Supporting Information for:

Improved voltage and solubility in non-aqueous redox flow batteries using a molecular 3,4-ethylenedioxythiophene (EDOT) derivative with stable radical cation state

Hee Kyung Hwang,[a] Yejoo Park,a Jisang Yeom, Yohan Ahn,[a] Yeasin Khan,[a,b] Jeewoo Lim,[a] Clément Cabanetos,[c] Jung Hwa Seo,[b] Je Seung Lee,[a] Bright Walker[a]

[a]Department of Chemistry, Kyung Hee University, Seoul, 02447, Republic of Korea

[b]Department of Physics, University of Seoul, Seoul, 02504, Republic of Korea

[c]Univ Angers, CNRS, Moltech-Anjou, SFR Matrix, F-49000 Angers, France.

E-mail: walker@khu.ac.kr, leejs70@khu.ac.kr

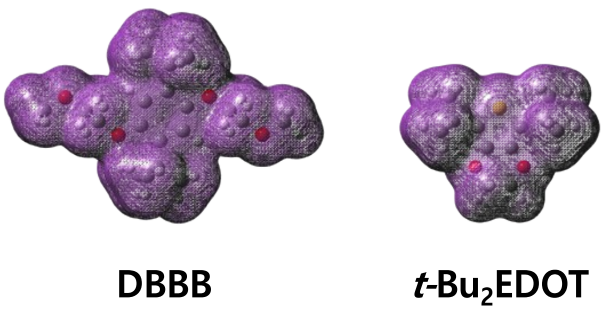


Figure S1. Predicted molecular volume of DBBB (3333.7 $Bohr^3$) and *t*-Bu_2EDOT (2209.4 $Bohr^3$).

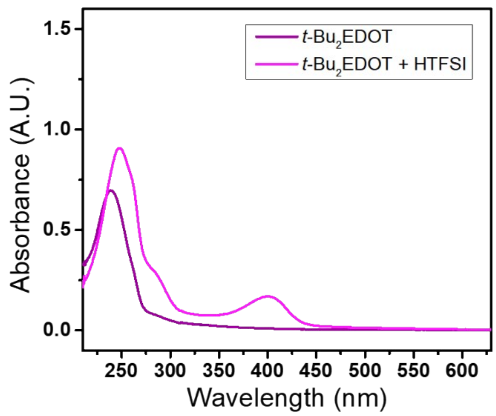


Figure S2. UV-Vis spectrum of only *t*-Bu_2EDOT and *t*-Bu_2EDOT with HTFSI. The purple line corresponds to 50 μM *t*-Bu_2EDOT and the pink line corresponds to 100 μM *t*-Bu_2EDOT with 50 μM of HTFSI. The changes in absorption spectrum are irreversible and indicate decomposition of tBu_2EDOT in the presence of acid.

