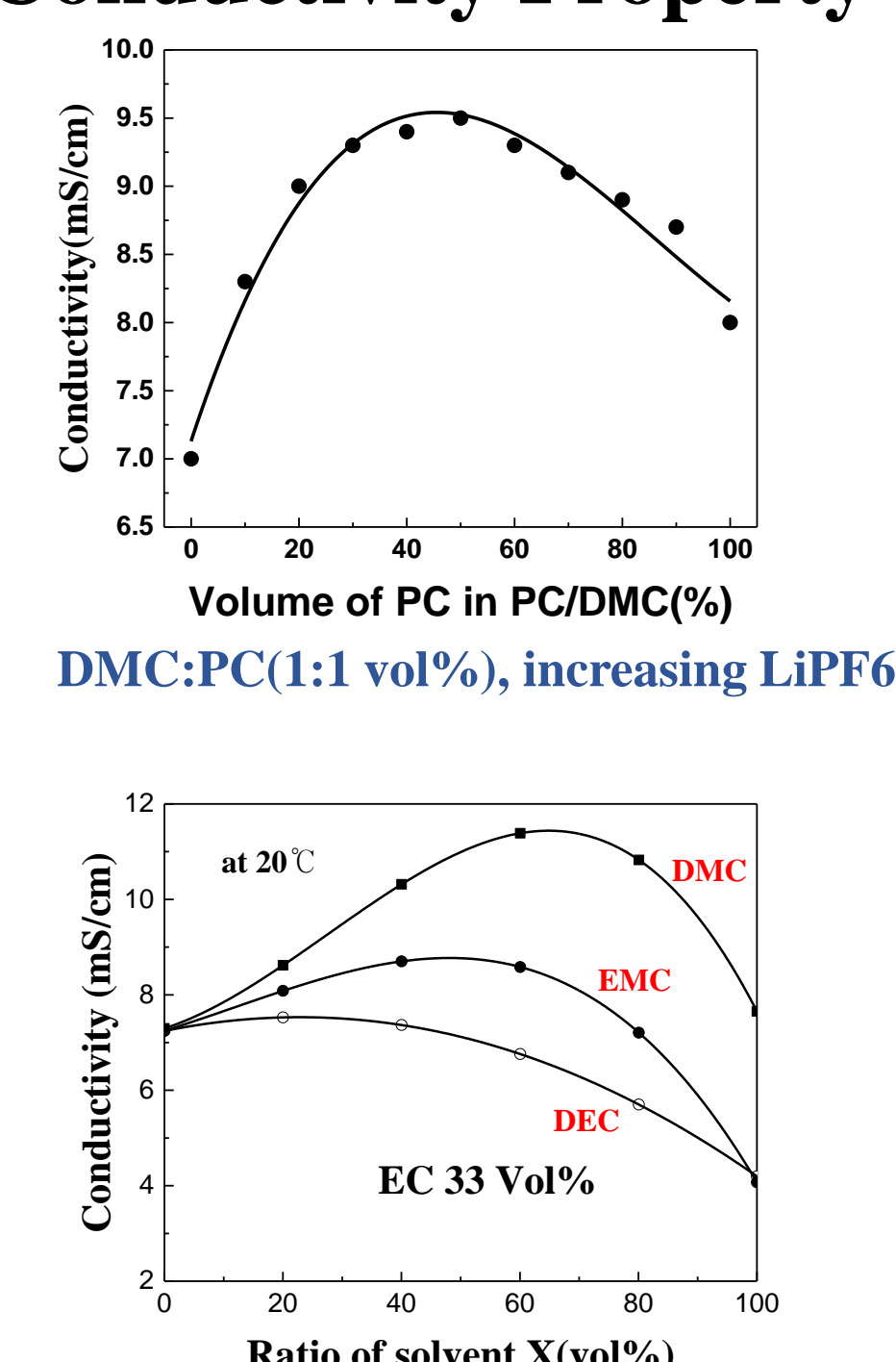
	Electrolyte	Dielectric constant	Viscosity (mPa)
Cyclic carbonate	Ethylene Carbonate(EC)	89.78	1.9
	Propylene Carbonate(PC)	64.92	2.53
Linear carbonate	Dimethyl Carbonate(DMC)	3.107	3.107
	Diethyl Carbonate(DEC)	2.805	2.805

