

Supplementary data for

# Origin of Li<sup>+</sup> Solvation Ability of Electrolyte Solvent: Ring Strain

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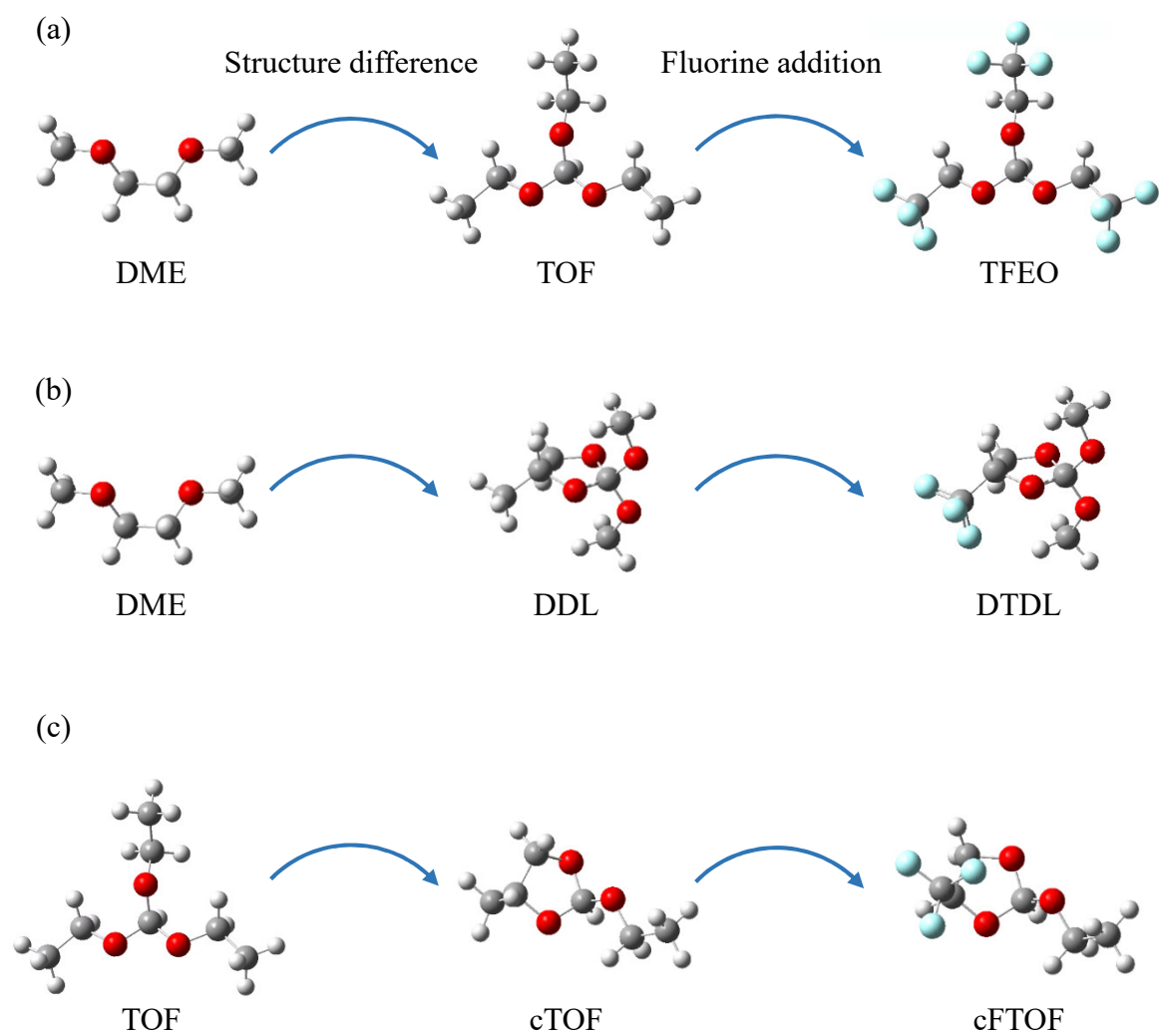


Figure S1. Optimized structures of (a) DME, TOF, and TFEO, (b) DME, DDL, and DTDL, and (c) TOF, cTOF, and cFTOF.

