Supporting Information

BF_3-Promoted Electrochemical Properties of Quinoxaline in Propylene Carbonate

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Keywords: *non-aqueous redox flow battery, quinoxaline, electrochemistry, Lewis acid, density functional theory*

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Table S1. Computed first and second redox potentials (V vs. Li/Li^+) of quinoxaline in the presence of various solvents. In the first strategy redox potentials were computed by optimizing the redox active molecules in the implicit solvent molecule. In the second strategy, optimization in the gas phase followed by a single point energy evaluation is performed.

Solvent	E^V_{redox} **(V vs. Li/Li^+): optimization in solvent**	E^V_{redox} **(V vs. Li/Li^+): optimization in gas phase and single point energy calculation in solvent**
water (ε = 78.35)	1.53, 1.01	1.55, 1.00
dimethyl sulfoxide (ε = 46.83)	1.50, 0.96	
methanol (ε = 32.61)	1.48, 0.92	
acetone (ε = 20.49)	1.44, 0.84	
diethyl ether (ε = 4.21)	1.03, 0.06	
n-hexane (ε = 1.88)	0.43, -0.01	
no solvent (ε = 0)	-0.47	-0.47

Figure S1. Voltammetry for 0.05 M quinoxaline (Q) in 0.5 M $LiPF_6$ / PC and 0.5 M $TEABF_4$ / ACN in a GC/Li/Li cell at a scan rate of 20 mV/s. Both solutions were dried to < 25 ppm H_2O using molecular sieves.

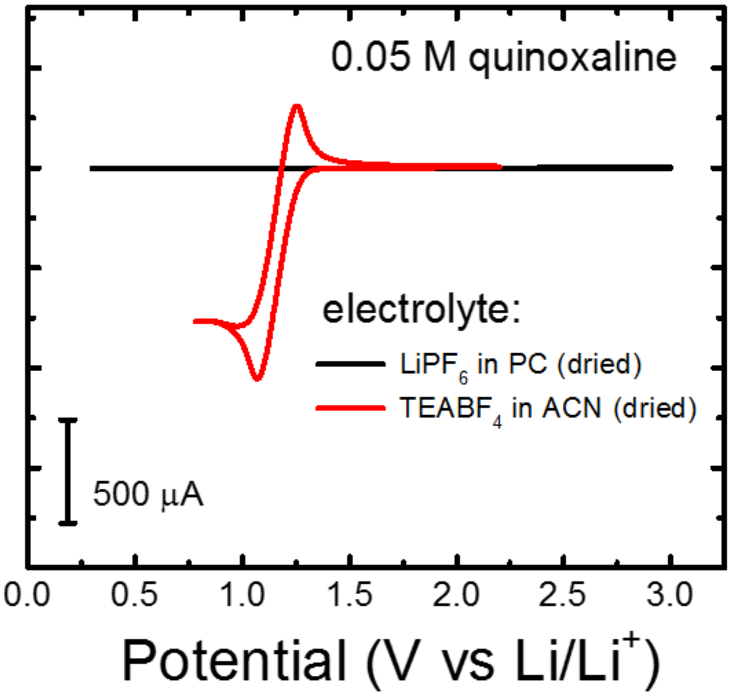


Figure S2. Voltammetry for 0.2 M TBABF4/PC only (black) and with 0.05 M quinoxaline (Q, red) in a GC/Li/Li cell at a scan rate of 20 mV/s.