Electrolytes are composed of mixed solvents, *Linear carbonate* and *Cyclic Carbonate*. Cyclic carbonate has high dielectric constant, so it cuts off PF_6^- interacting with Li^+ and solvates cation. Linear carbonate has low viscosity, and it drives solvation shell well in the LIB system.

Molecular Structure of solvation shell



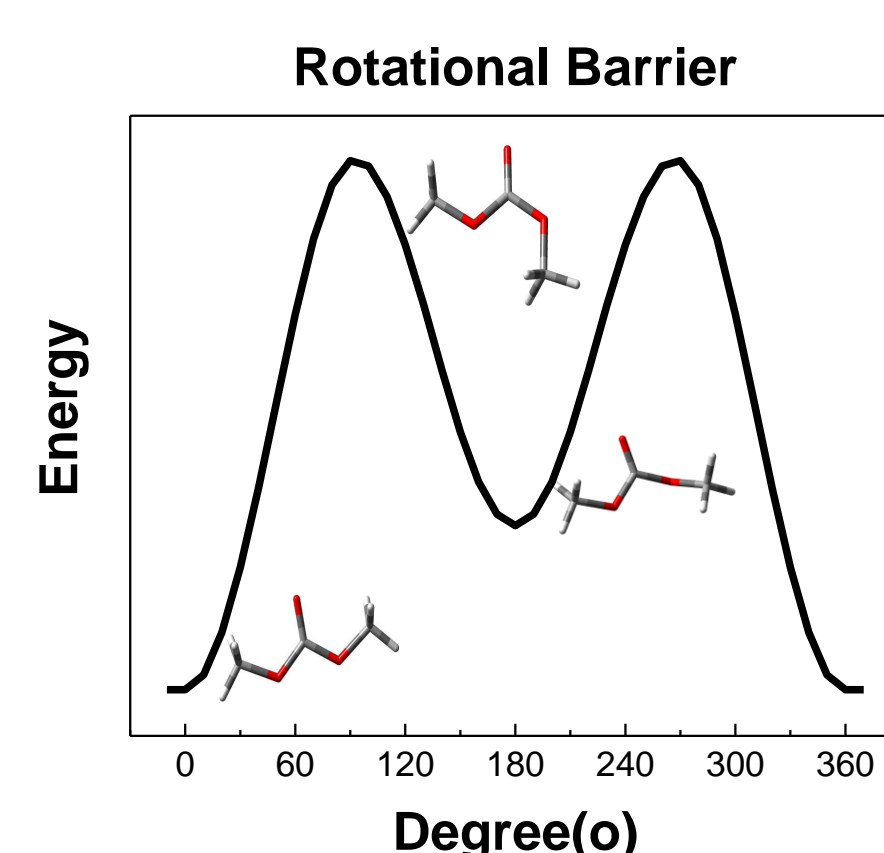
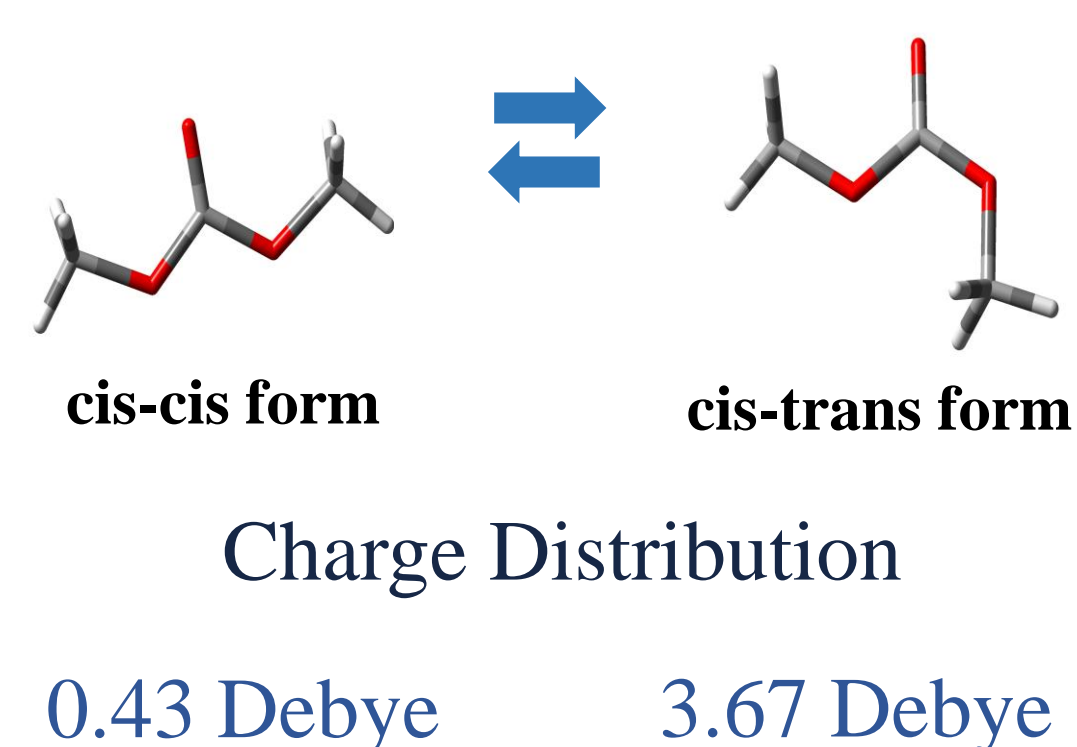
Conductivity Property of LIBs