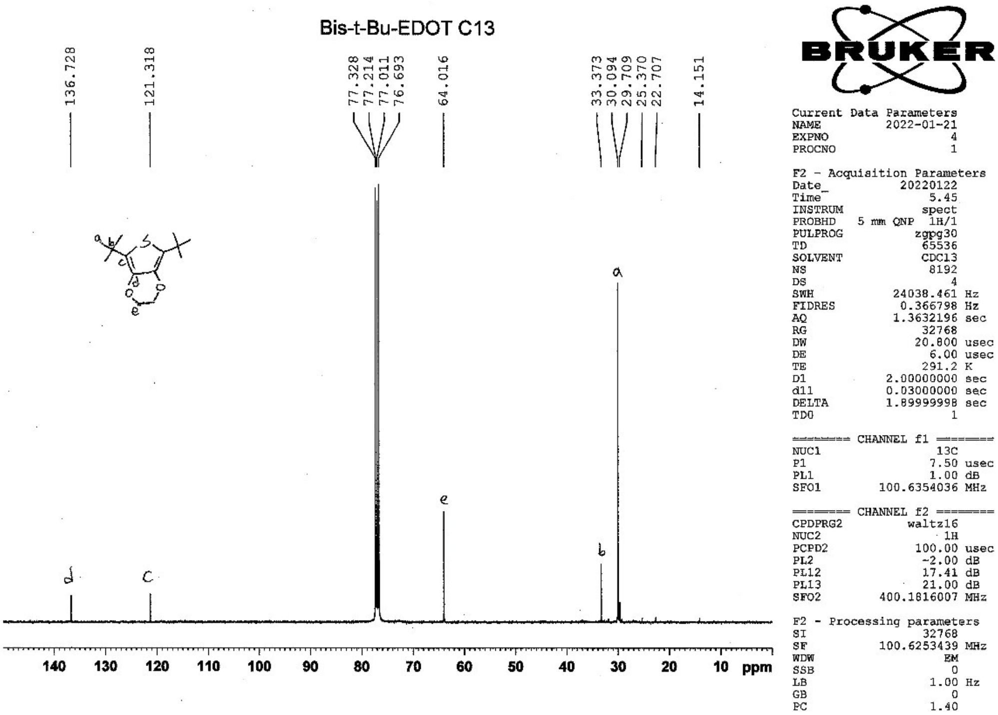


Figure S3. ^{13}CNMR spectrum of *t*Bu$_2$EDOT.

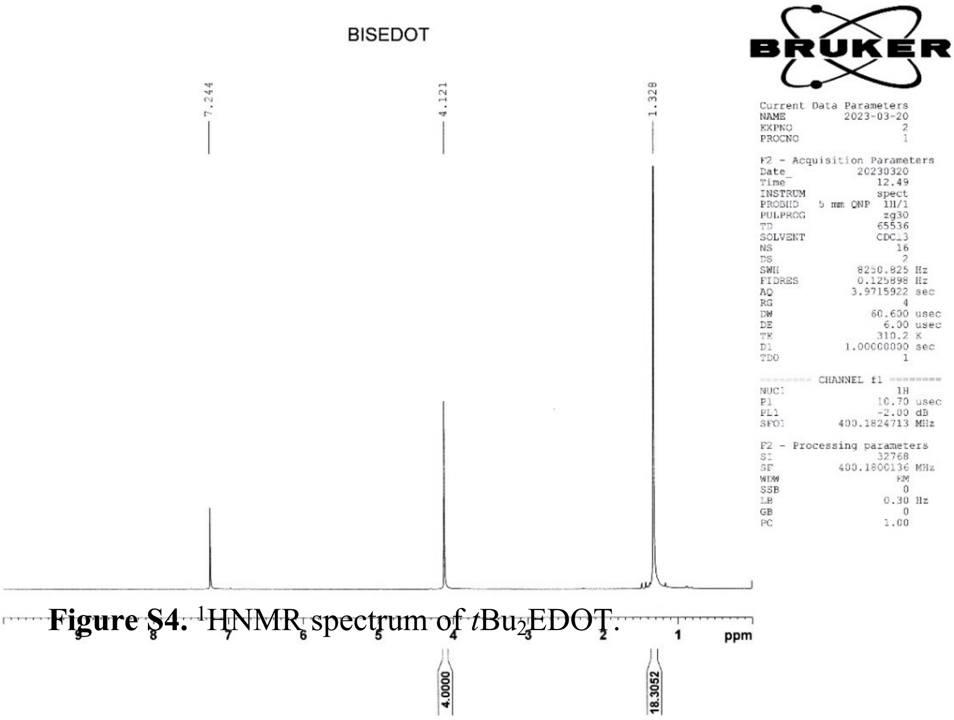


Figure S4. ^{1}HNMR spectrum of *t*Bu$_2$EDOT.

