Supporting Information

Tuning the Stability of Organic Active Materials for Non-Aqueous Redox Flow Batteries via Reversible, Electrochemically-Mediated Li⁺ Coordination

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Contents:

- 1. Figure S1: Ferrocene standards used to calibrate reference electrode potential in DME and PC
- 2. Figure S2: Supplemental voltammetric analysis
- 3. Table S1: Coulombic efficiencies from bulk electrolysis
- 4. Figure S3: IR absorbance bands, data from reaction mixture compared to NIST standards
- 5. Figure S4: Raw data from in situ SNIFTIRS studies
- 6. Table S2: electrochemical oxidation potentials and anion interactions
- 7. Table S3: Reaction free energies and dielectric effects
- 8. Figure S5: Optimized geometries and relative free energies of complexation from DFT/B3YLP
- 9. Figure S6. Computed IR absorbance spectra
- 10. Figure S7: Li⁺ solvation by TDT in DCM

Figure S1. Solutions of TDT in PC (top) and 1,2-DME (bottom) containing a ferrocene/ferrocenium (50:50) spike used to calibrate the reference scale potential. The experimental data was recorded using a Li/Li⁺ quasi-reference electrode consisting of a Li metal foil immersed in a 1.0 M solution of LiClO₄ in PC within a Vycor-fritted tube. The data was then plotted against the standard electrode potential for Li/Li⁺ (-3.04 V vs SHE) by taking into account the difference between the *measured* $E_{1/2}$ of the ferrocene/ferrocenium redox couple within the test solutions (below) and the standard electrode potential for ferrocene/ferrocenium (0.400 vs SHE, or 3.44 vs Li/Li⁺)



Figure S2. CV data for 0.005 M TDT in 1.0 M LiClO₄ in PC, recorded with a GC disk electrode.



Scan rate (mV/s)	$\Delta E_{\rm p}({\rm mV})$	ipc∕ipa ¹
2	60	0.97
5	61	0.92
10	57	0.93
20	57	0.96
50	59	0.95

 1 i_{PC}/i_{PA} was calculated by dividing the baseline-corrected cathodic peak current by the baseline-corrected anodic peak current. The baseline-corrected peak currents calculated using the CH Instruments software.

The peak potential difference, ΔE_P , was $58.9 \pm 1.8 \text{ mV}$, measured across all the scan rates as presented in Figure 1a, indicating electrochemically reversible behavior. The small (< 4 mV) variations in ΔE_P did not correlate with sweep rate. The ratio of peak currents, i_{PC}/i_{PA} was close to but less than unity, yet this also did not display any trends with sweep rate. If i_{PC}/i_{PA} is less than unity, this can indicate a side reaction. For example, a side reaction following the electrochemical reaction and resulting in loss or conversion of the active material into a side

product would manifest as a trend of decreasing i_{PC}/i_{PA} with decreasing scan rate. Background processes which non-uniformly impact the baseline current, such as electrolyte decomposition or changes in the electrode double-layer capacitance, also influence the measured peak currents. Upon further subtracting the baseline current, recorded in a solution containing only 1.0 M LiClO₄ in PC, from the peak currents, i_{PC}/i_{PA} change by no more than 0.01, which is not enough to account for the discrepancy in peak currents. While we cannot rule out side reactions following the electrochemical reaction, the lack of a clear trend in the i_{PC}/i_{PA} ratio suggests that these may be difficult to determine from CV alone. Figure S3. Electron Paramagnetic Resonance of chemically and electrochemically oxidized TDT. The first-derivative X band EPR spectra (9.431 GHz) were obtained from room temperature solutions using 2 mW microwave power, the modulation frequency of 0.2 G (1 G = 1e-4 T) and the modulation frequency of 100 kHz. Trace (a) was obtained in 70% aqueous H_2SO_4 containing 0.001 M of the catholyte molecule, while trace (b) was obtained by oxidation of the same compound (at the same concentration) in n-butyronitrile acidified with 1 M trifluoroacetic acid by PIFA ((bis(trifluoroacetoxy)iodo)benzene, 1:1 mol/mol). In both of these systems, the EPR spectra originated from the radical cation of the title compound with the g-factor of 2.0047. The hyperfine structure is partially resolved in trace a. The magnetic field is given in Gauss.



