

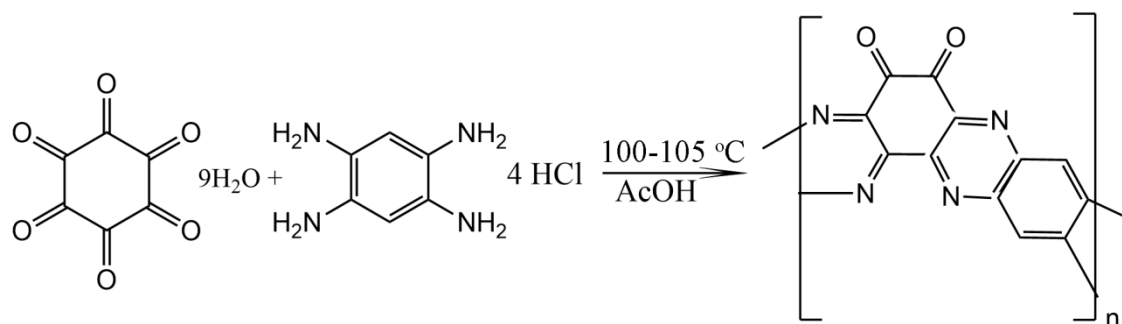
Electronic supplementary information

Influence of the Lithium Cation Desolvation Process at the Electrolyte/Electrode Interface on the Performance of Lithium Batteries

Olga V. Yarmolenko, Guzaliya R. Baymuratova, Kyunsylu G. Khatmullina, Galiya Z. Tulibaeva, Alena V. Yudina, Tatiana A. Savinykh, Igor K. Yakushchenko, Pavel A. Troshin, and Alexander F. Shestakov

Table of Contents

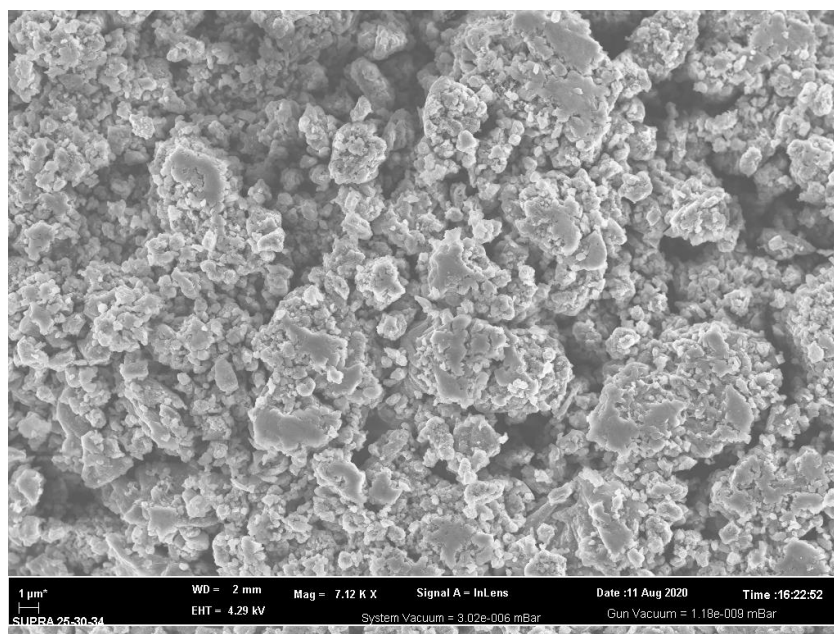
Scheme S1 Synthesis of PTTA	2
Figure S1 SEM images of the as-prepared PTTA powder at various scales: 1 μm (a); 200 nm (b)	3
Table S1 Structures and properties of the investigated solvents	4
Theoretical analysis	5
Figure S2 Calculated structures of the ion pairs $[\text{Li}^+(\text{DMC})_4] [\text{PF}_6^-]$ (a); $[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ (b)	6
Figure S3 Calculated structures of complexes $\text{PTTA4}[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]$ (a); $\text{PTTA4}[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ (b)	7
Figure S4 Calculated structure of complex $\text{PTTA4}\{[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]\}_2$	8
Figure S5 Calculated structures of complexes $(\text{PTTA3})_3[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]$ (a); $(\text{PTTA3})_3 [\text{Li}^+\text{G4}] [\text{PF}_6^-]$ (b)	9
Table S2 Calculated specific metalation energies ΔE_n of PTTA2 oligomer in eV	12
Figure S6 Calculated structures of the isomers $\text{PTTA2}(\text{Li})_2$ with Li atoms coordinated at (N,N) (a); (O,O) (b); (O,N) (c) and (N,O) chelate knot	13
Figure S7 Calculated structures of $\text{PTTA2}(\text{Li})_4$ (a) and $\text{PTTA2}(\text{Li})_6$ (b)	14
Figure S8 Calculated structures of dimers $[\text{PTTA2}(\text{Li}_4)]_2$ (a) and $[\text{PTTA2}(\text{Li}_6)]_2$ (b)	15



