Electronic Supplementary Information

The fluctuating standard potential of lithium in organic solvents

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S1. *Ab initio* calculation.

The geometrical optimizations of the solvent molecule (S = H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE) as well as the $Li^+(S)_n$ clusters were performed at M06-2X/6-31+G(d) level of theory[1] with D3 dispersion correction[2] in gas phase. The optimized structures were subjected to the normal mode analyses, and ensured that no imaginary frequency presents. The calculations of Gibbs free energies of Li-ions, solvent molecule S, and $Li^+(S)_n$ cluster in the gas-phase at standard condition (P = 1 atm and T = 298.15 K) are discussed in Sec. S2. The solvation free energies ($\Delta G^*(Li^+(s))$) of Li-ion in solvent (s) was obtained by cluster-continuum model,[3] as discussed in Sec. S3. The self-solvation Gibbs free energies of the solvent molecule S in its own solvent (s), $\Delta G^*(S(s))$, and the solvation Gibbs free energies of $Li^+(S)_n$ cluster, $\Delta G^*(Li^+(S)_n(s))$, were calculated by SMD solvation model[4] at M06-2X/6-31+G(d) level of theory.[1] Table S1 lists the descriptors that characterize the solvent in SMD solvation model. All the calculations were performed with Gaussian 16 program.[5]

Table S1. The descriptors[a] of H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE, in the *ab initio* calculations with SMD solvation model.[4]

S (s)	Abbr.	ε[b]	n_D[c]	γ[d]	β[e]
Water	H_2O	78.355[6]	1.3328[6]	-[f]	-[f]
Acetonitrile	AN	35.688[6]	1.3442[6]	41.25[6]	0.32[7]
Tetramethylene sulfone	TMS	44[8]	1.496[9]	69.02[10]	0.88[7, g]
Propylene carbonate	PC	65.5[8]	4.421[9]	66.77[10]	0.45[7, h]
1,3-Dioxolane	DOL	7.34[8]	1.399[9]	46.85[10]	0.41[7, i]
Tetrahydrofuran	THF	7.4257[6]	1.4050[6]	39.44[11]	0.48[7]
1,2-Dimethoxyethane	DME	7.22[6]	1.377[6]	33.18[12]	0.41[7, i]
N,N-dimethylformamide	DMA	37.219[6]	1.4305[6]	49.56[13]	0.74[7]
Dimethyl sulfoxide	DMSO	46.826[6]	1.4783[6]	61.78[6]	0.88[14]
Tetramethylurea	TMU	74.6[8]	1.450[6]	47.51[10]	0.74[7, j]

1,2-Dichloroethane	DCE	10.125[6]	1.4448[6]	45.86[6]	0.11[7]

[a]Abraham's hydrogen bond acidity, aromaticity, and electronegative halogenicity are all set to zero in the SMD solvation mode, except for DCE, which has Abraham's hydrogen bond acidity of 0.10;[7] [b]Dielectric constant; [c]Index of refraction; [d]Surface tension (cal·mol^{-1}·Å^{-2}); [e]Abraham's hydrogen bond basicity. For a solvent with unknown β, it is taken from a solvent of similar structure with known β; [f]Not needed by SMD for water; [g]Taken from DMSO; [h]Taken from esters; [i]Taken from diethyl ether; [j]Taken from DMA.

S2. The Gibbs free energy of Li-ion, solvent molecule (S), and Li$^+$(S)$_n$ cluster in the gas-phase.

In this section, we derive the Gibbs free energy of Li-ion, solvent molecule (S), and Li$^+$(S)$_n$ cluster in the gas-phase at standard condition (P = 1 atm and T = 298.15 K), based on that described by Hill,[15] with the vibrational entropy proposed by Grimme,[16] and the gas-phase substance is 1 mole.

Assuming an ideal-gas consisting of single component of Li$^+$, solvent molecule (S), or Li$^+$(S)$_n$, the partition function is

$$Q = \frac{q^{N_\mathrm{A}}}{N_\mathrm{A}!} \tag{S1}$$

in which q denotes the partition function of an isolated Li-ion, an isolated solvent molecule (S), or an isolated Li$^+$(S)$_n$ cluster in the gas-phase, and N_A = 6.02214179×10^{23} mol^{-1} is Avogadro's constant. $N_A!$ in the denominator is the correction factor, due to the translational invariance of the identical and indistinguishable an ensemble of Li-ions, solvent molecules, or Li$^+$(S)$_n$ clusters in the gas-phase.

Neglecting the coupling among the translational, rotational, vibrational, and electronic degrees of freedom, q can be expressed as

$$q = q_\mathrm{t} \cdot q_\mathrm{r} \cdot q_\mathrm{v} \cdot q_\mathrm{e} \tag{S2}$$

in which q_t, q_r, q_v, and q_e denote the translational, rotational, vibrational, and electronic partition function, respectively, for an isolated Li-ion, an isolated solvent molecule (S), or an isolated Li$^+$(S)$_n$ cluster in the gas-phase.