These macroscopic properties can account for conductivity trend of LIB. Increasing section of conductivity figure, the more PC is in electrolytes, the more Li^+ is soluble. Decreasing section, excessive PC increase the solution viscosity, so mobility of solution decreases. But these properties can't explain other phenomenon. Each linear carbonates have difference conductivities, though they have similar properties.

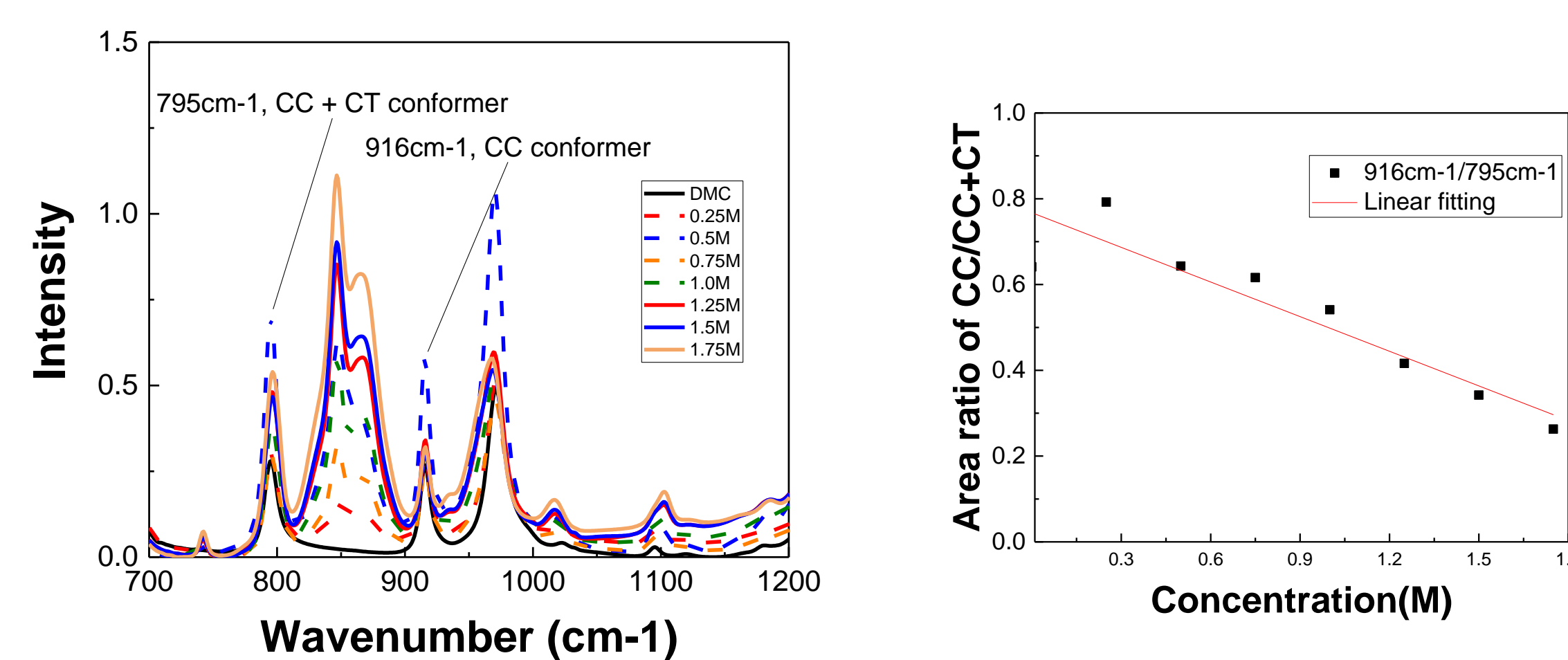
FTIR EXPERIMENT

Conformer Exchange



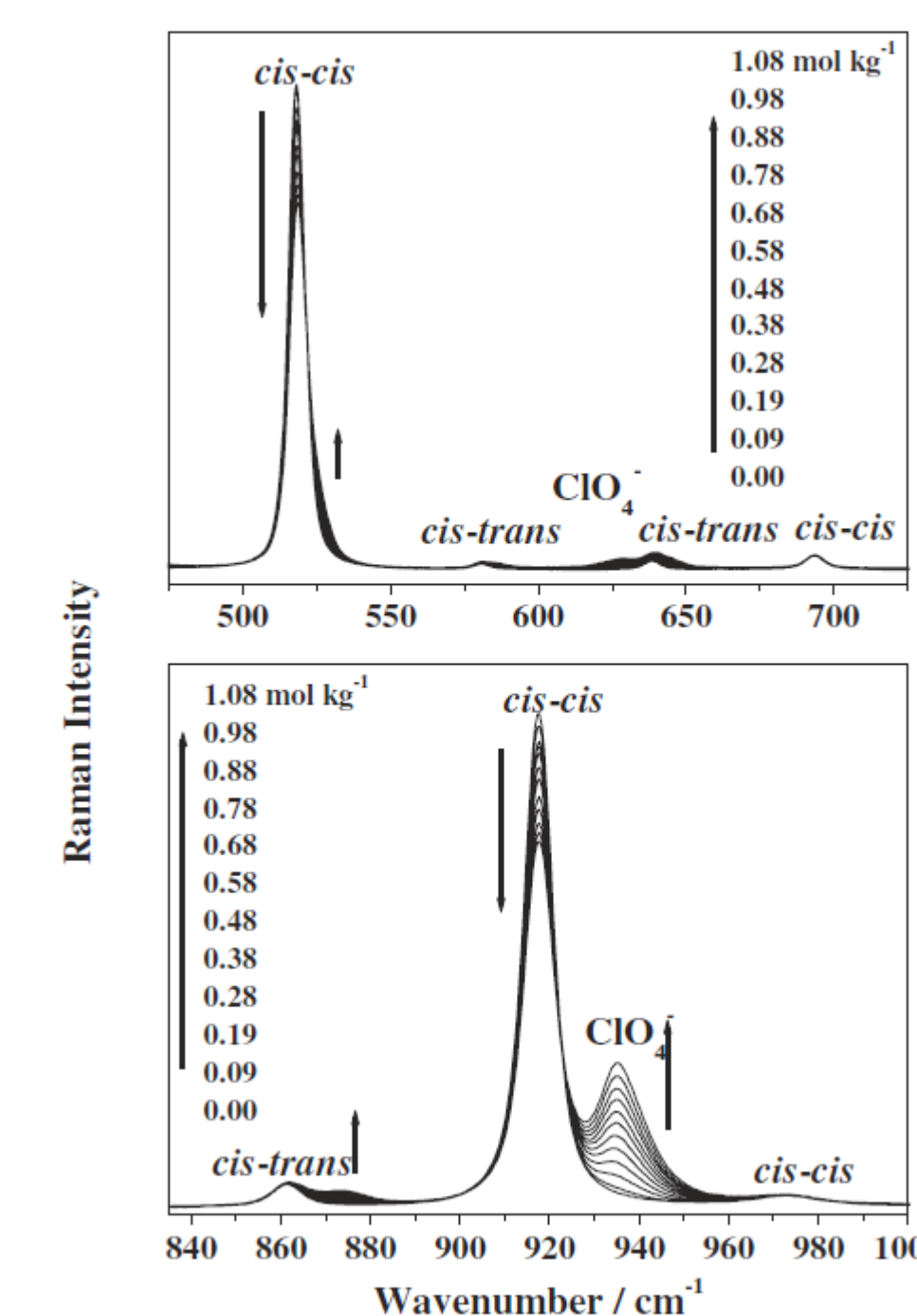
This phenomenon expects to be explained by microscopic properties. Linear carbonate has two kinds of stable conformer. In general, more stable cis-cis conformer is predominant in pure solvent. But in electrolytes, the ratio of conformer will change and this change will influence the LIB property.