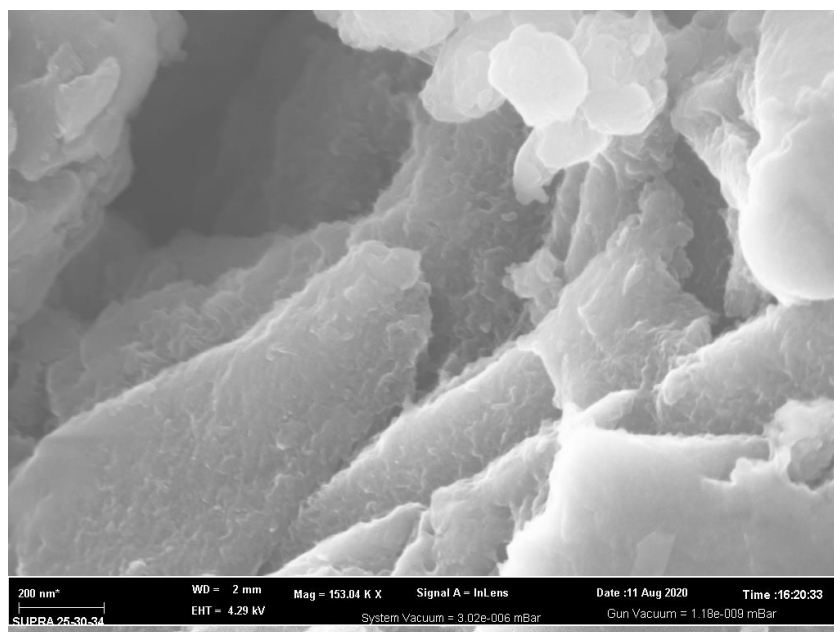
Scheme S1 Synthesis of PTTA

Synthesis of PTTA

A suspension of benzene-1,2,4,5-tetramine tetrahydrochloride and cyclohexane-1,2,3,4,5,6-hexone nonahydrate (both 4 mmol) in glacial acetic acid (50 ml) was heated to 50°C for 1 h, then anhydrous sodium acetate (16 mmol) was added, and the reaction mixture was stirred at 105-110°C for 5 h more. After cooling, water (50 ml) was added. The dark brown precipitate was filtered off and washed with water, DMF, methanol, and acetone. The resulting powder was dried *in vacuo* at 150°C for 5 h more. The target product (PTTA) was obtained in a yield of 72%.



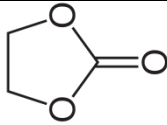
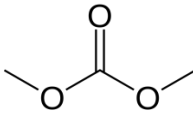
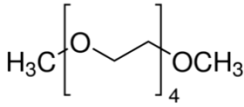
(a)



(b)

Figure S1 SEM images of the as-prepared PTTA powder at various scales: 1 μm (a); 200 nm (b)

Table S1 Structures and properties of the investigated solvents

Solvent	Solvent structure	T _{boil} , °C	T _{flesh} , °C	Viscosity, η , mPa·c	Dielectric constant
Dimethyl carbonate (DMC)		90	18	0.592	3.1
Ethylene carbonate (EC)		248	150	1.93	90
Tetraglyme (G4)		276	141	3.3-4.1	7.8

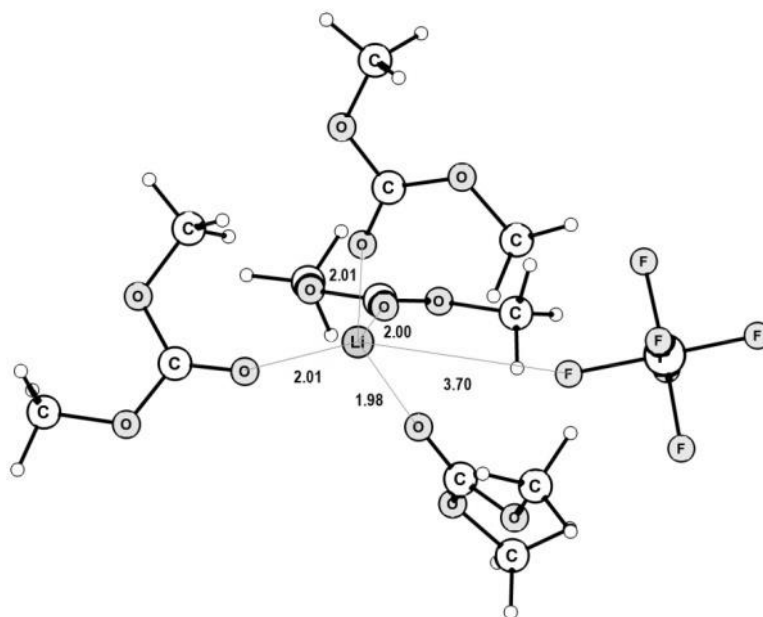
Theoretical analysis

To understand reasons for the fundamental difference in the behavior of PTTA in the first cycle in various solvents, we considered the interaction of model oligomers with Li^+ ions with solvate shells and ion pairs, including the PF_6^- counterion. The structures of the initial ion pairs $[\text{Li}^+(\text{DMC})_4] [\text{PF}_6^-]$ and $[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ are shown in Figure S2.

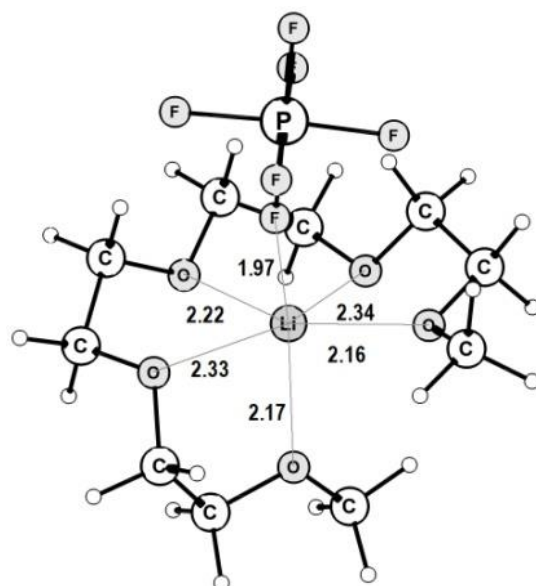
The dissociation energy of the ion pairs $\text{Li}^+(\text{DMC})_4 [\text{PF}_6^-]$ and $[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ is 66.5 and 74.2 kcal/mol, respectively. This difference is caused by the closer arrangement of Li^+ and the counterion in the solvate complex, which includes the G4 tetraglyme molecule, whose donor O atoms screen the Li^+ ion to a lesser extent.