Figure S4. (a) IR absorbance spectra of the reaction mixture, 0.1 M TDT in 1.0 M LiClO₄ in PC; (b) standard spectra representing the expected vibrational bands of various functional groups. The spectrum in (a) shows a broad absorbance background, with many closely spaced and overlapping peaks. Due to the high degree of overlap, interpretation of structural changes from this and similar spectra would be difficult. The standard IR transmittance spectra shown in (b) correspond to the individual organic functionalities present in the reaction mixtures we analyzed in this publication: propylene carbonate and dimethoxyethane solvent (top), and 1,2-dimethoxybenzene and 1,1-dimethylcyclohexane (bottom). 1,2-dimethoxybenzene and 1,1-dimethylcyclohexane represent the organic functionalities found in the TDT structure. From Figure S2a, we clearly see that the intensity of many individual features in the 1000-1800 cm⁻¹ spectral region are indistinguishable due to the high degree of overlap.

a)



b)







Figure S6. Background CVs in electrolyte-only solutions. The working electrode was a Au disk. The CVs all began at 3.2 V and were swept towards more positive potentials at a rate of 0.02 V/s.



Figure S7. Optimized geometries and relative free energies of complexation from DFT/B3YLP.



Table S1. Computed oxidation potentials (V vs. Li/Li⁺), enthalpies and free energies of select molecules and complexes. SMD solvation model with a dielectric of water is used to approximate solvation effects of PC. ^{*a*}: At the lower dielectric of DME, the computed oxidation potential of TDT is 4.23 V. Solution-phase enthalpies (ΔH) and free energies (ΔG) for forming TDT-anion complexes are reported here. The gas phase and solution phase free energies for the TDT-Li⁺ complexes are reported and discussed in the main text.

Species	Species Oxidation potential	
	$(V vs. Li/Li^+)$	
DME	5.48	
(DME-Li ⁺ -DME)	5.90	
TDT	3.92	
TDT ^a	4.23	
$(TDT-Li^{+})$	4.29	
(TDT-Li ⁺ -TDT)	4.33	
(TDT-Li ⁺ -DME)	4.22	
$(TDT:BF_4^{1-})$	4.14	
(TDT:ClO ₄ ¹⁻)	4.09	
(TDT:TFSI ¹⁻)	4.05	
TDT ^{•+}	4.44	
$(TDT^{+}:BF_4^{-1})$	4.98	
$(TDT^{+}:ClO_4^{-})$	5.10	
(TDT ^{•+} :TFSI ¹⁻)	5.19	

Solution-phase enthalpy (ΔH) and free energy (ΔG) of forming TDT: anion and TDT⁺: anion pairs

Species	$\Delta H (\mathrm{eV})$	ΔG (eV)
$(TDT:BF_4^{1-})$	0.11	0.49
$(TDT:ClO_4^{-1})$	0.10	0.51
(TDT:TFSI ¹⁻)	0.07	0.47
$(TDT^{+}:BF_4^{-})$	0.25	0.71
$(TDT^{+}:ClO_4^{1-})$	0.27	0.69
(TDT ^{•+} :TFSI ¹⁻)	0.16	0.60

Table S2. Computed free energies of selected reactions in the gas and solution (water dielectric, $\epsilon = 78$) phase.

Entry	Reaction	$\Delta G (eV)$	
		$\Delta G_{\rm gas}$	$\Delta G_{\rm solv}$
Ι	$(DME-Li^+-DME) + TDT \rightarrow (TDT-Li^+-DME) + DME$	-0.08	-0.02
II	$(TDT-Li^+-DME) + TDT \rightarrow (TDT-Li^+-TDT) + DME$	-0.12	0.01
III	$(TDT-Li^+ - TDT^{*+}) + 2DME \rightarrow (DME-Li^+ - DME) + TDT + TDT^{*+}$	-4.92	-0.73
IV	$(TDT-Li^+-TDT^{*+})+DME \rightarrow (TDT-Li^+-DME) + TDT^{*+}$	-3.71	-0.44
V	$(TDT^{+}-Li^{+}-DME) + DME \rightarrow (DME-Li^{+}-DME) + TDT^{+}$	-3.07	-0.28
VI	$(TDT^{\bullet+}-Li^+-DME) + TDT \rightarrow (TDT-Li^+-TDT) + TDT^{\bullet+}$	-3.10	-0.31

Figure S8. Simulated IR absorbance spectra and corresponding structural models. (a) Neutral TDT models; (b) TDT⁺; (c) comparison of Li⁺ complexes corresponding to Figure 3