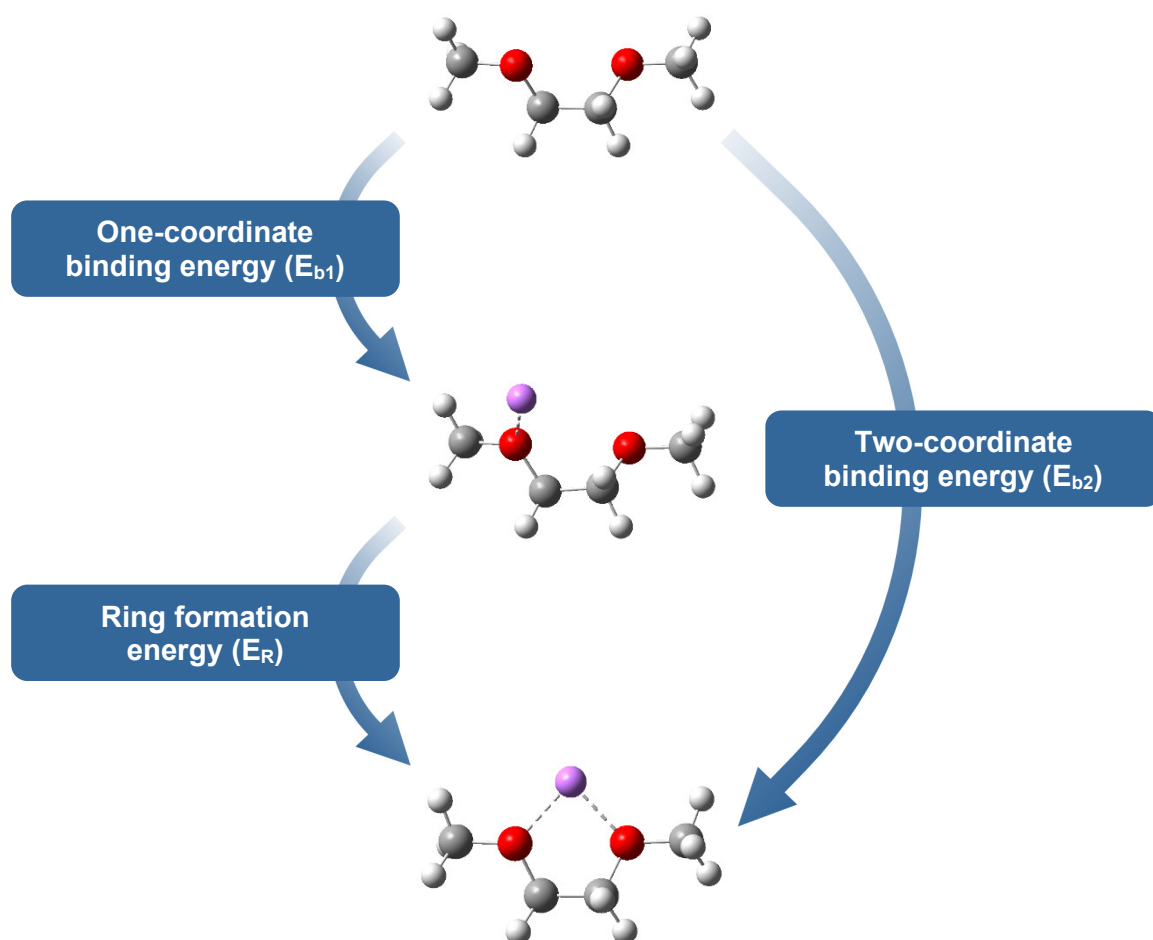


Figure S2. One- and two-coordinate binding energies between lithium ion and organic solvent, and ring formation energy.

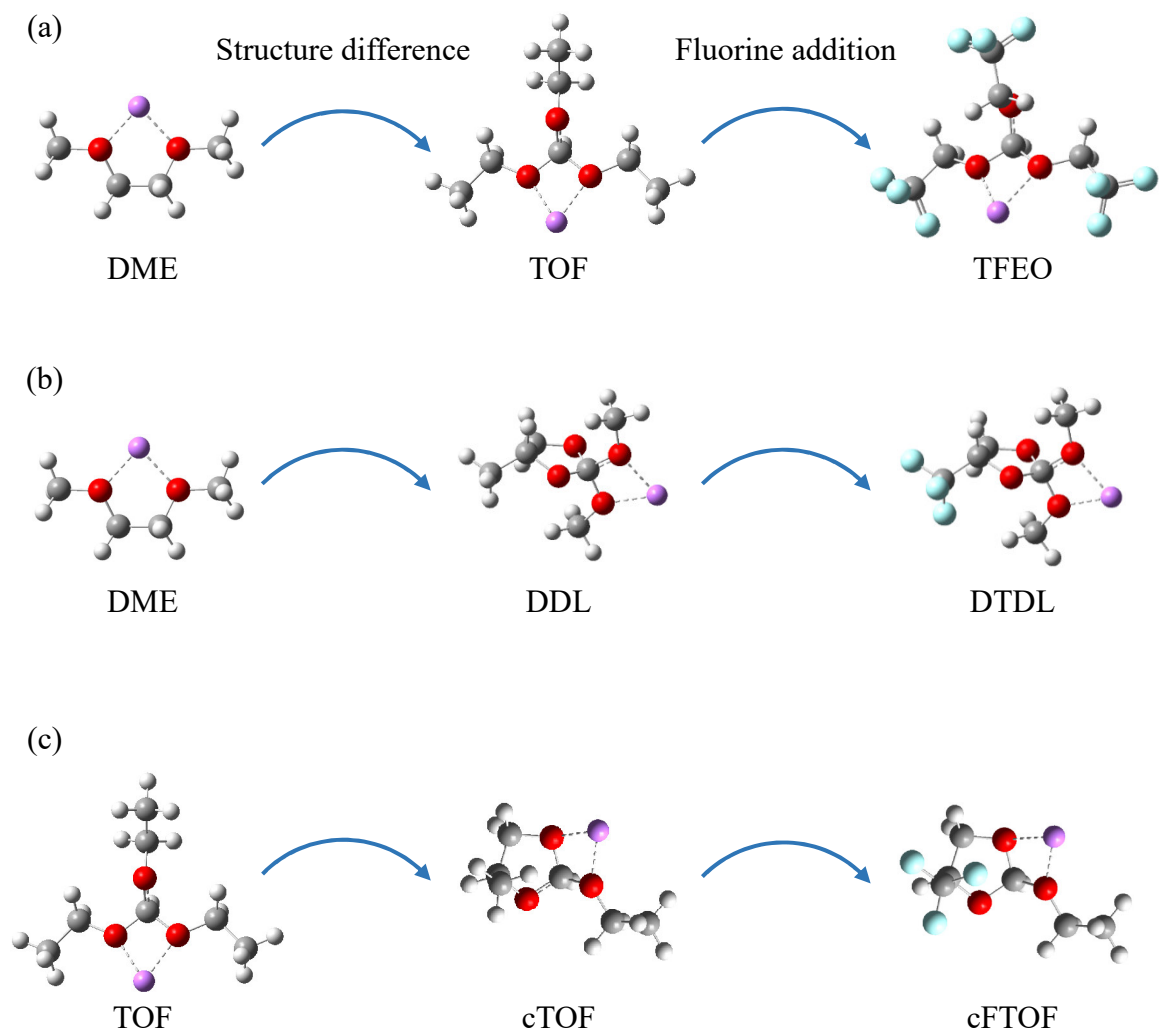


Figure S3. Optimized structures of (a) DME, TOF, and TFEO, (b) DME, DDL, and DTDL, and (c) TOF, cTOF, and cFTOF coordinated to  $\text{Li}^+$ .