The PTTA oligomers were used for quantum chemical modeling of processes at the electrolyte/electrode interface. The broken bonds were replaced by H atoms or NH_2 groups. A preliminary calculation showed that the electron affinity is 2.40, 3.41, and 4.25 eV for the oligomers with 1, 2, and 4 units with two terminal NH_2 groups, respectively. The replacement of the terminal NH_2 groups by H atoms has practically no effect on the electron affinity, which is 4.17 and 4.46 eV for the three-unit PTTA3 and four-unit PTTA4 oligomers, respectively. That is, the electron affinity, which is a key characteristic for redox processes, is saturated at 3-4 PTTA units.

There are two types of chelate sites in the PTTA4 molecules, and the coordination of the lithium ion over the N and O atoms is energetically preferable. The structures of the $\text{PTTA4}[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]$ and $\text{PTTA4}[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ complexes are shown in Figure S3.

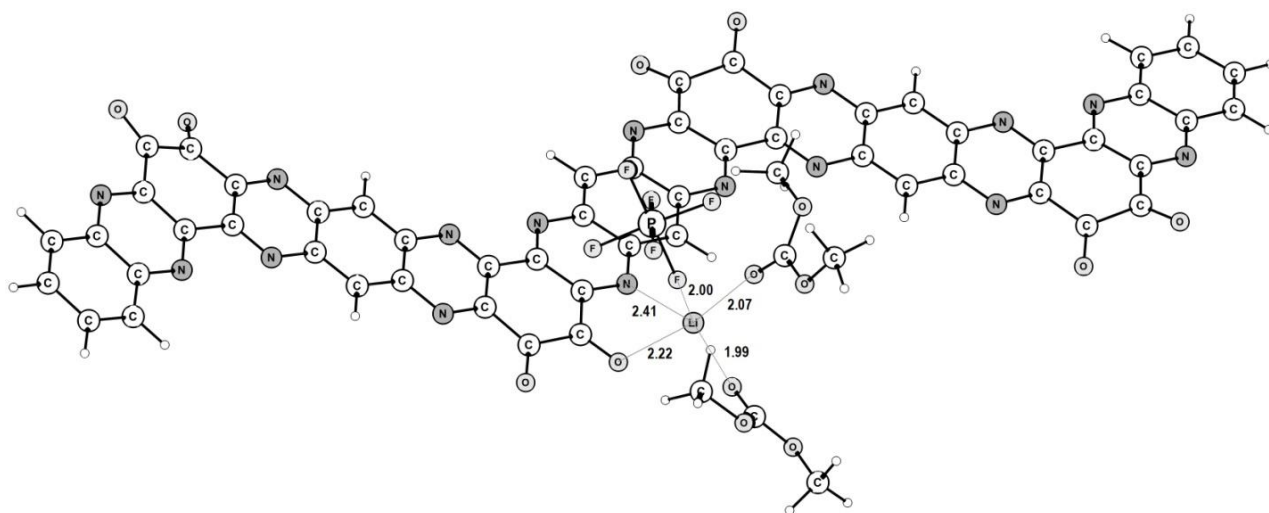


(a)

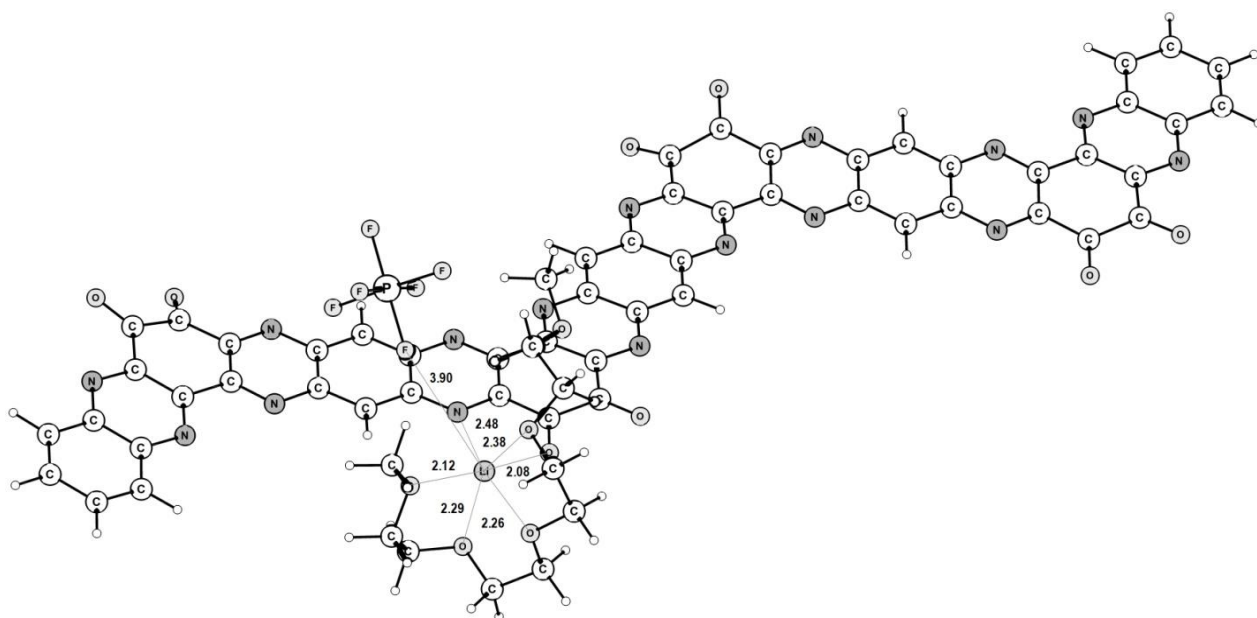


(b)