From Eqs. S1 and S2, the molar Helmholtz free energy of 1 mole (N_A) Li-ions, solvent molecules, or Li$^+$(S)$_n$ is

$$A = -kT\ln Q = -RT\left(\ln\frac{q_\mathrm{t}e}{N_\mathrm{A}} + \ln q_\mathrm{r} + \ln q_\mathrm{v} + \ln q_\mathrm{e}\right) = A_\mathrm{t} + A_\mathrm{r} + A_\mathrm{v} + A_\mathrm{e} \tag{S3}$$

in which A_t, A_r, A_v, and A_e are individual contribution to A from translational, rotational, vibrational and electronic degrees of freedom, k = 1.3806503 × 10^{-23} J·K^{-1} is Boltzmann's constant,$R = N_\mathrm{A}k =$ 8.31447187 J·K^{-1}·mol^{-1} is the ideal-gas constant, and e is the base of the natural logarithm. In deriving Eq. S3, Sterling approximation, $\ln N_\mathrm{A}! = N_\mathrm{A}\ln N_\mathrm{A} - N_\mathrm{A}$ is used.

S2.1. Translational contribution.

The translational partition function q_t of an isolated ion/molecule/cluster is

$$q_\mathrm{t} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \cdot V_A = \frac{V_A}{\Lambda^3} \tag{S4}$$

in which the de Broglie wavelength is

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} \tag{S5}$$

in which h = 6.6260696 × 10^{-34} J·s is Planck's constant, m is mass of a Li-ion, a solvent molecule (S), or a Li$^+$(S)$_\mathrm{n}$ cluster. In the above equation,

$$V_A = \frac{RT}{P} = 0.02446543\ \mathrm{m}^3 \tag{S6}$$

is the molar volume of the ideal-gas at P = 1 atm and T = 298.15 K.

From Eqs. S3 and S4, the translational contribution to A is

$$A_\mathrm{t} = -RT\ln\frac{V_A e}{\Lambda^3 N_\mathrm{A}} \tag{S7}$$

in which Λ is calculated by Eq. S5 with the molecular mass of Li-ion, solvent molecule (S), or Li$^+$(S)$_\mathrm{n}$ cluster of interest. For the Li-ions, the only thermodynamic correction in the free energy is the translational contribution.

S2.2. Rotational contribution.

For a nonlinear solvent molecule (S) or Li$^+$(S)$_\mathrm{n}$ cluster, the rotational partition function is

$$q_\mathrm{r} = \frac{\pi^{1/2}}{\sigma} \cdot \left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2} \tag{S8}$$

in which the characteristic rotational (Debye) temperatures are

$$\Theta_A = \frac{h^2}{8\pi^2 I_A k}, \qquad \Theta_B = \frac{h^2}{8\pi^2 I_B k}, \qquad \Theta_C = \frac{h^2}{8\pi^2 I_C k} \tag{S9}$$

in which I_A, I_B, and I_C are the principal moments of inertia of a solvent molecule (S) or $Li^+(S)_n$ cluster, and σ is rotational symmetry number as correction to the repeated counting of the indistinguishable configurations of rotation, as given below for the point group of the solvent molecule (S) or $Li^+(S)_n$ cluster of interest in this study.

Point group	C_n, C_{nv}	S_n	T_d
σ	n	$n/2$	12

From Eqs. S3 and S8, the rotational contribution to A is

$$A_r = -RT\ln\left[\frac{\pi^{1/2}}{\sigma}\cdot\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right] \tag{S10}$$

in which the Debye temperatures were calculated by Eq. S9, with the principal moments of inertia obtained from the *ab initio* optimized configuration of the solvent molecule (S) or $Li^+(S)_n$ cluster of interest in the gas-phase.

S2.3. Vibrational contribution.

The vibrational partition function of an isolated molecule/cluster is

$$q_v = \prod_{i=1}^{3N-6} q_{i,v} \tag{S11}$$

in which i denotes the ith vibrational mode ν_i and there are totally $3N-6$ such modes for a nonlinear solvent molecule (S) or $Li^+(S)_n$ cluster consisting of N atoms. The one-dimensional vibrational partition function of ν_i in Eq. S11 is given by the harmonic approximation, *i.e.*,

$$q_{i,v} = \frac{e^{-\Phi_i/2T}}{1-e^{-\Phi_i/T}} \tag{S12}$$

in which Φ_i is the vibrational characteristic (Einstein) temperature of ν_i, *i.e.*,

$$\Phi_i = \frac{h\nu_i}{k} \tag{S13}$$

From Eqs. S3 and S11, the vibration contribution to A, using harmonic approximation, is

$$A_{v,h} = -RT\ln\prod_{i=1}^{3N-6} q_{i,v} = \sum_{i=1}^{3N-6}\left[\frac{R\Phi_i}{2} + a_{i,h}\right] \tag{S14}$$

In the above equation, the first term on the last expression is the zero-point energy (ZPE) of ν_i, and the last term is the Helmholtz free energy of ν_i, which contributes to $A_{v,h}$ as

$$a_{i,\mathrm{h}} = RT\ln\left(1 - e^{-\frac{\Phi_i}{T}}\right) = u_{i,\mathrm{h}} - Ts_{i,\mathrm{h}} \tag{S15}$$

in which $a_{i,\mathrm{h}}$, $u_{i,\mathrm{h}}$, and $s_{i,\mathrm{h}}$ are the Helmholtz free energy, internal energy, and entropy of ν_i with Harmonic approximation, respectively.