Best	Name	Formula	m/z (prec.)	CAS	RT (DB)	RT Diff	Score	Score (Lib)	Score (Fwd)	Score (Rev)	Lib/DB
Yes	1,2,3,5,7-PENTAMETHYL-1H-PYRROLO[2,3-F]QUINOLIN-9-OL	C16H18N2O		2000330-78-7			68.34	68.34			W10N11.L

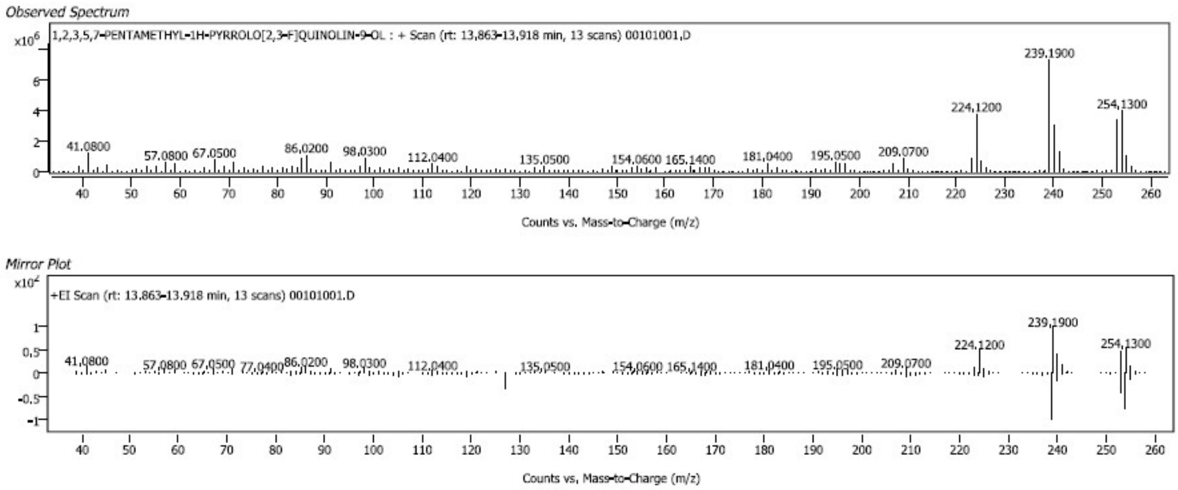


Figure S5. Mass spectrum of tBu_2EDOT. The named compound corresponds to the best fit for the observed spectrum among previously reported compounds, however, *t*-Bu_2EDOT has not been reported before.