Figure S2 Calculated structures of the ion pairs $[\text{Li}^+(\text{DMC})_4][\text{PF}_6^-]$ (a); $[\text{Li}^+\text{G4}][\text{PF}_6^-]$ (b)



(a)



(b)

Figure S3 Calculated structures of complexes PTTA4[Li⁺(DMC)₂] [PF₆⁻] (a); PTTA4[Li⁺G4] [PF₆⁻] (b)

Reactions of the formation of these complexes



slightly differ in energy but differ strongly in the change in entropy, since the number of particles increases by 1 in the first case and decreases by 1 in the second case. Based on Trouton's rule, it can be estimated that the entropy contribution to the free energy from the motion of a molecule

as a whole in a condensed medium is approximately 5.5 kcal/mol at room temperature. This estimate indicates that the change in the Gibbs free energy is noticeably negative (-9.8 kcal/mol) in the first case and positive (+5.2 kcal/mol) in the second case. Thus, it is only in a carbonate solvent where the possibility of strong chemisorption of ion pairs on the chelate sites of PTTA arises.

The attachment of the second ion pair to PTTA4 has practically no effect on the lengths of coordination bonds for the Li^+ ion (see Figure S4), and the addition reaction energy also changes slightly.

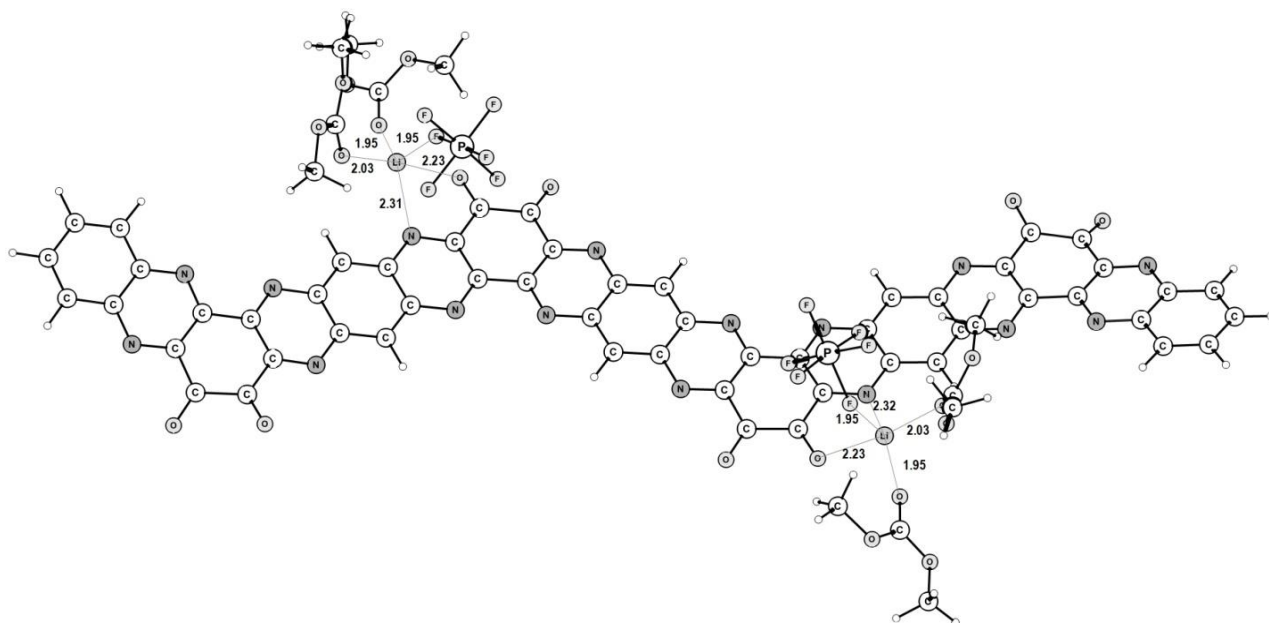
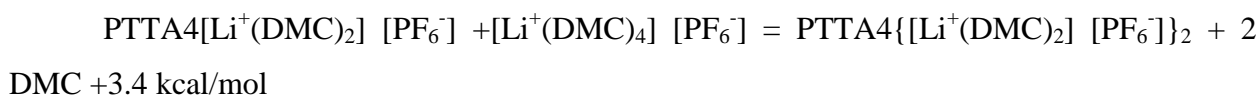
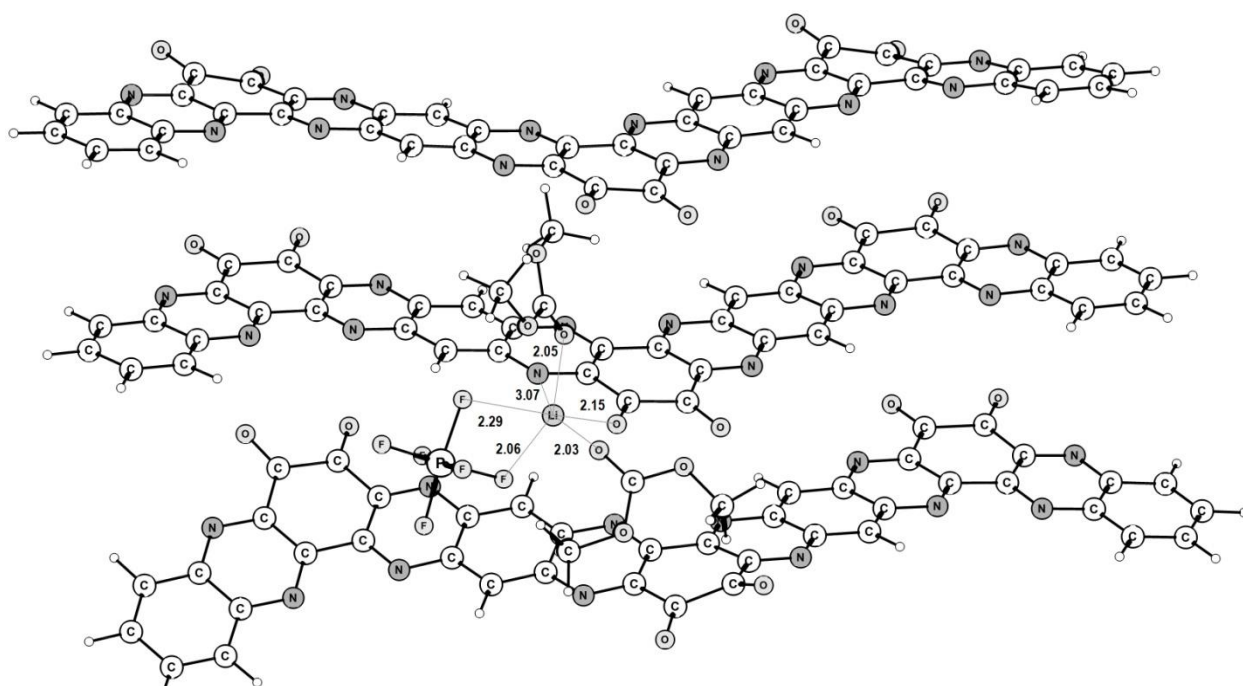
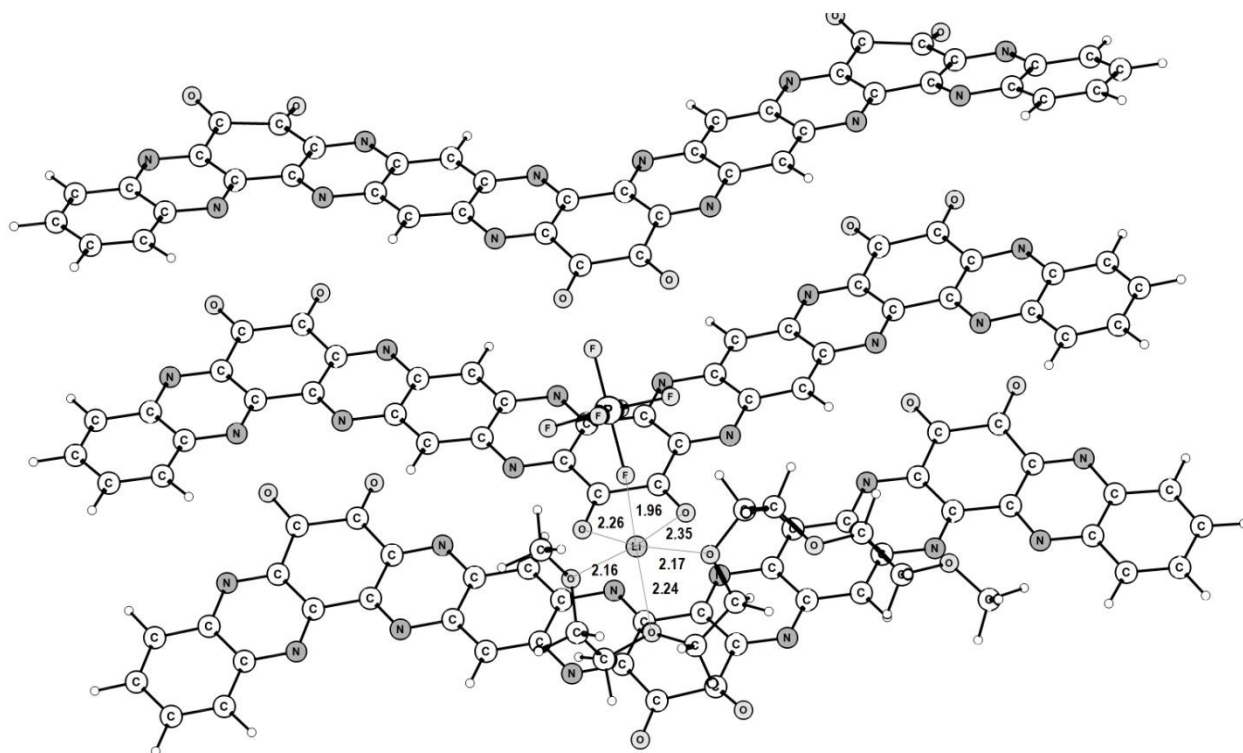


Figure S4 Calculated structure of complex $\text{PTTA4}\{[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]\}_2$

The tape PTTA polymers are stacked with an offset (Figure 8). The calculated energy of formation of the $(\text{PTTA3})_3$ trimer from three PPTA3 oligomers is 25.6 kcal/mol, or 12.8 kcal/mol per one pair interaction on the average. To study the possible effect of neighboring molecules in the stack, we considered the coordination of ion pairs to the internal molecule in the stack $(\text{PTTA3})_3$. The structures of complexes $(\text{PTTA3})_3[\text{Li}^+(\text{DMC})_2] [\text{PF}_6^-]$ and $(\text{PTTA3})_3[\text{Li}^+\text{G4}] [\text{PF}_6^-]$ are shown in Figure S5.