Since the harmonic approximation overestimates vibrational entropy, especially at low frequency, which is often attributed to the hindered rotation, Grimme proposed to interpolate vibrational entropy between harmonic approximation and rigid rotation,[16] *i.e.*,

$$s_{i,\mathrm{v}} = w_i s_{i,\mathrm{h}} + (1 - w_i) s_{i,\mathrm{r}} \tag{S16}$$

in which the weighting factor w_i is

$$w_i = \frac{1}{1 + (\nu_0/\nu_i)^\alpha} \tag{S17}$$

in which ν_0 = 100 cm^{-1} and α = 4 are empirically determined for the best interpolation.[16]

In Eq. S16, the harmonic vibrational contribution to $s_{i,\mathrm{v}}$ can be derived from Eq. S12, *i.e.*,

$$s_{i,\mathrm{h}} = R\ln q_{i,\mathrm{v}} + RT\left(\frac{\partial \ln q_{i,\mathrm{v}}}{\partial T}\right)_V = R\left[\frac{\Phi_i/T}{e^{\Phi_i/T} - 1} - \ln\left(1 - e^{-\Phi_i/T}\right)\right] \tag{S18}$$

Since the one-dimensional rotational partition function of frequency ν_i can be written as

$$q_{i,\mathrm{r}} = \left(\frac{\pi T}{\Theta_i}\right)^{1/2} \tag{S19}$$

in which the effective Debye temperature is

$$\Theta_i = \frac{h^2}{8\pi^2 \mu_i k} \tag{S20}$$

with the effective moment of inertia μ_i of ν_i being[16]

$$\mu_i = \frac{\mu_i' B_{\mathrm{av}}}{\mu_i' + B_{\mathrm{av}}}, \qquad and \ \ \mu_i' = \frac{h}{8\pi^2 \nu_i} \tag{S21}$$

in which B_{av} = 10^{-44} kg·m^2 corresponds to the average molecular moment of inertia and was empirically determined.[16]

From Eq. S19, the rigid rotor contribution to $s_{i,\mathrm{v}}$ in Eq. S16 is

$$s_{i,\mathrm{r}} = R\ln q_{i,\mathrm{r}} + RT\left(\frac{\partial \ln q_{i,\mathrm{r}}}{\partial T}\right)_V = \frac{R}{2}\left[1 + \ln\left(\frac{\pi T}{\Theta_i}\right)\right] \tag{S22}$$

Since $s_{i,\mathrm{h}}$ in Eq. S15 should be replaced by $s_{i,\mathrm{v}}$ in Eq. S16, as the corrected contribution to the Helmholtz free energy of ν_i proposed by Grimme,[16] $a_{i,\mathrm{h}}$ in Eq. S14 is correspondingly replaced by

$$a_{i,\mathrm{v}} = a_{i,\mathrm{h}} + Ts_{i,\mathrm{h}} - T\left[w_i s_{i,\mathrm{h}} + (1 - w_i)s_{i,\mathrm{r}}\right] = a_{i,\mathrm{h}} + (1 - w_i)T(s_{i,\mathrm{h}} - s_{i,\mathrm{r}}) \tag{S23}$$

Thus, corrected Helmholtz free energy is

$$A_{\mathrm{v,h}} = \sum_{i=1}^{3N-6}\left[\frac{R\Phi_i}{2} + a_{i,\mathrm{v}}\right] \tag{S24}$$

in which Einstein temperature can be calculated by Eq. S13, and the effective Debye temperature can be calculated by Eqs. S20 and S21, respectively, using the normal mode vibrational frequencies from the optimized structure of the solvent molecule (S) or $\mathrm{Li^+(S)_n}$ cluster of interest in the gas-phase by *ab initio* calculations.

S2.4. Electronic contribution.

For the closed shell ion/molecule/cluster with large electronic energy gap investigated in this study, only the electronic ground state is occupied with degeneracy of 1, so that the electronic partition function is

$$q_{\mathrm{e}} = e^{-\varepsilon_0/kT} \tag{S25}$$

in which ε_0 is the electronic energy of an isolated Li-ion, an isolated solvent molecule (S), or $\mathrm{Li^+(S)_n}$ cluster in the gas-phase.