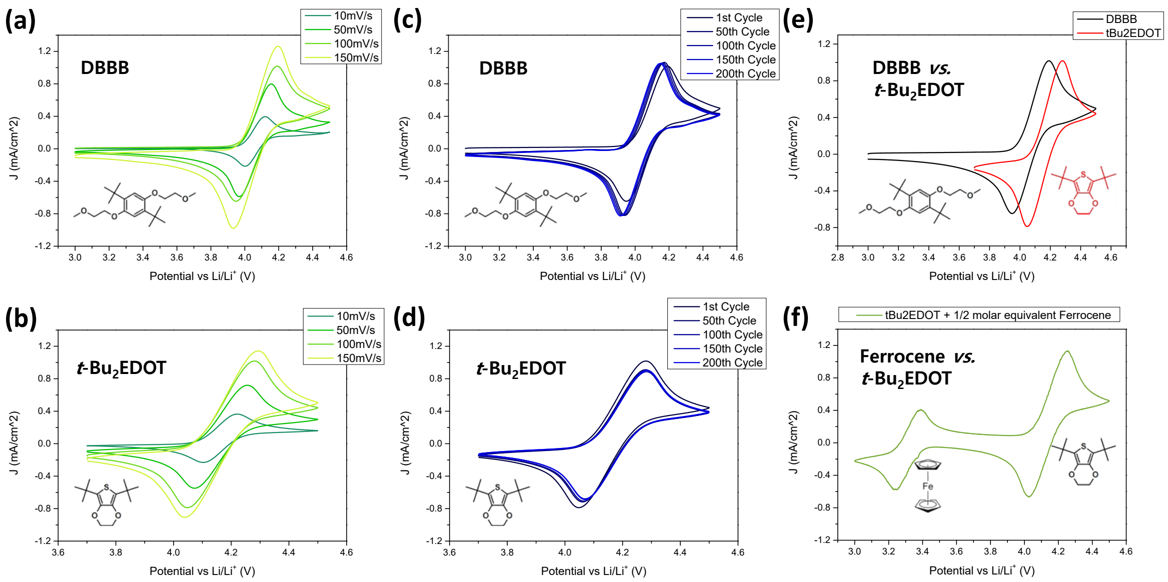


Figure S6. Cyclic voltammograms of DBBB (10 mM) and *t*-Bu_2EDOT (10 mM) using a lithium reference electrode under an Ar atmosphere in 100 mM LiTFSI in propylene carbonate. (a) DBBB and (b) *t*-Bu_2EDOT at different scan rates; (c) DBBB and (d) *t*-Bu_2EDOT over 200 scan cycles. (e) DBBB vs. *t*-Bu_2EDOT at a scan rate of 100 mV/s. (f) Ferrocene vs. *t*-Bu_2EDOT at a scan rate of 100 mV/s.

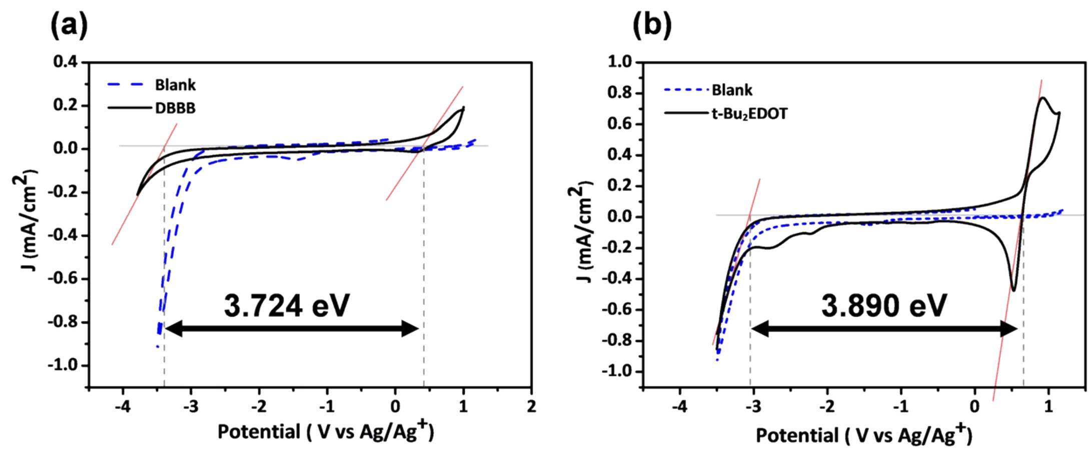


Figure S7. Cyclic voltammograms of 10 mM DBBB (a) and 10 mM *t*-Bu_2EDOT (b) using 100 mM LiTFSI/PC as an electrolyte solution over a wide potential range. Scans of electrolyte only are included for comparison..

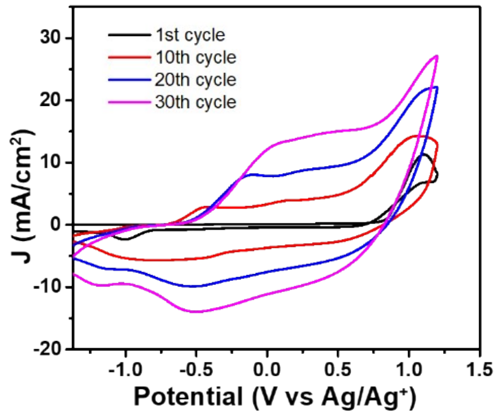


Figure S8. Cyclic voltammograms of 13 mM 3,4-ethylenedioxythiophene (EDOT) dissolved in 100 mM LiTFSI/PC solution over variable numbers of cycles.