4-membered ring    5-membered ring    6-membered ring    7-membered ring

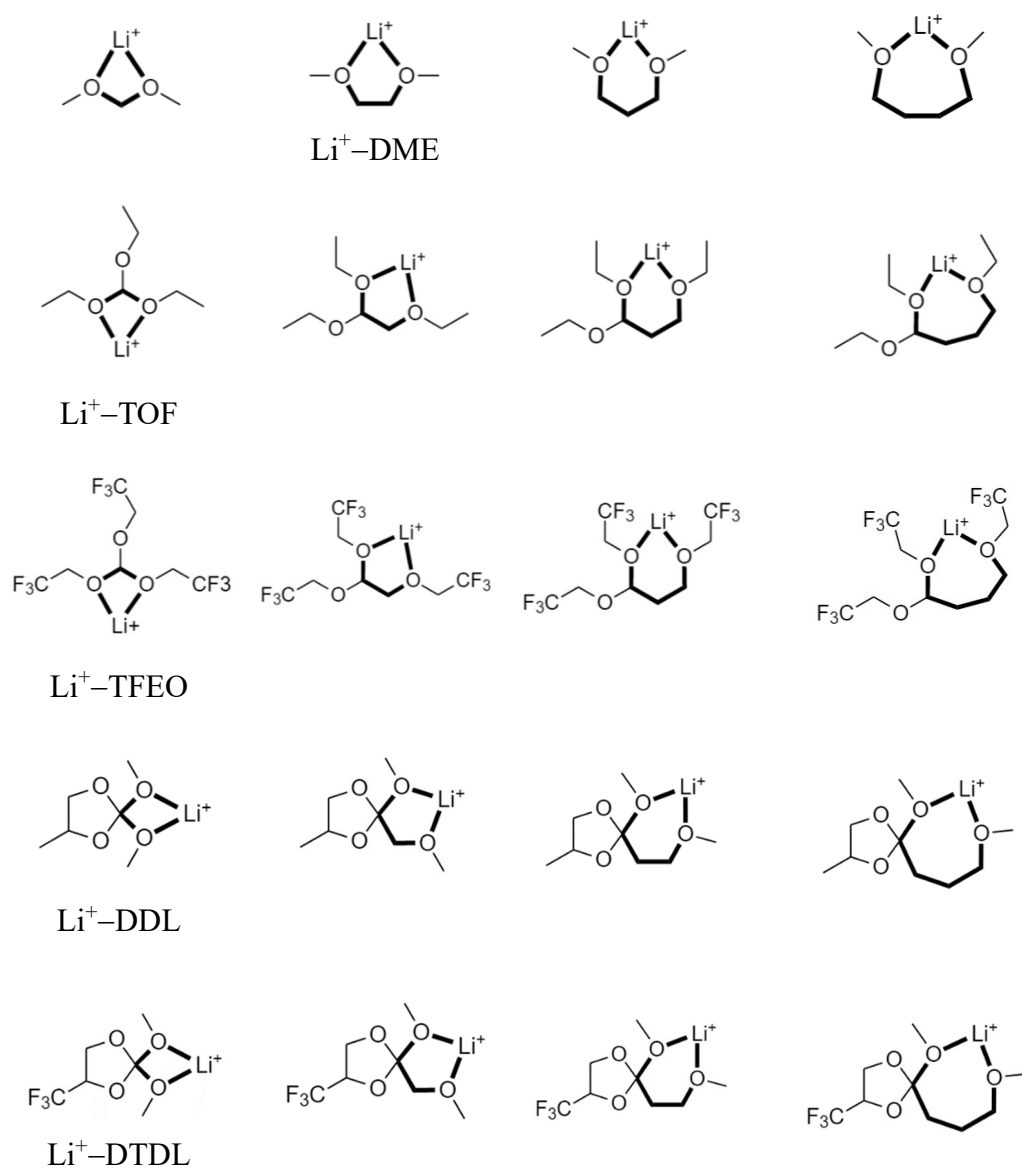


Figure S4.  $\text{Li}^+$ -coordinated structures of 4- to 7-membered 2D ring structures based on DME, TOF, TFEO, DDL, and DTDL molecules.

Table S1. The calculated Li–O–C bond angles, ring strain energies, and Li<sup>+</sup> binding energies of 4- to 7-membered ring based on (a) DME, TOF, and TFEO and (b) DME, DDL, and DTDL.

(a)					
N-membered ring		N = 4	N = 5	N = 6	N = 7
Li–O–C bond angle ( $\theta$ in degree)	DME	97.0	108.8	122.2	123.8
	TOF	97.3	110.7	119.8	122.0
	TFEO	99.1	111.7	118.0	123.2
Ring strain (kcal/mol)	DME	7.6	1.3	0.0	2.6
	TOF	3.6	0.7	0.0	2.3
	TFEO	2.7	0.3	0.0	1.4
Li <sup>+</sup> binding energy (kcal/mol)	DME	8.3	15.6	17.2	14.9
	TOF	11.5	14.4	15.1	12.7
	TFEO	3.6	6.3	6.9	5.7
(b)					
N-membered ring		N = 4	N = 5	N = 6	N = 7
Li–O–C bond angle ( $\theta$ in degree)	DME	97.0	108.8	122.2	123.8
	DDL	98.3	112.6	121.9	125.3
	DTDL	98.2	112.5	122.8	127.3
Ring strain (kcal/mol)	DME	7.6	1.3	0.0	2.6
	DDL	3.1	1.1	0.0	2.5
	DTDL	4.9	1.6	0.0	3.2
Li <sup>+</sup> binding energy (kcal/mol)	DME	8.3	15.6	17.2	14.9
	DDL	12.5	14.3	15.6	13.3
	DTDL	8.2	12.4	14.5	11.7