(b) **TDT**^{•+}



(c) comparison of Li⁺ complexes corresponding to Figure 3



From the simulated IR spectra, we are able to identify a few key features in the SNIFTIRS data (Figures 2 and 6) which can be related to structural changes during electrochemical cycling. Recall that the error in the calculated vibrational energy is about 60 cm⁻¹. The simulated spectrum of bare TDT displays C-C stretching and C-H rocking modes at 1200 cm⁻¹, asymmetrical aryl-O-C stretching at 1253 cm⁻¹, symmetrical aryl-C-O stretching at 1295 cm⁻¹ (Supporting Information, Figure S7). Upon Li⁺ coordination, the symmetrical aryl-C-O stretching band is comparatively much weaker and shifted to 1240 cm⁻¹. The simulated spectrum for TDT⁺⁺ displays only one prominent absorbance mode between 1200 cm⁻¹ and 1300 cm⁻¹ : the asymmetrical aryl-C-O stretching at 1295 cm⁻¹.

In the simulated *difference* spectra corresponding to conversion of the 3 different TDT models to TDT⁺ (Figure 6 a-c), we detect a unique feature between 1200 cm⁻¹ and 1300 cm⁻¹ which can be related to coordination of Li⁺ by TDT, followed by dissociation of Li⁺ from the complex upon oxidation. The peak at 1295 cm⁻¹ due to symmetrical aryl-C-O stretching of bare TDT has a higher intensity than the peak at 1295 cm⁻¹ due to asymmetric aryl-C-O stretching in TDT⁺⁺ and thus a mechanism in which bare TDT converts to TDT⁺⁺ should give rise to a disappearance peak at this energy (Figure 6a), alongside two other disappearance peaks at lower frequencies. Due to shifting of the aryl-C-O stretching mode to lower frequencies and the absence of a strong absorbance mode at 1295 cm⁻¹ as a result of Li⁺ coordination in the TDT-Li⁺-DME and TDT-Li⁺-TDT models ,conversion of the lithiated TDT models to TDT⁺⁺ manifests as a weak appearance peak at 1295 cm⁻¹ directly beside a disappearance peak at 1273 cm⁻¹, and a second, even weaker disappearance peak at 1240 cm^{-1} (Figure 6b-c). This feature is also apparent between 1200 cm⁻¹ and 1300 cm⁻¹ in the SNIFTIRS data (Figure 6d), and is more prominent in the spectrum recorded in LiClO₄ and PC (blue line in Figure 6d) than the spectrum recorded in LiClO₄ and DME (red line in Figure 6d). An additional disappearance peak around 1220 cm⁻¹ is more prominent in the DME solution, compared with PC, and this feature can be

related to oxidizing some bare TDT to TDT⁺⁺. This interpretation is reasonable considering that the bare and lithiated TDT models may exist in equilibrium (Figure 3).

Bare TDT shows 2 strong absorbance peaks between 1500 cm⁻¹ and 1600 cm⁻¹: in-ring stretching coupled with aromatic C-H rocking at 1563 cm⁻¹, and C-H bending modes around 1530 cm⁻¹. TDT-Li⁺-DME and TDT-Li⁺-TDT models also show C-H bending modes around 1530 cm⁻¹, but the in-ring stretch coupled with aromatic C-H rocking is shifted to 1545 cm⁻¹, resulting in a broad overlapping peak between 1500 cm⁻¹ and 1600 cm⁻¹, rather than the 2 wellseparated peaks as seen in the simulated data for bare TDT. The in-ring stretches for TDT⁺⁺ appear at 1527 cm⁻¹ and 1570 cm⁻¹. These are strongly absorbing modes and give rise to the most intense appearance peaks in spectroscopic signature at 4.4 V (Figure 6d), corresponding to oxidizing the neutral TDT models to TDT⁺⁺ (Figure 6a-d). TDT⁺⁺ has a 3rd slightly less intense peak around 1465 cm⁻¹ due to C-H bending which can also be seen in the simulations, and appears at 1430 cm⁻¹ in the measurements. Oxidizing the TDT-Li⁺-DME and TDT-Li⁺-TDT models to TDT⁺⁺ leads to a disappearance peak between 1500 cm⁻¹ and 1600 cm⁻¹, which is present in the simulated spectra (Figure 6b-c) and SNIFTIRS spectra (Figure 2a-b and Figure 6d). The presence of this disappearance peak in the simulations related to electrochemically oxidizing the lithiated TDT models, as well as in the SNIFTIRS measurements, provides further evidence for electrochemically-mediated Li⁺ coordination by TDT.

Figure S9. 10 mL of DCM following addition of 0.28g LiTFSI (left) and after subsequently adding 0.49 g TDT (right).