Li^+ Concentration Dependence



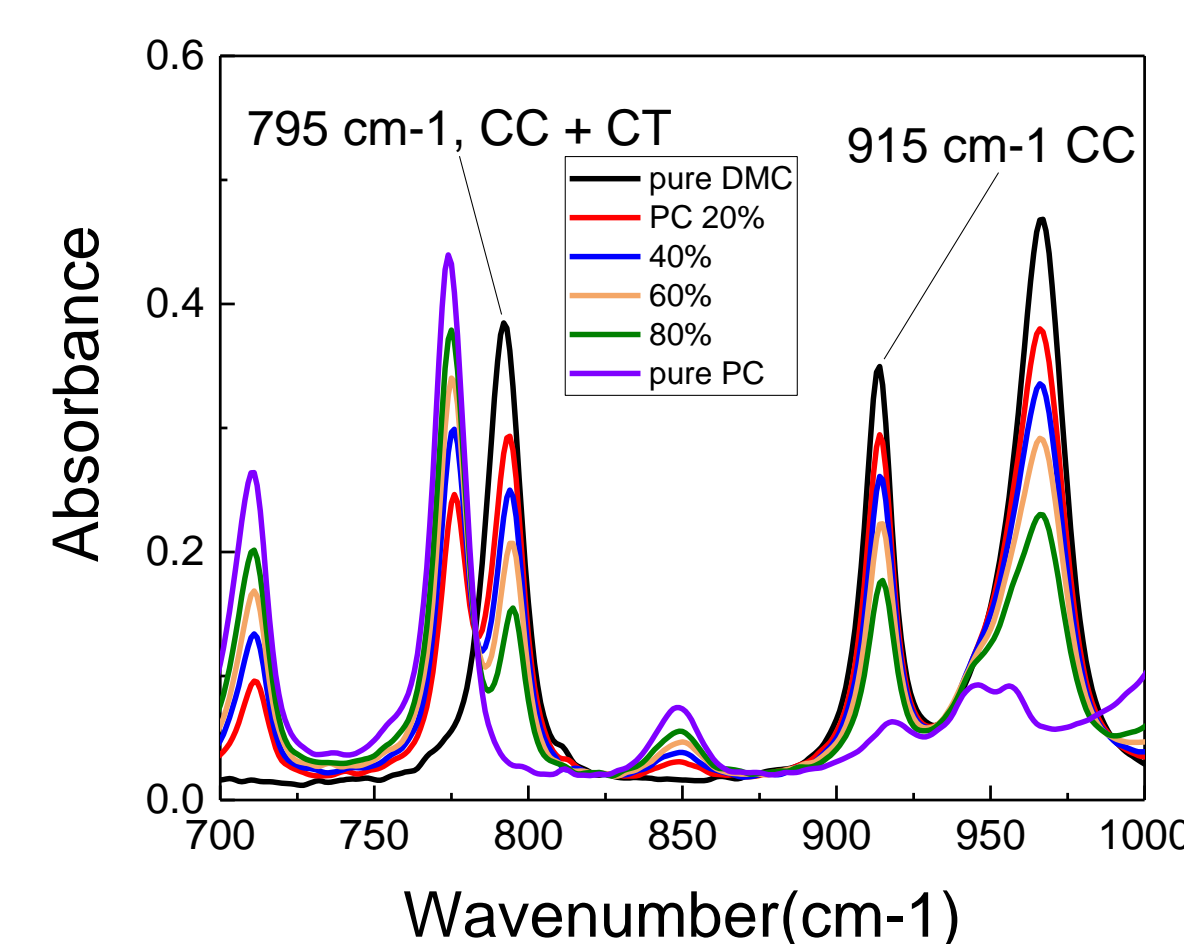
Increasing concentration of Lithium salt, the ration of cis-cis form reduce and cis-trans form grows up. We assume this phenomenon "*like dissolve like*" rule. Lithium salt raises polarity of electrolytes, and cis-trans form which is more polar than cis-cis form is grows up.