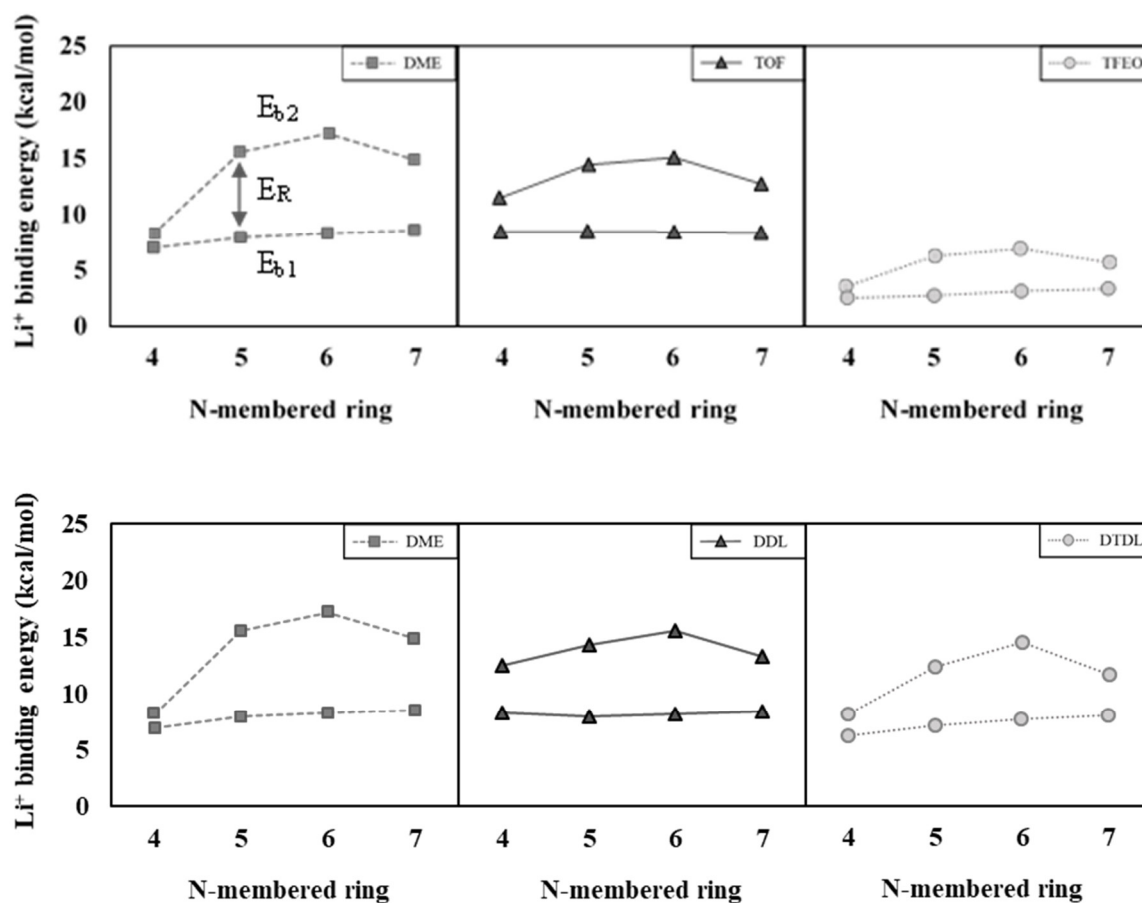


Figure S5. Comparison of one-coordinate ( $E_{b1}$ ) and two-coordinate ( $E_{b2}$ ) binding energies of 4- to 7-membered ring structures. The ring formation energy ( $E_R$ ) is the reaction energy when  $\text{Li}^+$  is converted from a one-coordinate to a two-coordinate form with the solvent molecules. Units are in kcal/mol.

Table S2. The calculated values of one ( $E_{b1}$ ) and two-coordinated ( $E_{b2}$ )  $\text{Li}^+$  binding energies, ring formation energies ( $E_R$ ) of 4- to 7-membered ring based on (a) DME, TOF, and TFEO and (b) DME, DDL, and DTDL. Units are in kcal/mol.

(a)

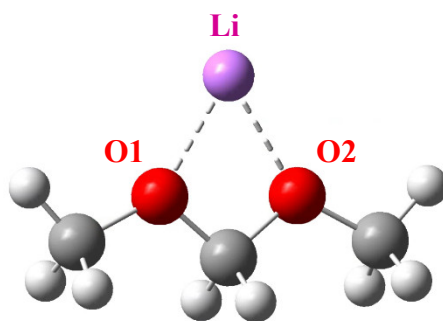
N-membered ring		N = 4	N = 5	N = 6	N = 7
DME	$E_{b1}$	7.0	7.9	8.3	8.6
	$E_R$	1.3	7.7	8.9	6.3
	$E_{b2}$	8.3	15.6	17.2	14.9
TOF	$E_{b1}$	8.5	8.5	8.4	8.4
	$E_R$	3.0	5.9	6.7	4.3
	$E_{b2}$	11.5	14.4	15.1	12.7
TFEO	$E_{b1}$	2.5	2.8	3.1	3.3
	$E_R$	1.1	3.5	3.8	2.4
	$E_{b2}$	3.6	6.3	6.9	5.7

(b)

N-membered ring		N = 4	N = 5	N = 6	N = 7
DME	$E_{b1}$	7.0	7.9	8.3	8.6
	$E_R$	1.3	7.7	8.9	6.3
	$E_{b2}$	8.3	15.6	17.2	14.9
DDL	$E_{b1}$	8.3	8.0	8.3	8.5
	$E_R$	4.2	6.3	7.3	4.8
	$E_{b2}$	12.5	14.3	15.6	13.3
DTDL	$E_{b1}$	6.2	7.2	7.7	8.1
	$E_R$	1.9	5.2	6.8	3.6
	$E_{b2}$	8.2	12.4	14.5	11.7



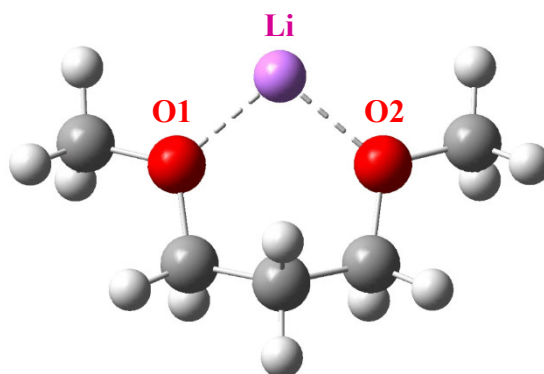
(a)



Donor (i)	Acceptor (j)	E2 <sup>a</sup> (kcal/mol)	E(j) – E(i) <sup>b</sup> (a.u.)	F(i,j) <sup>c</sup> (a.u.)
LP (1) O1	LP* (1) Li	4.92	0.77	0.06
	LP* (3) Li	2.41	0.76	0.04
LP (1) O2	LP* (1) Li	4.92	0.77	0.06
	LP* (3) Li	2.41	0.76	0.04

<sup>a</sup> E2 represent the stabilization energy.<sup>b</sup> The energy difference between donor (i) and acceptor (j) orbitals.<sup>c</sup> The interaction element between donor (i) and acceptor (j) orbitals.

(b)



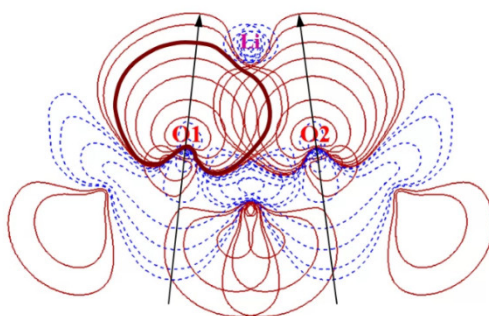
Donor (i)	Acceptor (j)	E2 (kcal/mol)	E(j) – E(i) (a.u.)	F(i,j) (a.u.)
LP (1) O1	LP* (1) Li	7.23	0.78	0.07
	LP* (2) Li	4.52	0.76	0.05
LP (1) O2	LP* (1) Li	7.23	0.78	0.07
	LP* (2) Li	4.52	0.76	0.05

Figure S6. Second order perturbation theory analysis through NBO analysis in (a) 4-membered ring and (b) 6-membered ring.

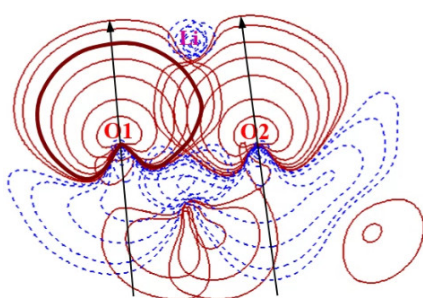
Table S3. The calculated Li–O–C bond angles and Li<sup>+</sup> binding energies of 4- to 7-membered basic ring based on TOF, cTOF, and cFTOF.