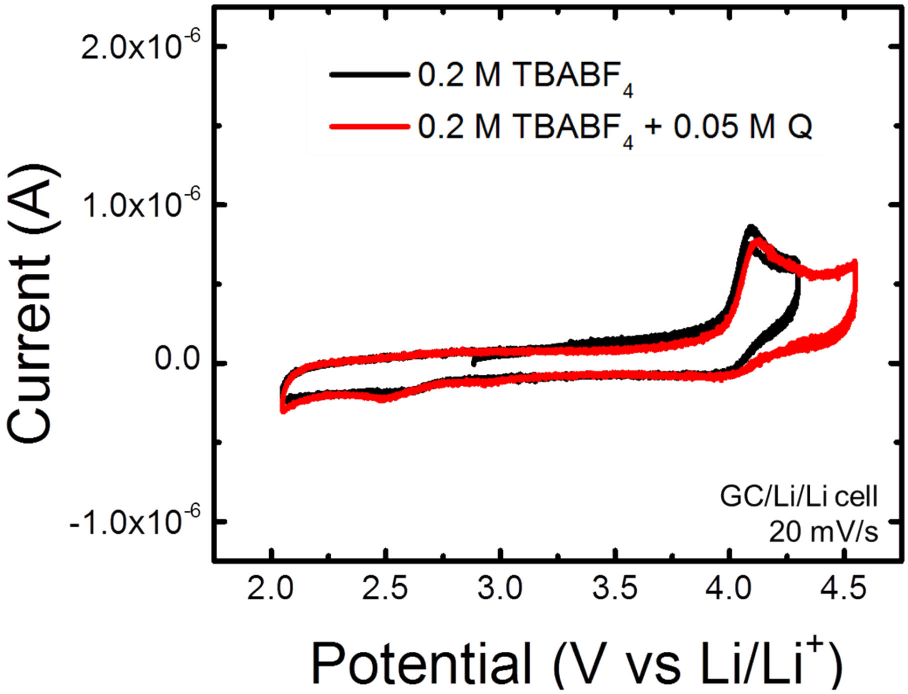


Figure S3. Voltammetry for 0.005 M 2,3,6-TMQ in 0.2 M $LiBF_4$ / PC on different working electrodes and Li foil counter and reference electrodes. The scan rate was 100 mV/s.

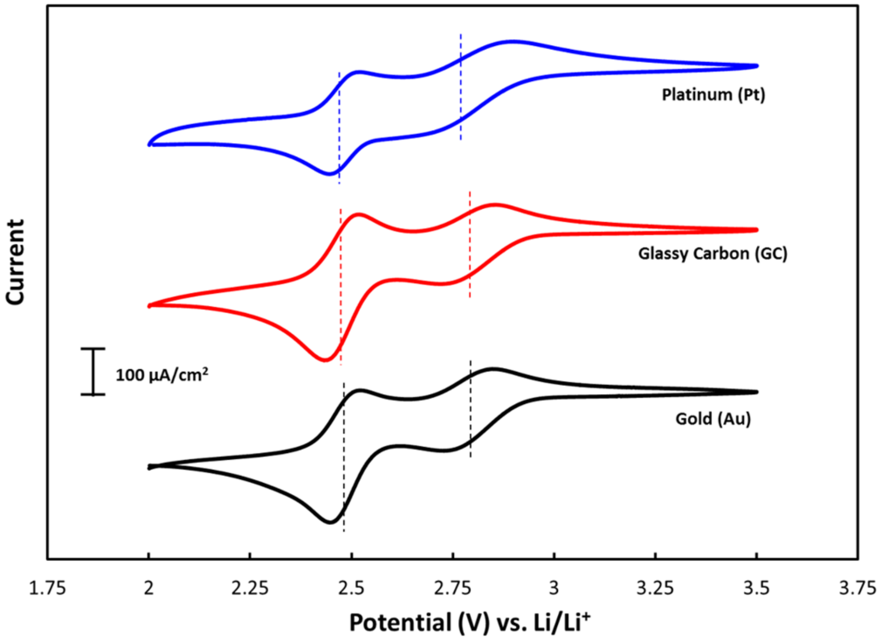


Figure S4. Voltammetry data corresponding to the plots in Figure 2.