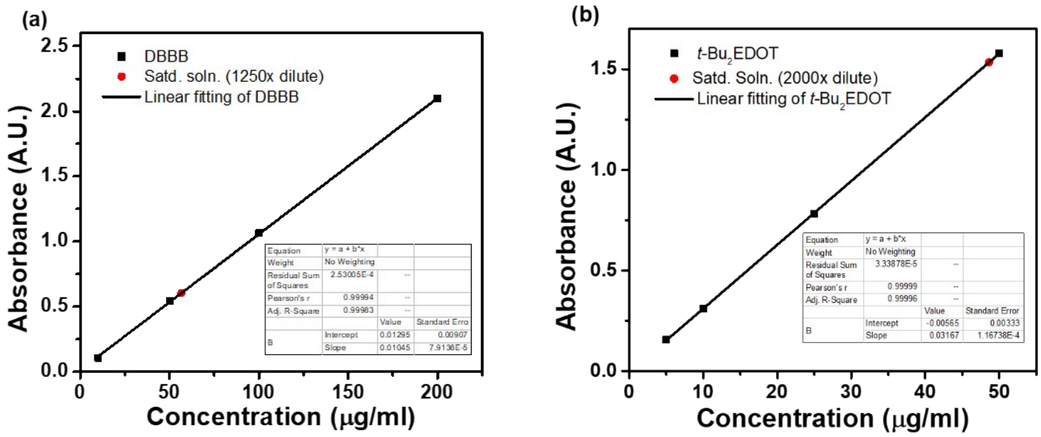


Figure S9. Calibration curves and Beer-Lambert fits of concentration vs absorbance for (a) DBBB, (b) t-Bu_2EDOT.

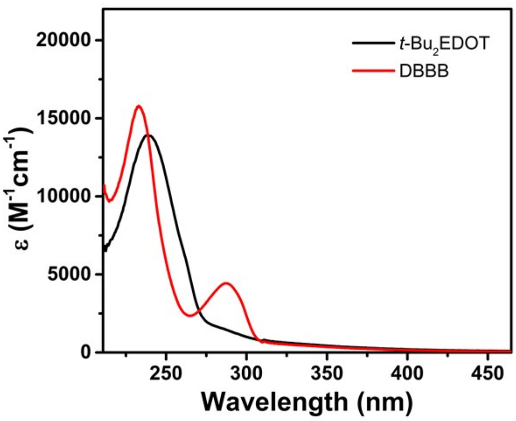


Fig. S10. UV-vis absorbance of *t*-Bu_2EDOT (black line) and DBBB (red line) solutions (50 μM) in PC.