From Eqs. S3 and S25, the electronic contribution to A is

$$A_{\mathrm{e}} = N_A\varepsilon_0 = E_0 \tag{S26}$$

in which the relation $N_A = R/k$ is used, and E_0 is the molar electronic energy of Li-ions, or the optimized structure of solvent molecule (S) or $\mathrm{Li^+(S)_n}$ cluster by *ab initio* calculations.

S2.5. Gibbs free energy in the gas-phase.

Once Helmholtz free energy in Eq. S3 is calculated by the individual contribution from Eqs. S7, S10, S24, and S26, Gibbs free energy can be calculated as

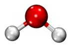
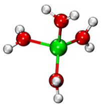
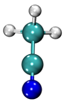
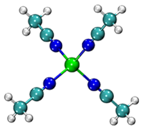
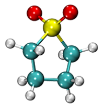
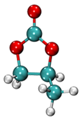
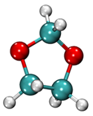
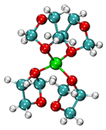
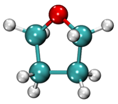
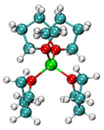
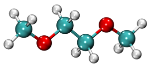
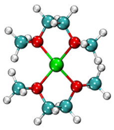
$$G = A + PV = A + RT \tag{S27}$$

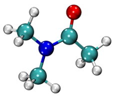
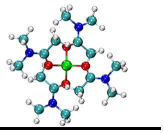
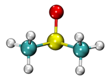
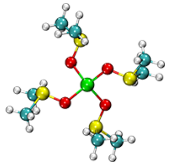
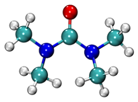
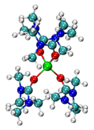
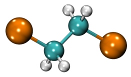
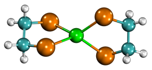
in which the relation $PV = RT$ for 1 mole ideal-gas is used.

S2.6. Gibbs free energies of Li-ion, solvent molecule (S), and Li$^+$(S)$_n$ cluster, as well as the formation Gibbs free energies of Li$^+$(S)$_n$ in the gas-phase.

Table S2 lists the Gibbs free energies of Li-ion, solvent molecule (S = H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE), and the corresponding Li$^+$(S)$_n$ clusters, obtained by *ab initio* calculation at M06-2X/6-31+G(d) level of theory[1] with D3 dispersion correction[2] in the gas-phase. According to previous study,[17] Li$^+$(S)$_n$ clusters were optimized with Li$^+$ coordinating with 4 electronegative atoms, contributed from different solvent molecules with n = 2, 3, or 4.

Table S2. Gibbs free energy of Li-ion, solvent molecule (S = H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE), and Li$^+$(S)$_n$ cluster, and the Gibbs free energy of formation of Li$^+$(S)$_n$ clusters in the gas-phase at standard condition (*P* = 1 atm and *T* = 298.15 K).

Rxn.	$G^\circ(\mathrm{Li}^+)^a$		$\mathrm{n}G^\circ(\mathrm{S})^a$	$\Delta G_f^{\circ b}$	$G^\circ(\mathrm{Li}^+(\mathrm{S})_\mathrm{n})^a$	S^c	$\mathrm{Li}^+(\mathrm{S})_\mathrm{n}{}^d$
1	Li$^+$ (*g*)	+	$4H_2O$ (*g*)	→	Li$^+$(H_2O)$_4$ (*g*)		
			C_{2v}		$C_1{}^e$		
	-7.293797		-305.519887	**-78.14**	-312.938215		
2	Li$^+$ (*g*)	+	4AN (*g*)	→	Li$^+$(AN)$_4$ (*g*)		
			C_{3v}		T_d		
			-530.697487	**-81.17**	-538.120639		
3	Li$^+$ (*g*)	+	3TMS (*g*)	→	Li$^+$(TMS)$_3$ (*g*)^f		
			C_2		C_2		
			-2116.684064	**-91.50**	-2124.123675		
4	Li$^+$ (*g*)	+	4PC (*g*)	→	Li$^+$(PC)$_4$ (*g*)		
			C_1		C_2		
			-1526.007717	**-85.34**	-1533.437513		
5	Li$^+$ (*g*)	+	4DOL (*g*)	→	Li$^+$(DOL)$_4$ (*g*)		
			C_1		S_4		
			-1072.687338	**-73.86**	-1080.098846		
6	Li$^+$ (*g*)	+	4THF (*g*)	→	Li$^+$(THF)$_4$ (*g*)		
			C_2		S_4		
			-929.012142	**-82.46**	-936.437354		
7	Li$^+$ (*g*)	+	2DME (*g*)	→	Li$^+$(DME)$_2$ (*g*)		
			C_2		C_2		
			-617.213223	**-86.13**	-624.6442827		
8	Li$^+$ (*g*)	+	4DMA (*g*)	→	Li$^+$(DMA)$_4$ (*g*)		
			C_1		S_4		