N-membered basic ring		N = 4	N = 5	N = 6	N = 7
Li–O–C bond angle ( $\theta$ in degree)	TOF	97.3	97.3	97.3	97.3
	cTOF	94.5	95.5	95.9	96.9
	cFTOF	94.5	95.8	96.1	97.2
Li <sup>+</sup> binding energy (kcal/mol)	TOF	11.5	11.5	11.5	11.5
	cTOF	5.5	8.8	11.7	13.2
	cFTOF	2.1	7.6	9.6	11.2

TOF: Low structural strain



cTOF: High structural strain



cFTOF: High structural strain

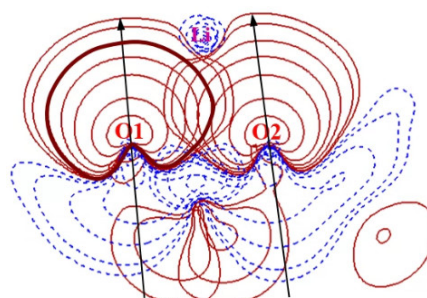
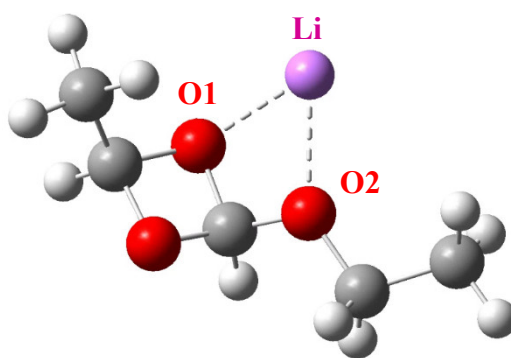


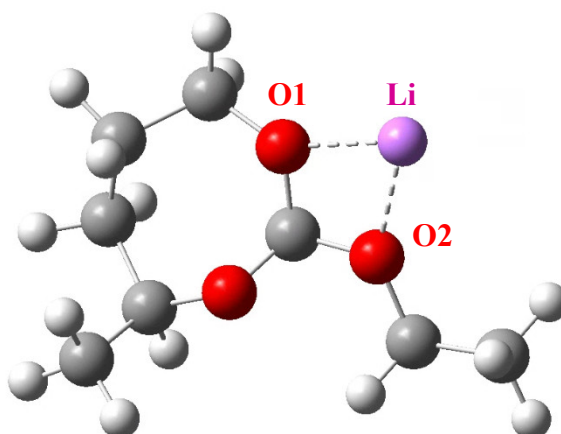
Figure S7. Contour plots of oxygen lone pair orbitals and lithium antibonding lone pair orbitals of TOF, cTOF, and cFTOF coordinated to  $\text{Li}^+$ . The black arrows represent the direction of lone pair orbitals of the oxygen binding sites. The bold red lines are the 0.020 isovalue lines of oxygen lone pair orbitals.

(a)



Donor (i)	Acceptor (j)	E2 (kcal/mol)	E(j) – E(i) (a.u.)	F(i,j) (a.u.)
LP (1) O1	LP* (1) Li	3.28	0.81	0.05
	LP* (2) Li	3.45	0.79	0.05
LP (1) O2	LP* (1) Li	4.85	0.72	0.05
	LP* (2) Li	1.43	0.70	0.03

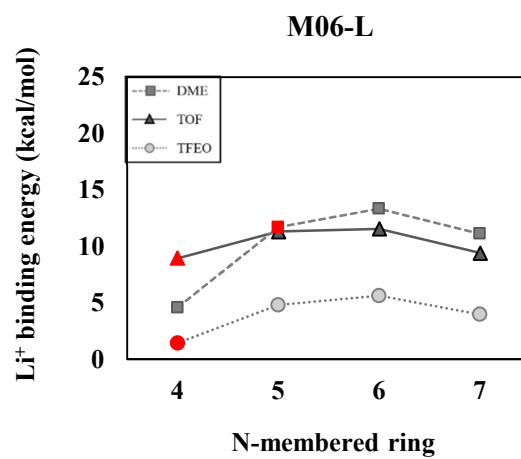
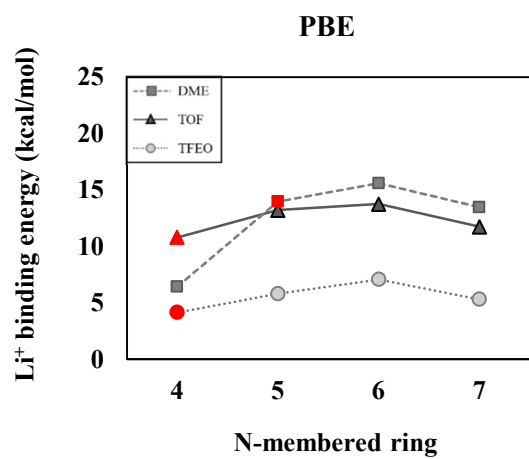
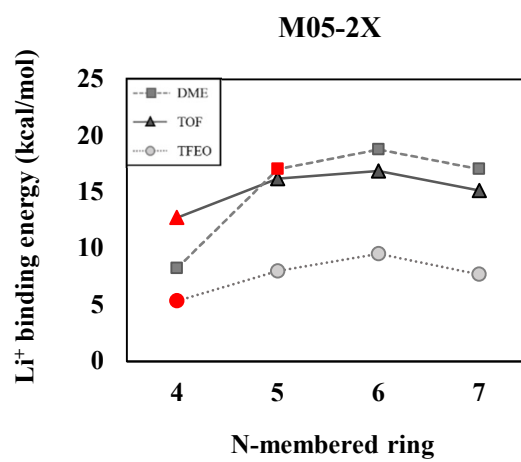
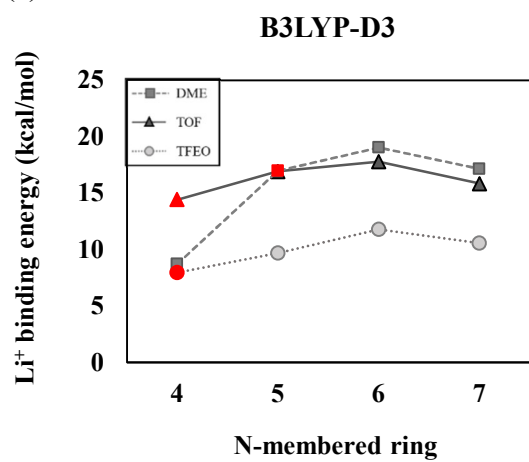
(b)