Raman Spectroscopy



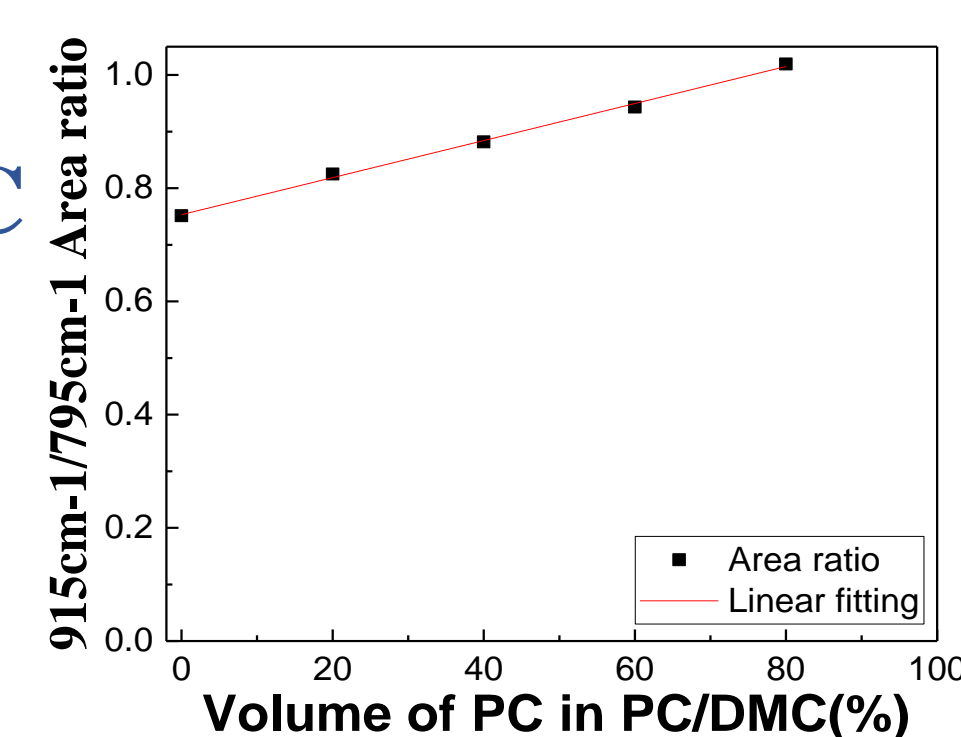
FUTURE WORK

PC volume Ratio increase

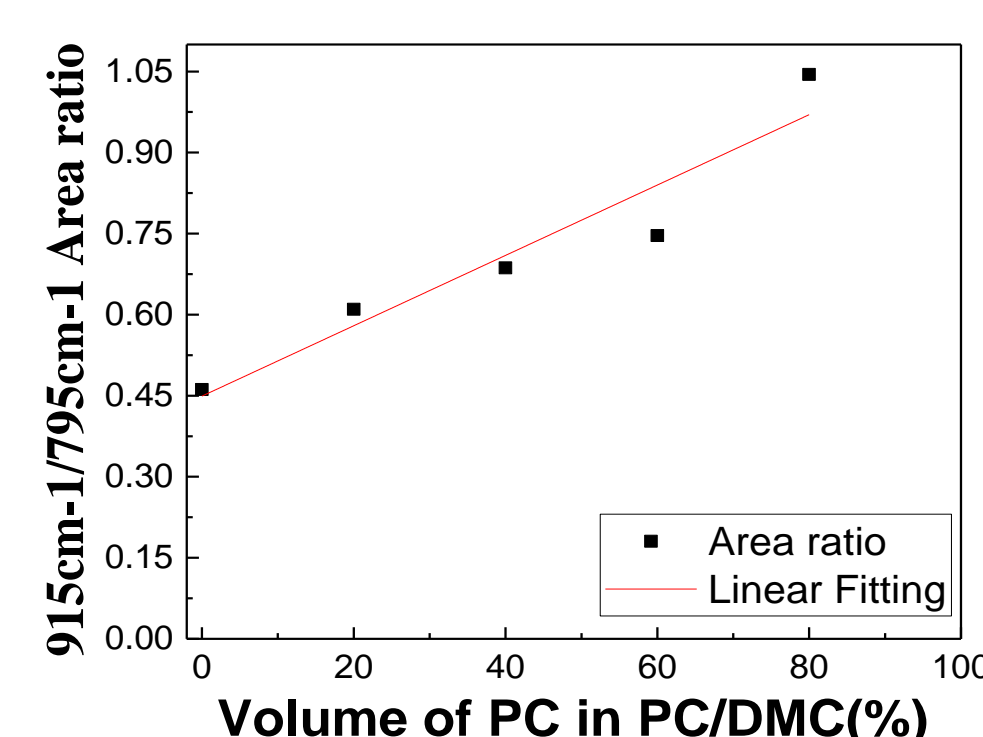


We predict a mount of PC raises up the ratio of cis-trans form because of its high polarity. However, the result of pure PC/DMC and 1M electrolyte system is reverse.