			-1150.400604	**-100.13**	-1157.853967		
9	Li^+ (*g*)	+	4DMSO (*g*)	→	$Li^+(DMSO)_4$ (*g*)		
			C_1		S_4		
			-2212.095478	**-112.77**	-2219.568984		
10	Li^+ (*g*)	+	4TMU (*g*)	→	$Li^+(TMU)_4$ (*g*)		
			C_2		C_2		
			-1528.715400	**-102.20**	-1536.172065		
11	Li^+ (*g*)	+	2DCE (*g*)	→	$Li^+(DCE)_2$ (*g*)		
			C_2		C_2		
			-1997.865796	**-51.08**	-2005.240275		

[a]*Ab initio* calculations of Li-ion, solvent molecule (S), and $Li^+(S)_n$ cluster were performed at M06-2X/6-31+G(d) level of theory[1] with D3 dispersion correction,[2] with the Gibbs free energy (a.u., and 1 a.u. = 627.5095 kcal·mol^{-1}) of $G°(\mathrm{Li}^+)$, $G°(\mathrm{S})$, and $G°(\mathrm{Li}^+(\mathrm{S})_\mathrm{n})$ in the gas-phase calculated by Eq. (S27); [b]Gibbs free energy of formation (kcal·mol^{-1}) of $\mathrm{Li}^+(\mathrm{S})_\mathrm{n}$ cluster in the gas-phase, calculated by $\Delta G_f^\circ = G°(\mathrm{Li}^+(\mathrm{S})_\mathrm{n}) - G°(\mathrm{Li}^+) - \mathrm{n}G°(\mathrm{S})$; [c]Optimized structure of the solvent molecule in the gas-phase by *ab initio* calculation. The white, cyan, blue, red, yellow, and orange balls denote hydrogen, carbon, nitrogen, oxygen, sulfur, and chlorine atoms, respectively; [d]Optimized structure of $\mathrm{Li}^+(\mathrm{S})_\mathrm{n}$ cluster in the gas-phase by *ab initio* calculation. The green ball denotes lithium atom; [e]Attempts on optimizing $Li^+(H_2O)_4$ with higher symmetry, such as C_2 and S_4, result in imaginary frequencies with M06-2X/6-31+G(d) with D3 employed in this study, though S_4 symmetry should be more reasonable;[18] [f]For $Li^+(TMS)_n$, ΔG_f° = -73.21 kcal·mol^{-1} for n = 2 with D_2 symmetry, which is much higher than that for n = 3 by 18.29 kcal·mol^{-1}. Thus, the computation of the Gibbs free energy of solvation of Li^+ in TMS was performed with $Li^+(TMS)_3$ using cluster-continuum model.[3]

S3. Thermodynamic cycle for calculating the Gibbs free energy of solvation, $\Delta G^*(\mathrm{Li}^+(s))$, of Li-ion in solvent (*s*) by cluster-continuum model.

The solvation of Li-ion from the gas-phase to solution phase can be represented by the following equilibrium,

$$\mathrm{Li}^+(g) \rightarrow \mathrm{Li}^+(s), \qquad \Delta G^*(\mathrm{Li}^+(s)) \tag{S28}$$

in which $\mathrm{Li}^+(g)$ denotes that Li-ions the gas-phase and $\mathrm{Li}^+(s)$ denotes Li-ion the solution phase of a specific solvent (s), both at condition with c_0 = 1 M and T = 298.15 K, according to the convention proposed by Ben-Naim.[19]

Though the Gibbs free energy of solvation $\Delta G^*(\mathrm{Li}^+(s))$, corresponding to Eq. S28, may be calculated directly by SMD solvation model[4] with *ab initio* calculations described in Sec. S1, the accuracy of such direct calculation is often not satisfactory due to the ionic nature of Li^+. This is because a polarizable continuum model can not fully capture the strong interactions between a bare ion and the implicit solvents.[3] In order to calculate $\Delta G^*(\mathrm{Li}^+(s))$ accurately, we further employed the cluster-continuum model,[3] because it includes explicitly the coordination structure of a solvated ion, and can remedy the nonunique definition of cavity or ion-solvent boundary in implicit solvation model.

$$\begin{tikzcd}
\mathrm{Li}^+(g) \arrow[d, "\text{Eq. S28}"', "\Delta G^*(\mathrm{Li}^+(s))"] & + & \mathrm{nS}(g) \arrow[r, dashed, "\Delta G_f^{\circ\prime}", "\text{Eq. S29}"'] \arrow[d, dashed, "\text{Eq. S30}"', "\mathrm{n}\Delta G^*(\mathrm{S}(s))"] & \mathrm{Li}^+(\mathrm{S})_\mathrm{n}(g) \arrow[d, dashed, "\text{Eq. S31}"', "\Delta G^*(\mathrm{Li}^+(\mathrm{S})_\mathrm{n}(s))"] \\
\mathrm{Li}^+(s) & + & \mathrm{nS}(s) \arrow[r, dashed, "\Delta G_f^*", "\text{Eq. S32}"'] & \mathrm{Li}^+(\mathrm{S})_\mathrm{n}(s)
\end{tikzcd}$$

Figure. S1. Thermodynamic cycle for the cluster-continuum model,[3] in which s denotes a solvent molecule (H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE) and $\mathrm{Li}^+(\mathrm{S})_\mathrm{n}$ denotes the cluster consisting of Li-ion coordinating with n solvent molecules (S), while (s) and (g) denotes the solution phase and the gas-phase, respectively. The individual reactions and the Gibbs free energies are described in the text with the corresponding equation numbers.