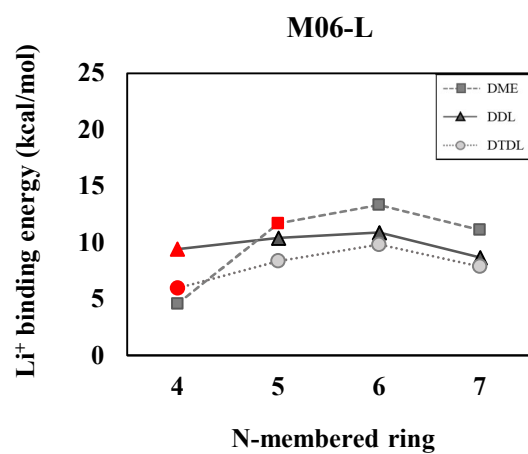
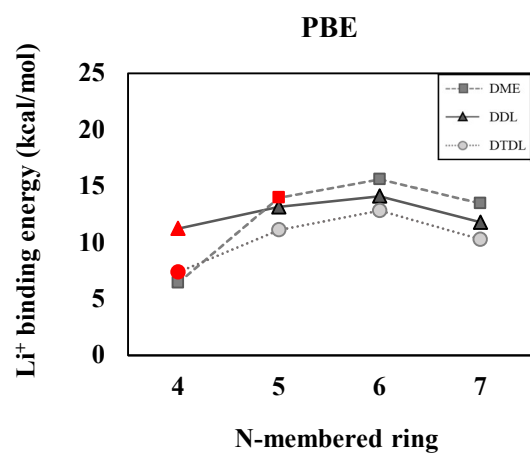
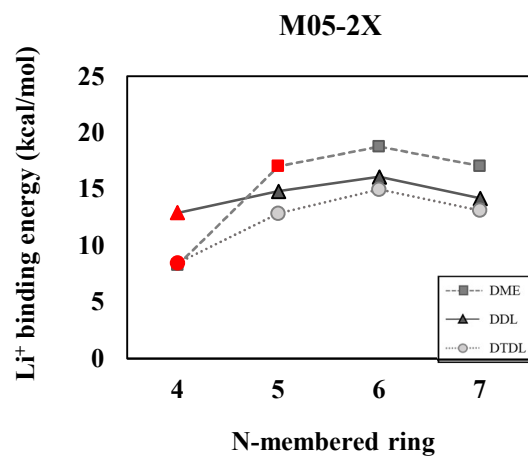
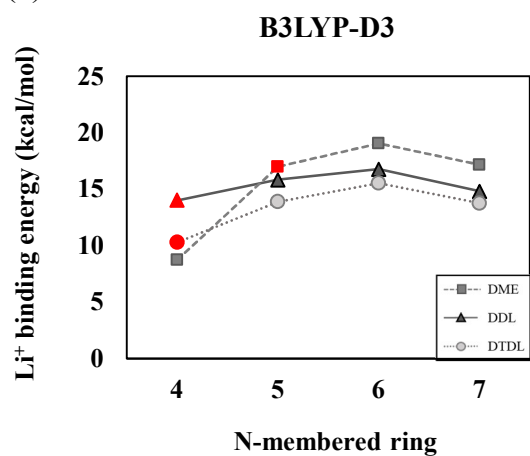
Donor (i)	Acceptor (j)	E2 (kcal/mol)	E(j) – E(i) (a.u.)	F(i,j) (a.u.)
LP (1) O1	LP* (1) Li	4.03	0.74	0.05
	LP* (2) Li	2.66	0.74	0.04
LP (1) O2	LP* (1) Li	5.64	0.75	0.06
	LP* (2) Li	1.89	0.74	0.03

Figure S8. Second order perturbation theory analysis through NBO analysis in (a) 4-membered basic ring and (b) 7-membered basic ring.

(a)



(b)



(c)