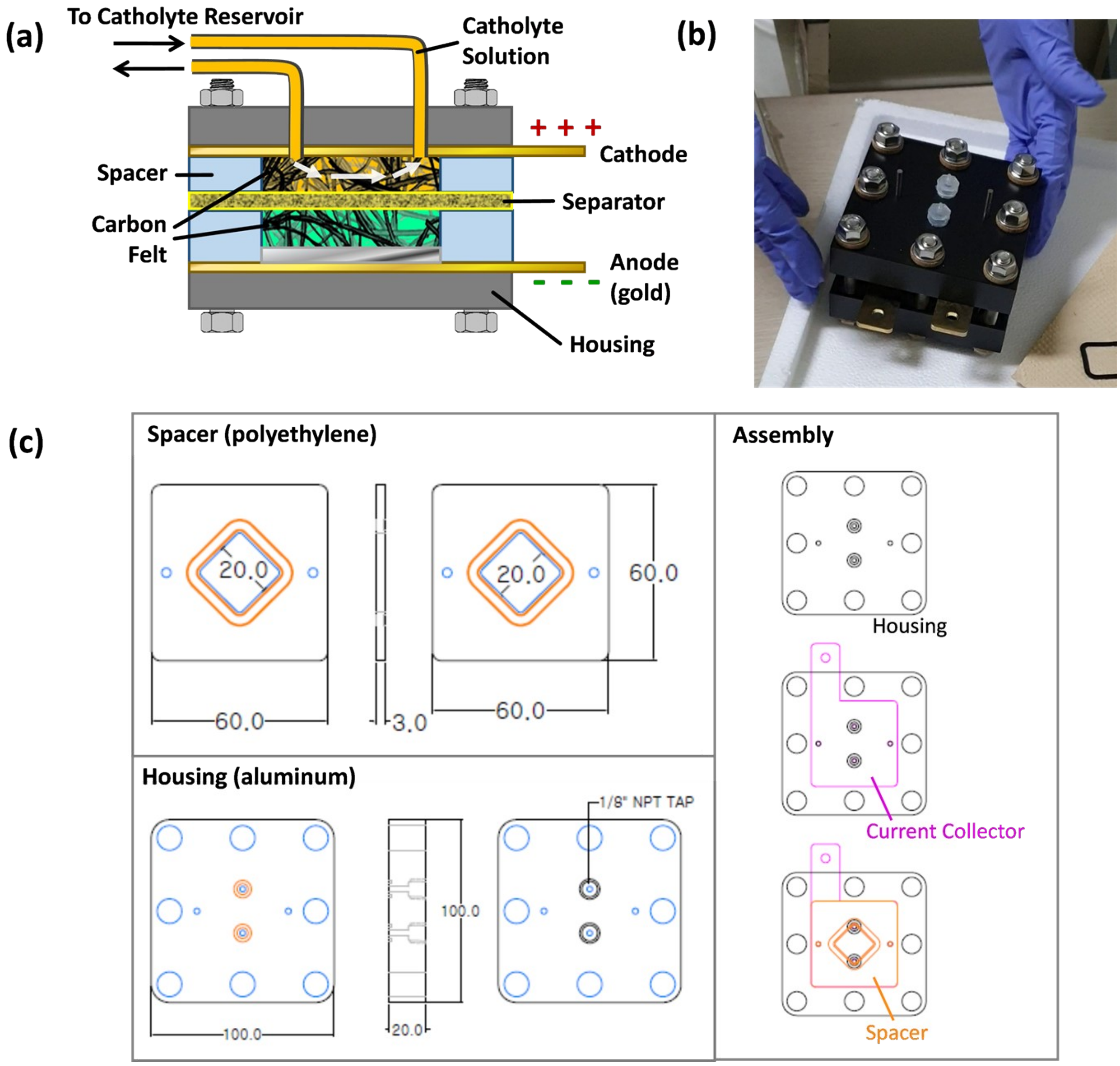


Figure S11. Redox flow cell design. (a) Diagram showing components. (b) Photograph showing assembled cell. (c) Diagrams showing dimensions (in mm) of spacer, housing and current collector.

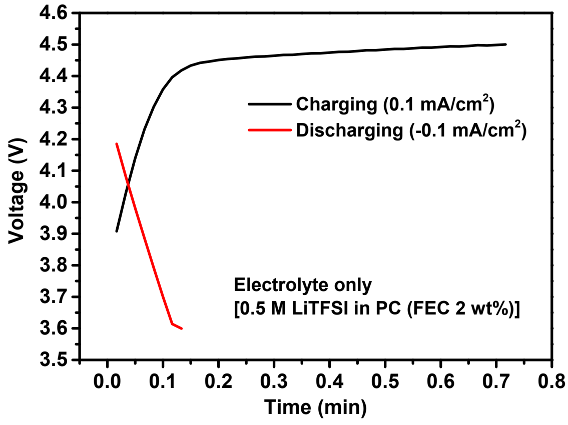


Figure S12. Charging and discharging curves for the battery containing electrolyte only.