(a)

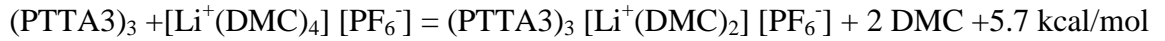


(b)

Figure S5 Calculated structures of complexes $(\text{PTTA3})_3[\text{Li}^+(\text{DMC})_2][\text{PF}_6^-]$ (a); $(\text{PTTA3})_3[\text{Li}^+\text{G4}][\text{PF}_6^-]$ (b)

The Li-N distances in $(\text{PTTA3})_3[\text{Li}^+(\text{DMC})_2][\text{PF}_6^-]$ increase from 3.48 to 3.07 Å due to steric hindrances. In this case, the loss of the coordination interaction with the N atom is

compensated by the transition to the bidentate coordination of the anion with Li-F distances of 2.29 and 2.08 Å. In the (PTTA3)₃ [Li⁺G4] [PF₆⁻] complex, the coordination of Li⁺ at two carbonyl groups becomes the most favorable, and only three coordination bonds with the O atoms of the tetraglyme molecule remain due to steric hindrances. In this case, the PF₆⁻ anion enters the inner coordination sphere, and the Li-F distance decreases from 3.90 to 1.96 Å. Despite these structural differences, the energy effect in the coordination of ion pairs changes slightly.



Therefore, the cardinal influence of the entropy factor does not change qualitatively.

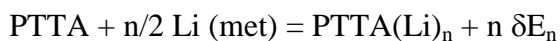
Thus, it can be assumed that when a polymer electrode contacts with an electrolyte, the significant chemisorption of the ion pairs on the chelate groups of surface PTТА molecules occurs only in the case of the carbonate solvent. As a result, the concentration of [PF₆⁻] in the electrode mass becomes much higher than that in the case of the tetraglyme solvent.

The ionization potential of PTТА4 is 7.1 eV, and a close value of 6.6 eV was found for (PTТА3)₃. The binding energy of the radical cation of PTТА4⁺ and [PF₆⁻] (65.4 kcal/mol) practically coincides with the dissociation energy of the [Li⁺(DMC)₄] [PF₆⁻] ion pair and is 9 kcal/mol lower than that for the [Li⁺G4] [PF₆⁻] ion pair. Therefore, the transfer of the anion to the oxidized polymer is a thermoneutral reaction in the carbonate solvent and an energy-consuming reaction in tetraglyme.

Upon the ionization of the PTТА oligomers, the electron density decreases uniformly for different units. Therefore, the interaction energy of [Li⁺(DMC)₄] [PF₆⁻] with the PTТА4⁺ radical cation is only 4.4 kcal/mol lower than that for the neutral oligomer. This obvious effect will promote the desorption of the ion pairs during polymer oxidation.

Based on these data, one can interpret the difference between the discharge and charge capacities in the first cycles for the cell with the carbonate solvent (Figure 3).

The calculation of specific metalation energies ΔE_n of PTТА oligomers was carried out on the basis of the found energies for attachment of the corresponding number of diatomic Li₂ molecules per one unit of PTТА



and the experimental value of the sublimation of metallic Li in the form of diatomic molecules

$\text{Li}(\text{metal}) \rightarrow 0.5 \text{Li}_2 - Q_{\text{Li}}$, where $Q_{\text{Li}}=1.079 \text{ eV}$,

Then the final formula looks like

$$\Delta E_n = \delta E_n - Q_{\text{Li}} \text{ (eV)}$$

Neglecting (small) entropy effects, the quantities of these energies in eV correspond to the potentials of redox transitions in the organic cathode relative to Li^+/Li in V. The ΔE_n values, $n=1,2,3,4,6$, for PTTA2 oligomers are shown in Table S2 .

The isomeric structures of $\text{PTTA2}(\text{Li})_2$ and $\text{PTTA2}(\text{Li})_n$, $n=4,6$ are shown in Figs S6 and S7, respectively. The greatest energy gain is observed when a Li atom is attached to chelate sites containing an O atom. For a chelate site with two N atoms, the specific energy is lower by 0.4 eV. Due to edge effects (the effect of donor amino groups), the energy effect for the (N, O) chelate sites located at its ends decreases in the short PTTA2 oligomer. To evaluate the effect of intermolecular interactions on the value of the specific energy of metalation, the structure and energy of formation of dimers $[\text{PTTA2}(\text{Li}_4)]_2$ and $[\text{PTTA2}(\text{Li}_6)]_2$, 4.07 and 7.03 eV, respectively, were considered (see Fig. S8). Assuming that the magnitude of the pair interaction is kept constant in infinite stacks of dimers $[\text{PTTA2}(\text{Li}_4)]_m$ and $[\text{PTTA2}(\text{Li}_6)]_m$, $m \gg 1$, we get the estimate for 1D structures given in Table S2.