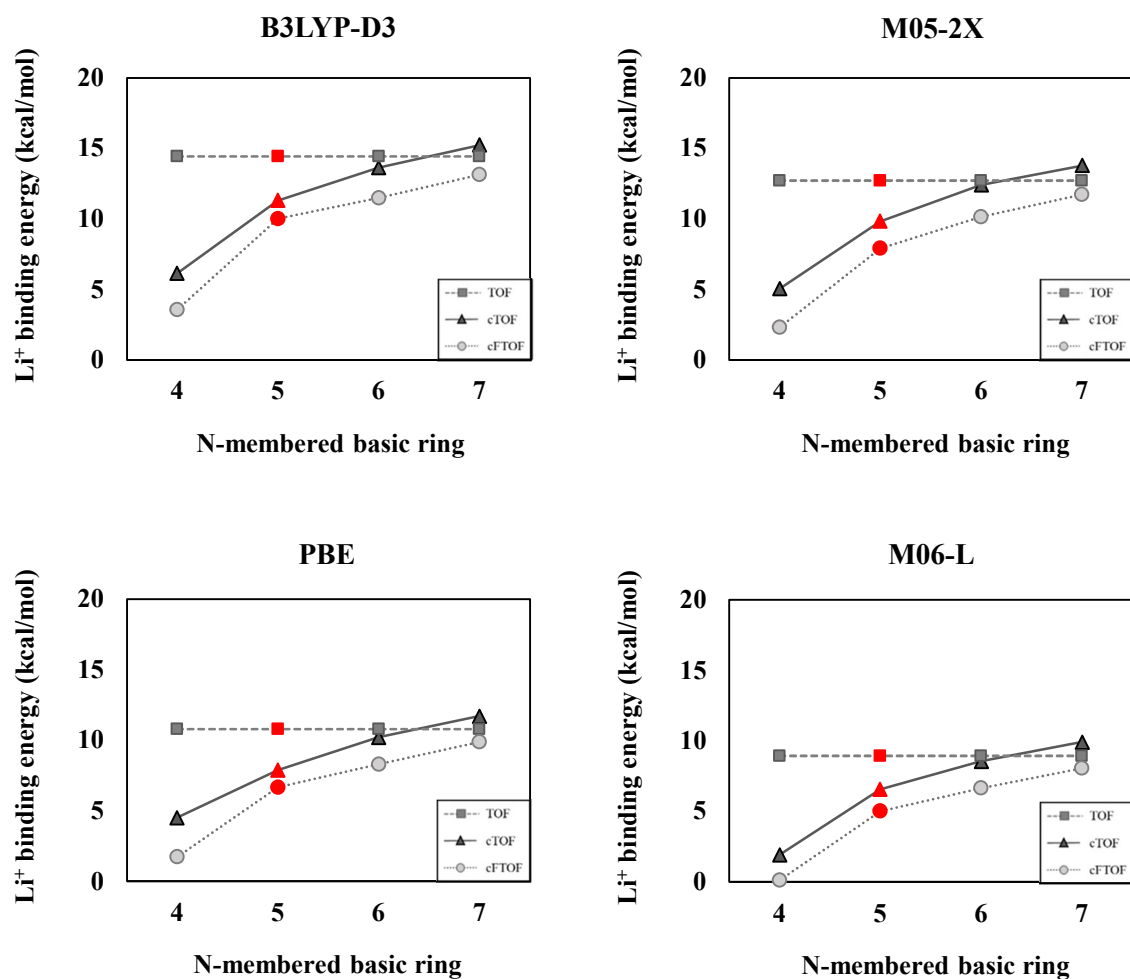


Figure S9. Calculated  $\text{Li}^+$  binding energies according to the N of (a) DME, TOF, TFEO, (b) DME, DDL, DTDL, and (c) TOF, cTOF, and cFTOF at the B3LYP-D3, M05-2X, PBE, and M06-L levels of theory. The DME, TOF, TFEO, DDL, DTDL, cTOF, and cFTOF results are highlighted in red.

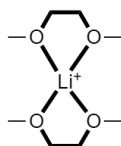
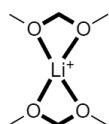
(a)

4-membered ring

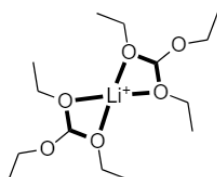
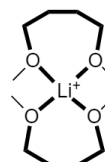
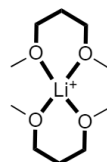
5-membered ring

6-membered ring

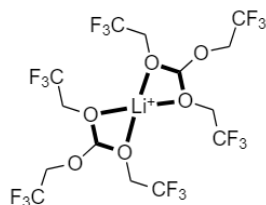
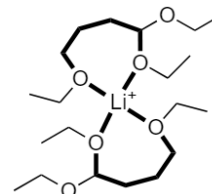
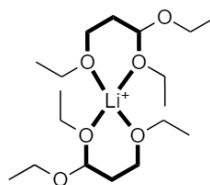
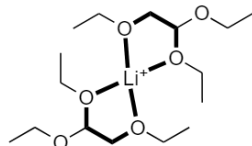
7-membered ring



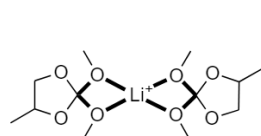
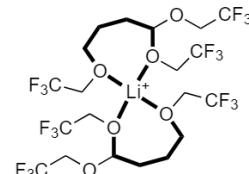
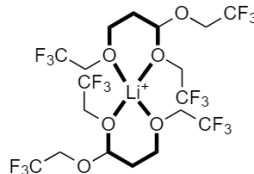
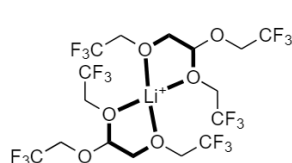
$\text{Li}^+(\text{DME})_2$



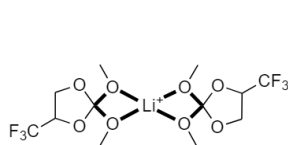
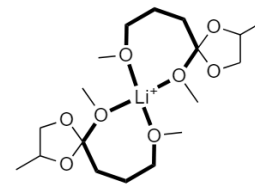
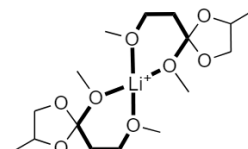
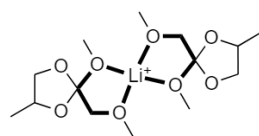
$\text{Li}^+(\text{TOF})_2$



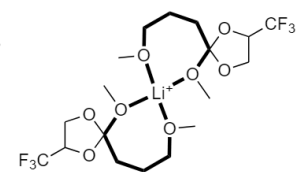
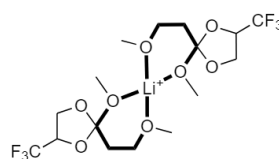
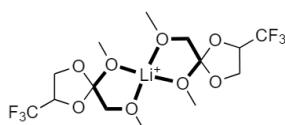
$\text{Li}^+(\text{TFEO})_2$



$\text{Li}^+(\text{DDL})_2$



$\text{Li}^+(\text{DTDL})_2$





(b)

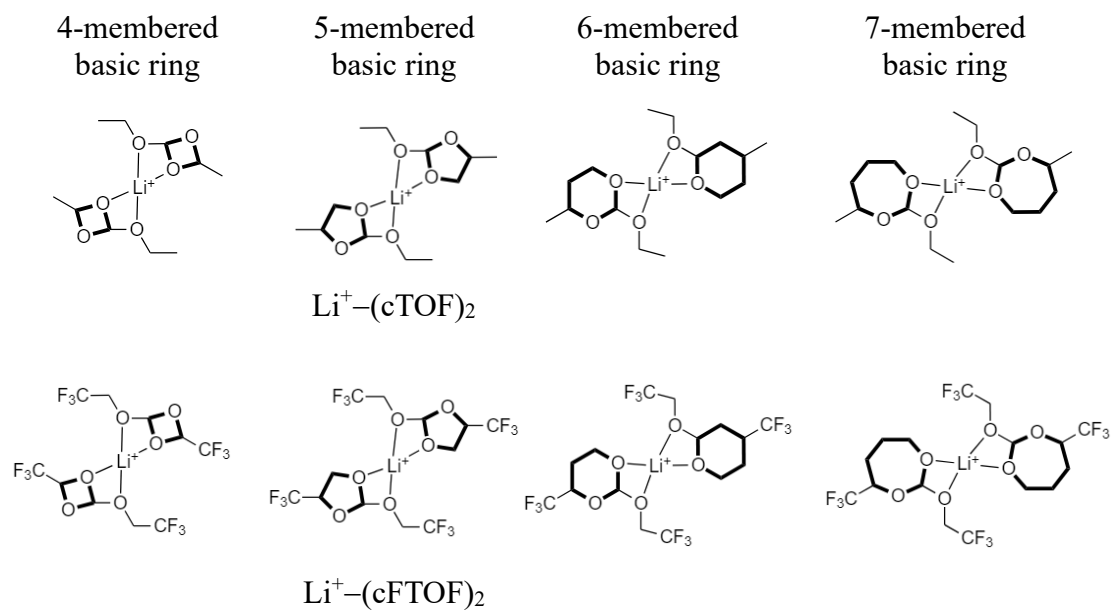


Figure S10. Two solvent-coordinated  $\text{Li}^+$  structures of 4- to 7-membered 2D ring structures based on (a) DME, TOF, TFEO, DDL, and DTDL, and (b) cTOF and cFTOF molecules.