The calculation of $\Delta G^*(\mathrm{Li}^+(s))$ in Eq. S28 with cluster-continuum model[3] is illustrated by the thermodynamic cycle in Figure S1. Apart from Eq. S28, the other reactions in Figure S1, with the corresponding free energies, are

$$\mathrm{Li}^+(g) + \mathrm{nS}(g) \rightarrow \mathrm{Li}^+(\mathrm{S})_\mathrm{n}(g), \qquad \Delta G_f^{\circ\prime} \tag{S29}$$

$$\mathrm{nS}(g) \rightarrow \mathrm{nS}(s), \qquad \mathrm{n}\Delta G^*\big(\mathrm{S}(s)\big) \tag{S30}$$

$$\mathrm{Li}^+(\mathrm{S})_\mathrm{n}(g) \rightarrow \mathrm{Li}^+(\mathrm{S})_\mathrm{n}(s), \qquad \Delta G^*\big(\mathrm{Li}^+(\mathrm{S})_\mathrm{n}(s)\big) \tag{S31}$$

$$\mathrm{Li}^+(s) + \mathrm{nS}(s) \rightarrow \mathrm{Li}^+(\mathrm{S})_\mathrm{n}(s), \qquad \Delta G_f^* \tag{S32}$$

in which $\mathrm{Li}^+(\mathrm{S})_\mathrm{n}(g)$ is the optimized cluster in the gas-phase, with n the coordinating solvent molecules, as depicted in Table S2.

In Eq. S29, $\Delta G_f^{\circ\prime}$ is the Gibbs free energy of formation of $\mathrm{Li^+(S)_n}$ cluster in gas phase, which can be obtained by consulting Table S2, with an additional conversion, $\Delta G^{\circ\to\circ\prime}$, in order to transform from the gas-phase standard state (P = 1 atm and T = 298.15 K) to the Ben-Naim convention (c_0 = 1 M and T = 298.15 K),[19] *i.e.*,

$$\Delta G^{\circ\to\circ\prime} = RT\ln\frac{V_A}{V_0} = 1.89\ \mathrm{kcal\cdot mol^{-1}} \tag{S33}$$

in which V_A is given by Eq. S6 and $V_0 = 0.001\ \mathrm{m^3}$. Thus,

$$\Delta G_f^{\circ\prime} = \Delta G_f^{\circ} - \mathrm{n}\cdot\Delta G^{\circ\to\circ\prime} \tag{S34}$$

in which ΔG_f° is tabulated in Table S2.

The self-solvation Gibbs free energies of the solvent molecule S in its own solvent (s), $\Delta G^*\big(\mathrm{S}(s)\big)$, and the Gibbs free energy of solvation of the $\mathrm{Li^+(S)_n}$ cluster in solvent (s) $\Delta G^*\big(\mathrm{Li^+(S)_n}(s)\big)$ in Eqs. S30 and S31 were calculated with SMD solvation model,[4] using the solvent descriptors listed in Table S1. $\Delta G^*\big(\mathrm{S}(s)\big)$ can be calculated accurately with SMD solvation model for the neutral molecule within 1 kcal·mol^{-1}.[4] For the $\mathrm{Li^+(S)_n}$ cluster, since $\mathrm{Li^+}$ is embedded in the explicit n coordinating solvent molecules (S), $\Delta G^*\big(\mathrm{Li^+(S)_n}(s)\big)$ can also be calculated accurately.[20]

Eq. S32 represents a hypothesis reaction for the formation of the $\mathrm{Li^+(s)_n}$ cluster in the solvent. Assuming ideal solution, the corresponding equilibrium constant is

$$K = \frac{[\mathrm{Li^+(S)_n}]}{[\mathrm{Li^+}][\mathrm{S}]^{\mathrm{n}}} = \frac{1}{[\mathrm{S}]^{\mathrm{n}}} \tag{S35}$$

in which $[\mathrm{Li^+(S)_n}] = [\mathrm{Li^+}] = 1$ M for the concentration corresponding to the standard state of solution, and $[\mathrm{S}]$ is the concentration of the solvent. Neglecting the change of volume on dissolving $\mathrm{Li^+}$ salt, $[\mathrm{S}]$ remains the same as that of the neat solvent, *i.e.*,

$$[\mathrm{S}] = \frac{\rho_s}{M_s} \tag{S36}$$

in which ρ_s and M_s are the mass density of the neat solvent[21] and the molar mass of the solvent, respectively. Thus, the corresponding Gibbs free energy of formation of $\mathrm{Li^+(S)_n}$ cluster in solution for the reaction in Eq. S32 is

$$\Delta G_f^{*} = -RT\ln K = \mathrm{n}RT\ln[\mathrm{S}] \tag{S37}$$

Since the reference standard state in solution corresponds to c_0 = 1 M, $\ln[\mathrm{S}]$ is understood to be dimensionless since the unit of the concentration in M is cancel with that of the standard state.