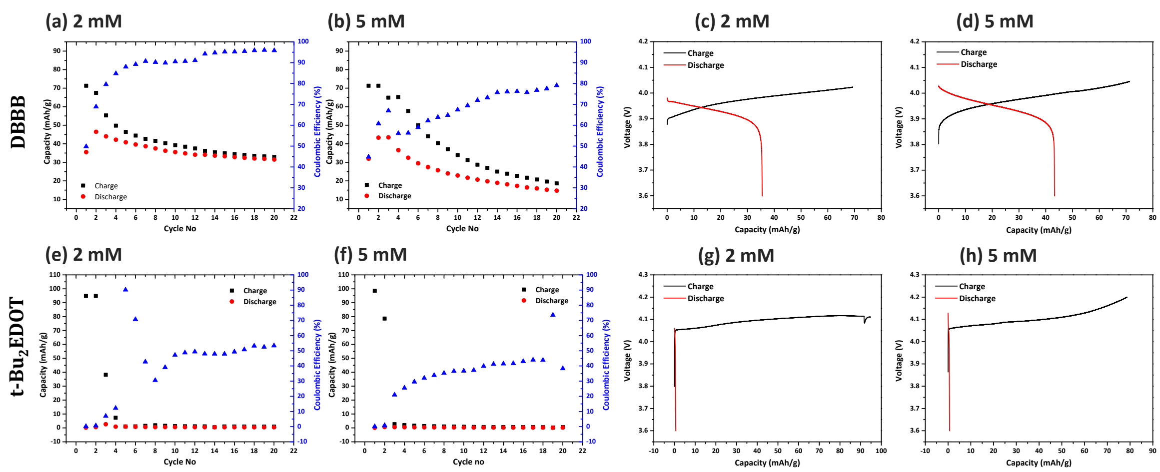
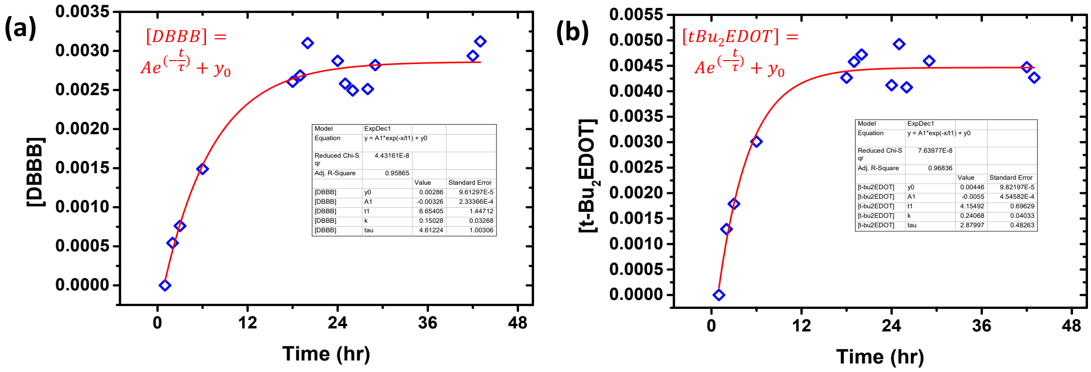


Figure S13. Battery characteristics of (a – d) DBBB and (e-h) tBu_2EDOT at at 2 mM (a, c, e, g) and 5 mM (b, d, f, h) concentration. Capacity and efficiency over repeated charge cycles are shown in (a, b, e, f) and representative charge / discharge curves (voltage vs charge capacity) are shown in (c, d, g, h).



$$initial \frac{d[DBBB]}{dt} = 4.22 \pm 1.32 \times 10^{-4}\ M/hr$$

$$initial \frac{d[tBu_2EDOT]}{dt} = 1.04 \pm 0.25 \times 10^{-3}\ M/hr$$

Figure S14. Crossover experiment involving running the flow cell with an initial concentration of 10.0 mM in the catholyte reservoir and 0 mM concentration in the anolyte reservoir, without charging. Anolyte concentration vs time data are shown for of (a) DBBB and (b) t-Bu_2EDOT, which were calculated from changes in UV-vis spectra of aliquots taken from the anolyte side using a volumetric micropipette. The data show that both DBBB and t-Bu_2EDOT cross the separator membrane to the anolyte side over the course of several hours.