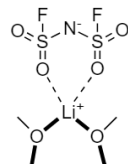
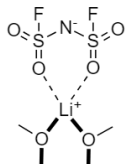
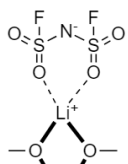
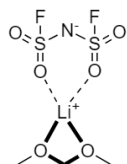
(a)

4-membered ring

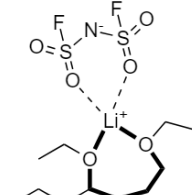
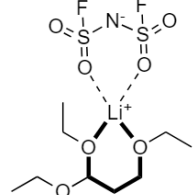
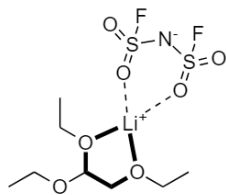
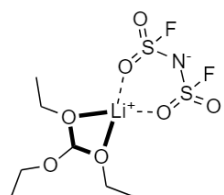
5-membered ring

6-membered ring

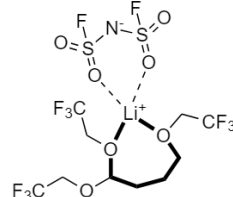
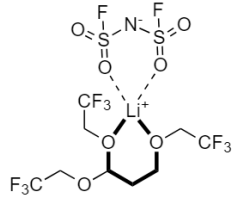
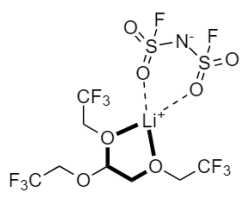
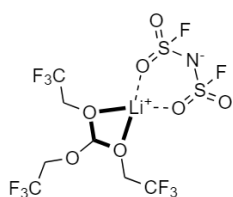
7-membered ring



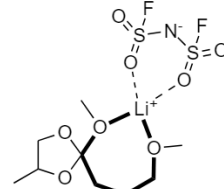
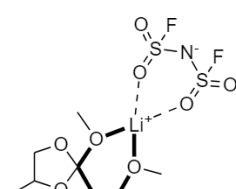
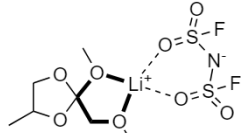
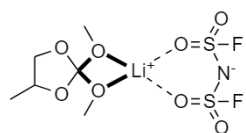
LiFSI-DME



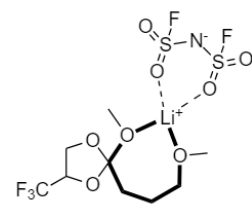
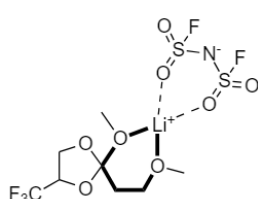
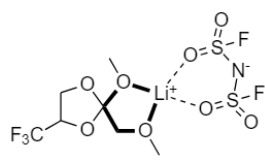
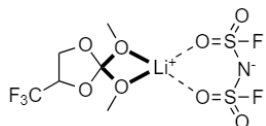
LiFSI-TOF



LiFSI-TFEO



LiFSI-DDL



LiFSI-DTDL

(b)

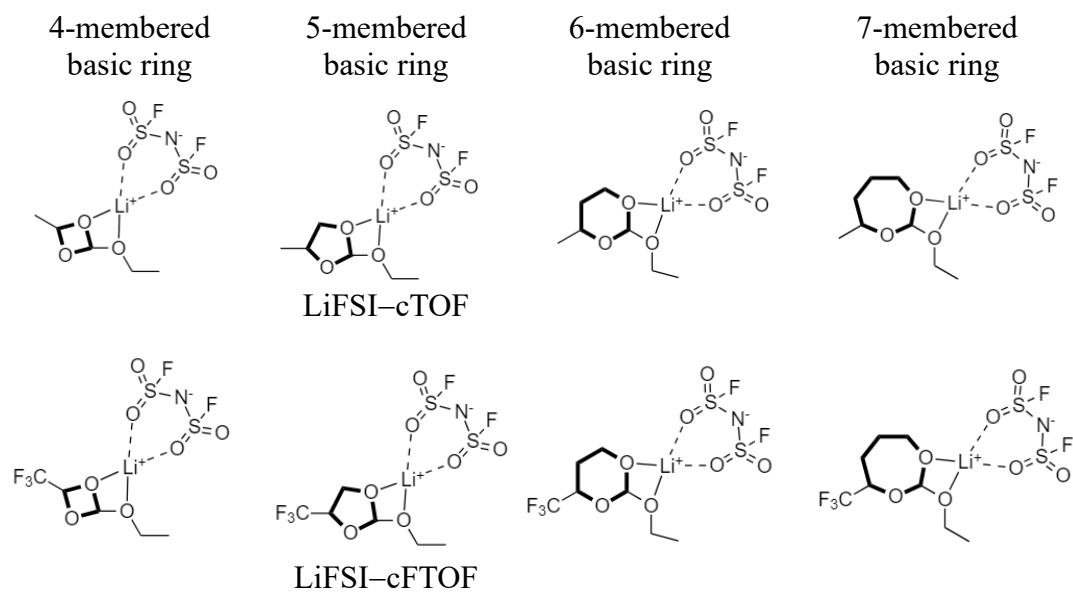
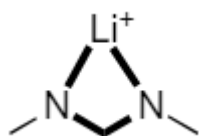
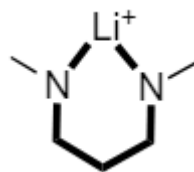


Figure S11. One solvent and FSI anion-coordinated  $\text{Li}^+$  solvation structures of 4- to 7-membered 2D ring structures based on (a) DME, TOF, TFEO, DDL, and DTDL and (b) cTOF and cFTOF molecules.

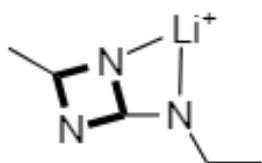
4-membered ring: 13.4



6-membered ring: 19.2



4-membered basic ring: 13.1



7-membered basic ring: 14.1

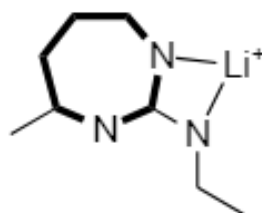


Figure S12. 2D structures and calculated  $\text{Li}^+$  binding energies of the  $\text{Li}^+$  coordinated solvent molecules where oxygens are substituted with NH groups. Units are in kcal/mol.