As demonstrated in Figure S1, Eq. S28 can be represented by

$$\mathrm{Eq.\,S28} = \mathrm{Eq.\,S29} - \mathrm{Eq.\,S30} + \mathrm{Eq.\,S31} - \mathrm{Eq.\,S32},$$

the corresponding $\Delta G^{*}(\mathrm{Li}^{+}(s))$ in a solvent (s = H_2O, AN, TMS, PC, DOL, THF, DME, DMA, DMSO, TMU, and DCE) can be calculated by

$$\Delta G^{*}\big(\mathrm{Li}^{+}(s)\big) = \Delta G_f^{\circ\prime} - \mathrm{n}\cdot\Delta G^{*}\big(\mathrm{S}(s)\big) + \Delta G^{*}\big(\mathrm{Li}^{+}(\mathrm{S})_{\mathrm{n}}(s)\big) - \Delta G_f^{*} \qquad \text{(S38)}$$

in which $\Delta G_f^{\circ\prime}$ and ΔG_f^{*} are given by Eqs. S34 and S37, respectively, and $\Delta G^{*}\big(\mathrm{S}(s)\big)$ and $\Delta G^{*}\big(\mathrm{Li}^{+}(\mathrm{S})_{\mathrm{n}}(s)\big)$ are calculated by the SMD solvation model[4] using the solvent descriptors listed in Table S1.

Table S3 lists the Gibbs free energies of the individual reactions corresponding to the thermodynamic cycle in Figure S1. It is of interest to note that $\Delta G^{*}(\mathrm{Li}^{+}(\mathrm{S})_{\mathrm{n}}(s))$ of THF, DME, DMA, DMSO, and TMU are very similar, and such observation is in agreement with TATB assumption,[22] in the sense that the Gibbs free energy of solvation of a bulk ion with embedded ionic center surrounded by large neutral functional groups are insensitive to the solvent. Meanwhile, an accurate gas-phase Gibbs free energy of formation, $\Delta G_f^{\circ\prime}$, is important for the calculation of $\Delta G^{*}(\mathrm{Li}^{+}(s))$ with the cluster-continuum model.[23]

Table S3. $\Delta G_f^{\circ\prime}$, $\Delta G^{*}(\mathrm{S}(s))$, $\Delta G^{*}(\mathrm{Li}^{+}(\mathrm{S})_{\mathrm{n}}(s))$, ΔG_f^{*}, and $\Delta G^{*}(\mathrm{Li}^{+}(s))$ in (kcal·mol^{-1}), corresponding the reactions in the thermodynamic cycle in Figure S3.

S (s)	$\Delta G_f^{\circ\prime a}$	$\Delta G^{*}(\mathrm{S}(s))^{b}$	$\Delta G^{*}(\mathrm{Li}^{+}(\mathrm{S})_{\mathrm{n}}(s))^{b}$	ΔG_f^{*c}	$\Delta G^{*}(\mathrm{Li}^{+}(s))^{d}$
H_2O	-85.70	-9.56	-64.15	9.51	-121.12
AN	-88.73	-6.51	-45.60	6.99	-115.3
TMS	-97.17	-12.63	-53.09	4.19	-116.6
PC	-92.90	-9.41	-50.53	5.85	-111.6
DOL	-81.42	-4.12	-42.91	6.31	-114.2
THF	-90.02	-4.26	-41.46	5.94	-120.4
DME	-89.91	-4.70	-40.89	2.68	-124.1
DMA	-107.69	-7.72	-41.16	5.64	-123.6
DMSO	-120.33	-8.76	-41.46	6.27	-133.0
TMU	-109.76	-8.76	-41.84	5.03	-121.6
DCE	-54.86	-7.52	-52.31	3.01	-95.14

[a]Eq. S34; [b]Calculated by SMD solvation model[4] at M06-2X/6-31+G(d) level of theory,[1] using the gas-phase optimized structure at the same level of theory; [c]Eq. S37; [d] Eq. S38.

S4. $\Delta_{\mathrm{fus}}S$ of the solvent.