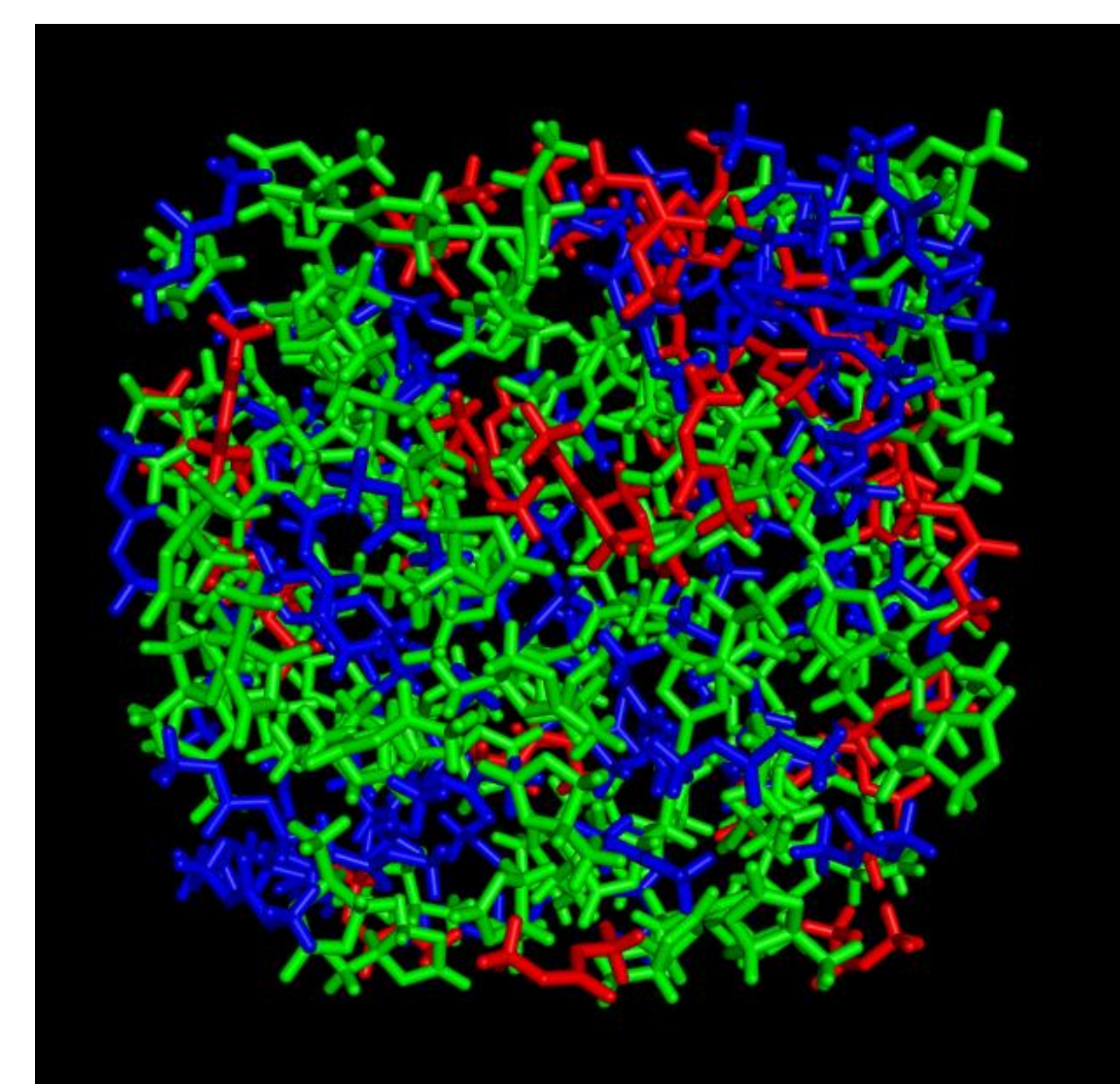
Pure DMC:PC



1M LiPF6 DMC:PC



MD simulation



Therefore, We propose two assumption: First, although lithium salt has high polarity, solvated Li^+ has less influence out of solvation shell. Second, there is PC-DMC interaction and it changes the conformer ratio increasing cis-trans form. To find out evidence of these arguments, we has calculated MD simulation and taken spectrum using IR or NMR

CONCLUSION

1. In polar environment, the cis-trans conformer increases by increasing lithium salt but decreases by increasing PC.
2. Li^+ is screened by solvation structure. Out of the solvation shell, environment of electrolyte might be similar with pure PC/DMC solution because the trend of conformer exchange is same.
3. There might be PC-DMC interaction to increase cis-cis conformer, and this interaction affects LIB property.

REFERENCE & ACKNOWLEDGMENT

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2. Structural Chemistry, Vol. 16, No. 3, June 2005

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