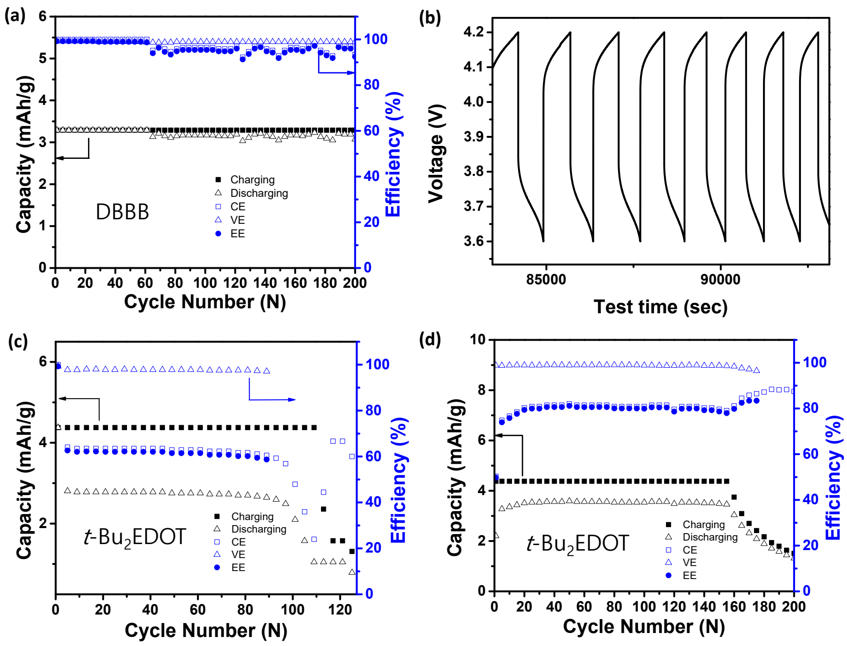


Figure S15. Rapid charge/discharge tests. Catholytes were prepared by using 1 mM DBBB (a) and 1 mM t-Bu_2EDOT (b), (c), (d) with 0.5 M LiTFSI in PC. Cells were charged and discharged at 4 % of theoretical capacity at a current density was of 1.25 μA/cm^2. In (a), (b) and (c), Tygon-LFL tubing is used, while Viton is used in (d). (b) Shows a close-up of voltage vs time plots for several charge / discharge cycles for t-Bu_2EDOT, corresponding to the efficiencies shown in plot (c).

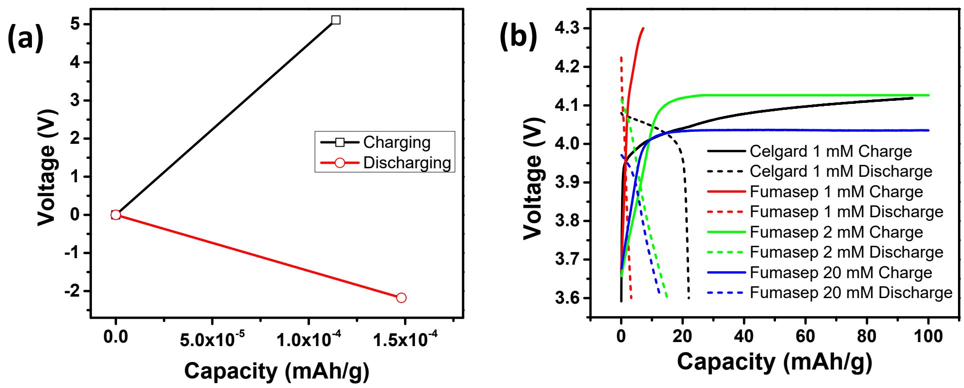


Figure S16. Battery tests using anion exchange membranes. (a) Charging / discharging characteristics using Selemion AMVN anion exchange membrane. (b) Charging / discharging characteristics using Fumasep FAP-450 anion exchange membrane.