The melting of solvent (s) is the equilibrium between solid and liquid phases, *i.e.*,

$$s(solid) \rightarrow s(liquid) \tag{S39}$$

Since the chemical potentials of $s(solid)$ and $s(liquid)$ are equal at the melting point, the Gibbs free energy of fusion $\Delta_{\text{fus}}G$ is zero, i.e.,

$$\Delta_{\text{fus}}G = \Delta_{\text{fus}}H - T_{\text{fus}}\Delta_{\text{fus}}S = 0 \tag{S40}$$

in which $\Delta_{\text{fus}}H$ is the enthalpy of fusion of solvent (s), and T_{fus} is the melting point, both of which can obtained by check NIST chemistry webbook,[21] and listed in Table S4. From Eq. S40, the entropy of fusion of solvent (s) $\Delta_{\text{fus}}S$ can be calculated by

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} \tag{S41}$$

The calculated $\Delta_{\text{fus}}S$ of different solvent (s), along with $\Delta_{\text{fus}}H$ and T_{fus}, are listed in Table S4.

Table S4. List of $\Delta_{\text{fus}}H$, T_{fus}, and $\Delta_{\text{fus}}S$ of solvent (s).

s	$\Delta_{\text{fus}}H^{a}$	$T_{\text{fus}}{}^{b}$	$\Delta_{\text{fus}}S^{c}$
H_2O	1.44	273.2	5.27
AN	1.95	229.3	8.52
TMS	0.33	301.7	1.09
PC	2.14	220.3	9.72
DOL	1.57	175.9	8.93
THF	2.04	164.8	12.39
DME	3.00	203.9	14.72
DMA	2.44	254.2	9.59
DMSO	3.35	291.7	11.77
TMU	3.43	272.1	12.30
DCE	2.11	273.2	7.72

[a]Enthalpy of fusion (kcal·mol^{-1});[21] [b]Melting temperature (K);[21] [c]Entropy of fusion by Eq. S41 (cal ·mol^{-1}·K^{-1}).

S5. The physical meaning of the fitting parameters in Eqs. (4) and (5) in the main text.

As shown in the inset of Fig. 2 in the main text, the fitted $b = 3.05$ may be considered as the effective coordination number of the solvents. Though different solvent may favour different coordination number as demonstrated in Table S2, it is not easily justified *a priori*. We thus adopt a universal b, and suggest to use the modified donor number by entropy of solvation, i.e., DN' defined in Eq. (4) in the main text, as indicator of $\Delta G^{*}(\text{Li}^{+}(s))$ or $E^{\ominus}(\text{Li/Li}^{+}(s))$.The correlation between the newly defined DN' and $\Delta G^{*}(\text{Li}^{+}(s))$ or $E^{\ominus}(\text{Li/Li}^{+}(s))$ is reflected in the fitness of Eq. (5) in the main text, as shown in Fig. 2 in the main text.

In Tables S1 – S4, we also list the relevant parameter of DCE as well as the computed $\Delta G^*(\mathrm{Li}^+(\mathrm{DCE}))$, though it is not generally adopted as solvent in lithium-metal battery. Since DCE is defined to be the reference with $DN(\mathrm{DCE}) = 0$ kcal·mol^{-1},[24] it may be employed to understand the physical meaning of the fitting parameters of $a = -0.81$ and $c = -106.33$ kcal·mol^{-1}. Taking $\Delta_{\mathrm{fus}}S(\mathrm{DCE}) = 7.72$ cal·mol^{-1}·K^{-1} from Table S4, $DN'(\mathrm{DCE}) = -7.02$ kcal·mol^{-1} according to Eq. (4) in the main text with $T = 298.15$ K. Further applying a, b, and $DN'(\mathrm{DCE})$ in Eq. (5) in the main text, we have the extrapolated Gibbs free energy of solvation of Li$^+$ in DCE, $\Delta G^*(\mathrm{Li}^+(\mathrm{DCE})) = -100.64$ kcal·mol^{-1}, which is in accord with the computed $\Delta G^*(\mathrm{Li}^+(\mathrm{DCE})) = -95.14$ kcal·mol^{-1} in Table S3. From the above observation, the physical meaning of c may be attributed to the enthalpy of solvation of Li$^+$ in DCE. For fitted a = –0.81, is the universal scaling parameter that measures the negative relation between DN' and $\Delta G^*(\mathrm{Li}^+(s))$. Though the physical meaning needs more in-depth understanding, it reflects the negative correlation between $DN'$and $\Delta G^*(\mathrm{Li}^+(s))$ or $E^{\ominus}(\mathrm{Li/Li}^+(s))$.

Based on the above discussion, it can be seen that while DN proposed by Gutmann[24] is a measure of the Lewis basicity of a solvent in terms of enthalpy of solvation, DN' measures Lewis basicity of a solvent in terms of Gibbs free energy of solvation. Thus, it is reasonable that the correlation between DN' and $\Delta G^*(\mathrm{Li}^+(s))$ or $E^{\ominus}(\mathrm{Li/Li}^+(s))$ is improved, and a higher DN' correlates with more negative $\Delta G^*(\mathrm{Li}^+(s))$ as well as $E^{\ominus}(\mathrm{Li/Li}^+(s))$ in an unambiguous manner.

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