Table S2 Calculated specific metalation energies ΔE_n of PTTA2 oligomer in eV*

n=1		n=2	n=3	n=4	n=6
(N,N) site	1.566	1.756	1.495	1.341 (1.85)	0.725 (1.31)
(O,O) site	1.968				
(O,N) site	1.928				
(N,O) site	1.590				

* Estimated values for infinite stacks of PTTA2 are given in brackets

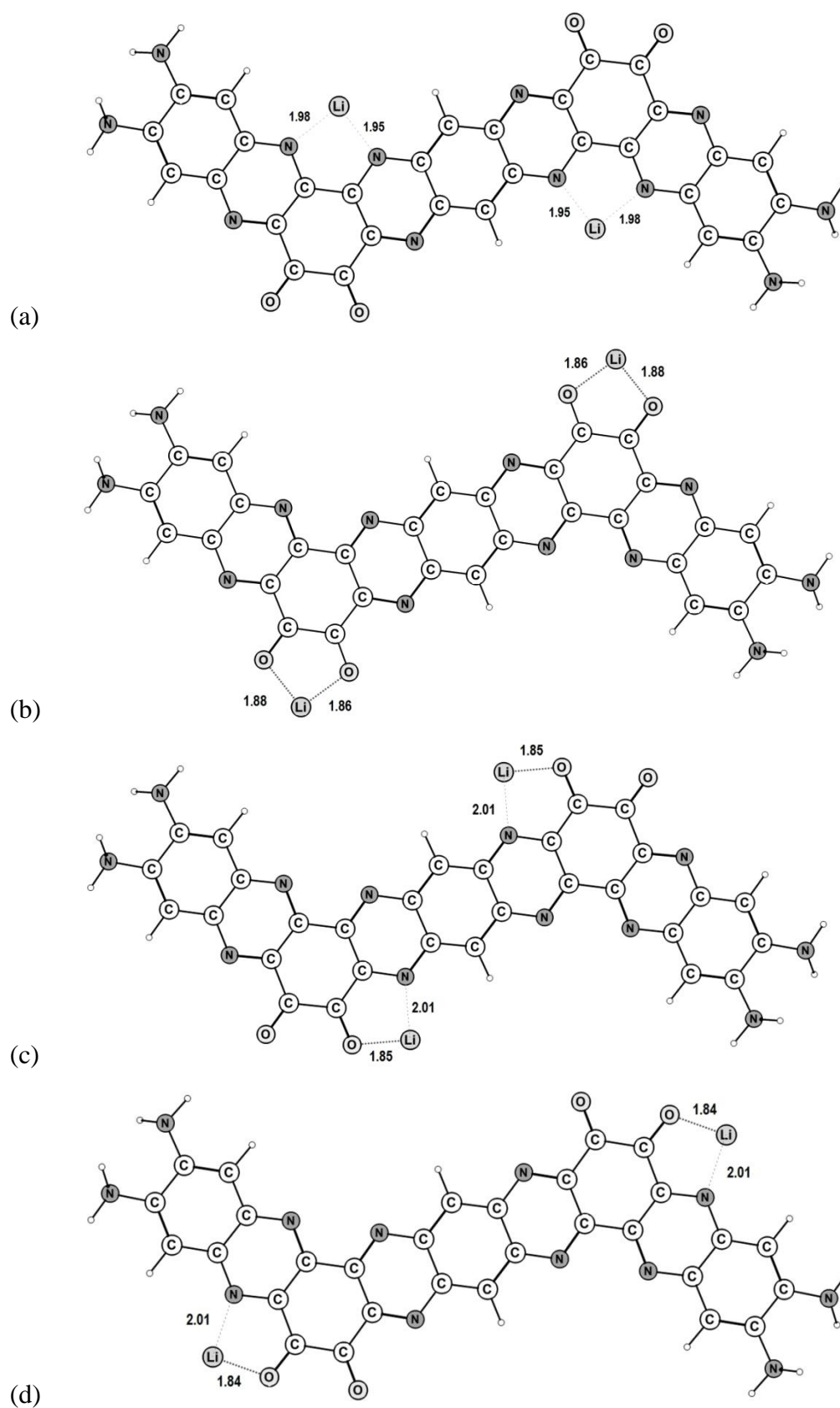


Figure S6 Calculated structures of the isomers PTTA2(Li)₂ with Li atoms coordinated at (N,N) (a); (O,O) (b); (O,N) (c) and (N,O) chelate knot

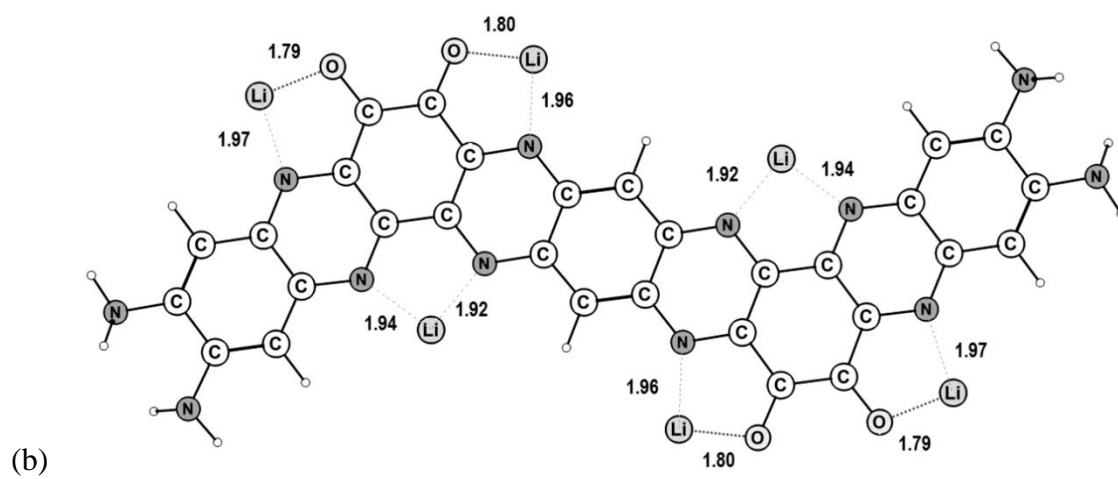
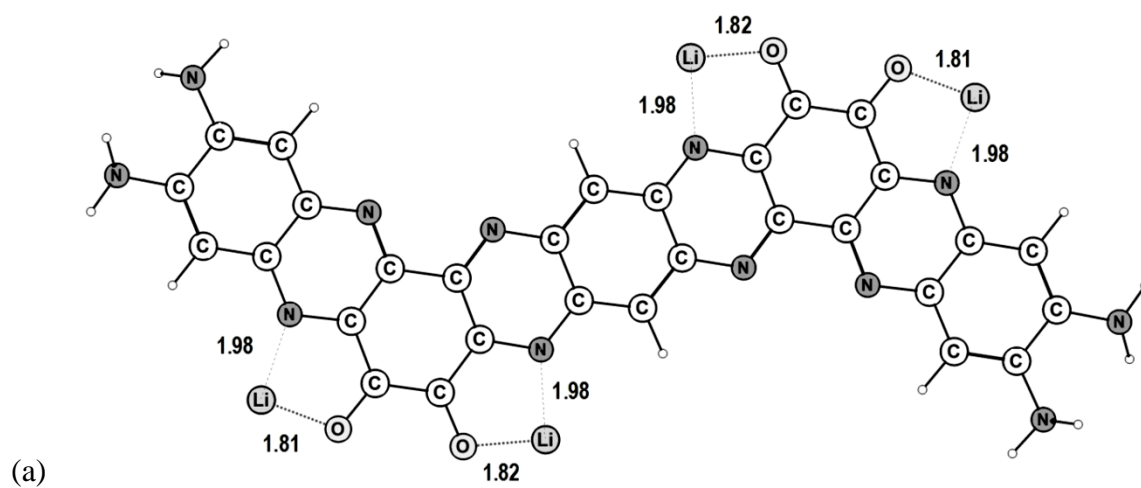
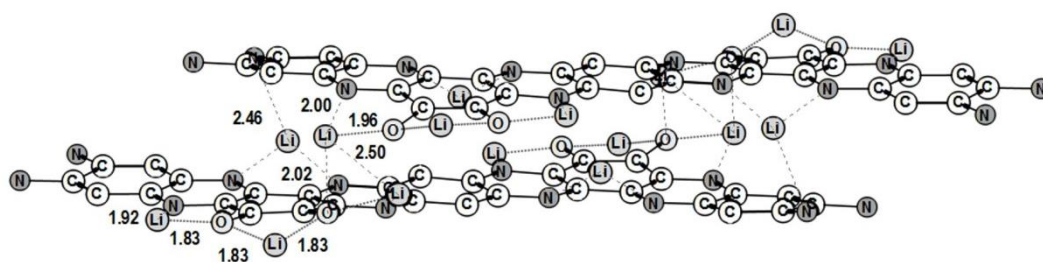
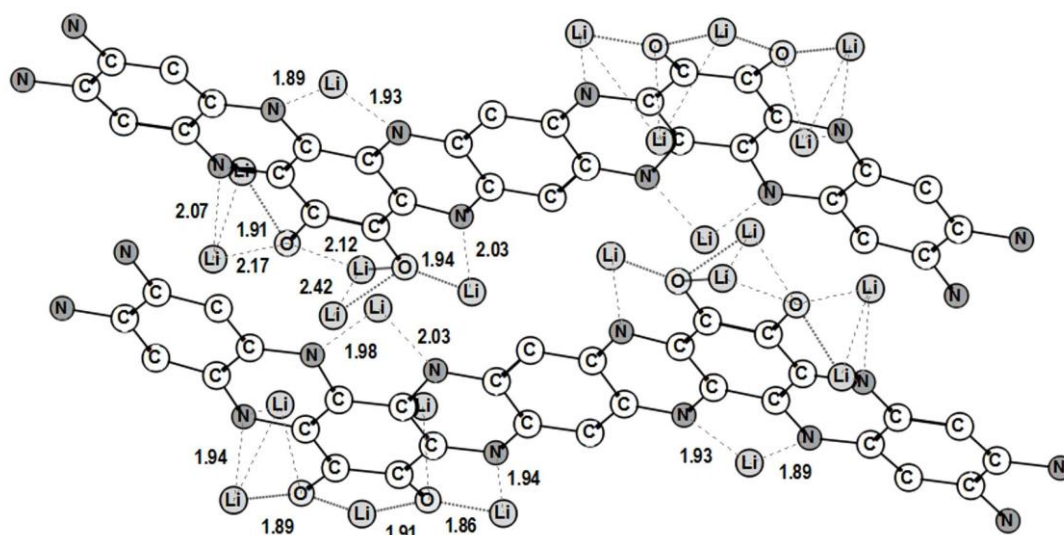


Figure S7 Calculated structures of PTTA2(Li)₄ f(a) and PTTA2(Li)₆ (b)



(a)



(b)

Figure S8 Calculated structures of dimers $[\text{PTTA2}(\text{Li}_4)]_2$ (a) and $[\text{PTTA2}(\text{Li}_6)]_2$ (b)