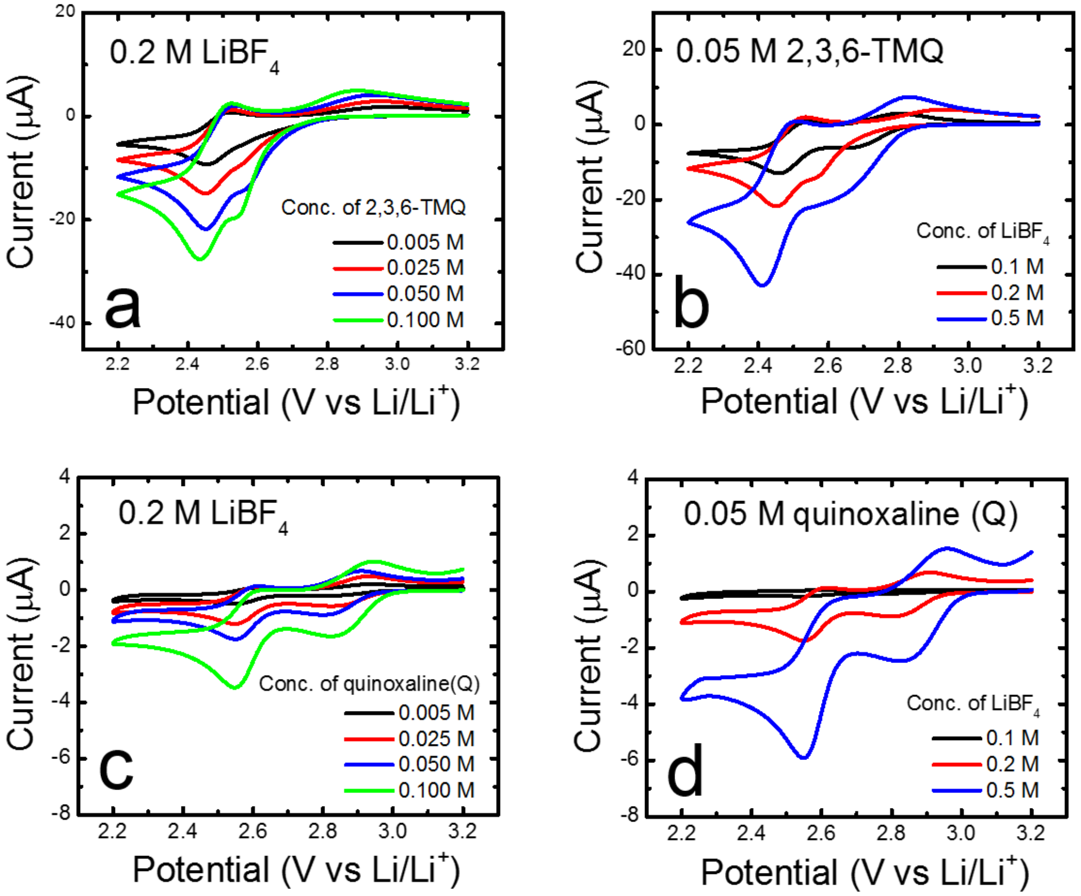


Figure S5. Electrochemical data for 0.2 M BF_3•OEt_2 in PC only (black) and in PC with 0.05 M quinoxaline (red) in a GC/Li/Li cell at a scan rate of 20 mV/s. The solutions did not contain any additional supporting salt. The voltammogram indicated in red began at 4.3 V and the voltage was swept towards negative potentials.

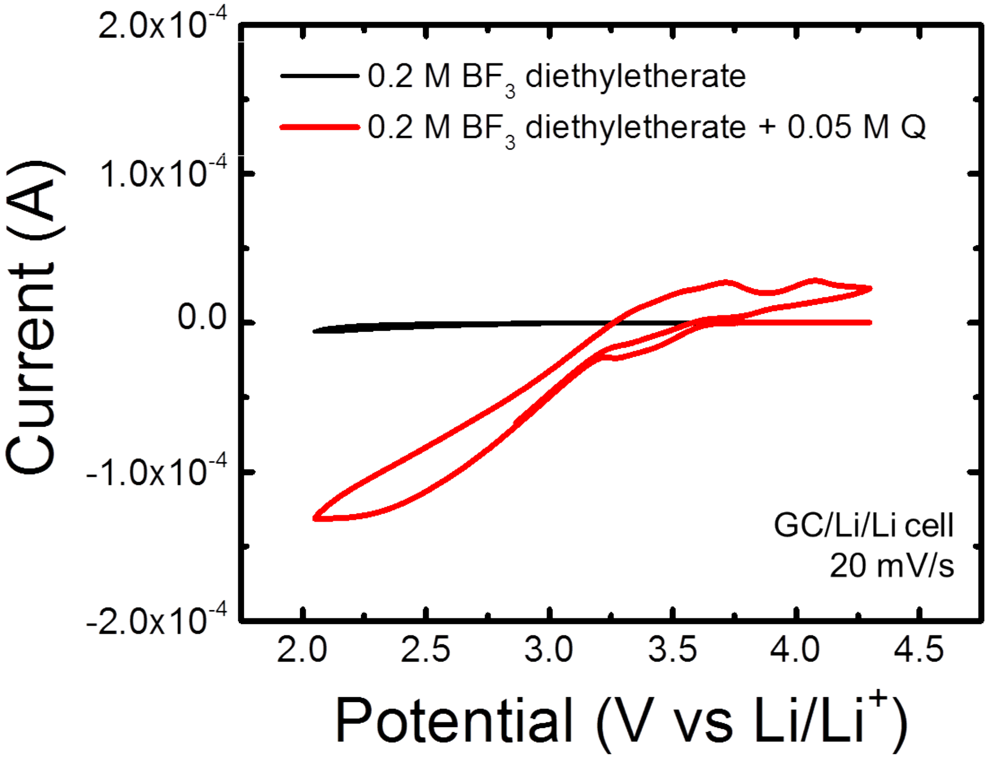


Figure S6. Cyclic voltammetry of dried (black line) and as-prepared (red line) solutions of quinoxaline in 0.5 M $LiBF_4$ / PC electrolyte. The data were recorded at a sweep rate of 20 mV/s using a glassy carbon working electrode, a fritted Li/Li^+ reference electrode, and an Au wire counter electrode.

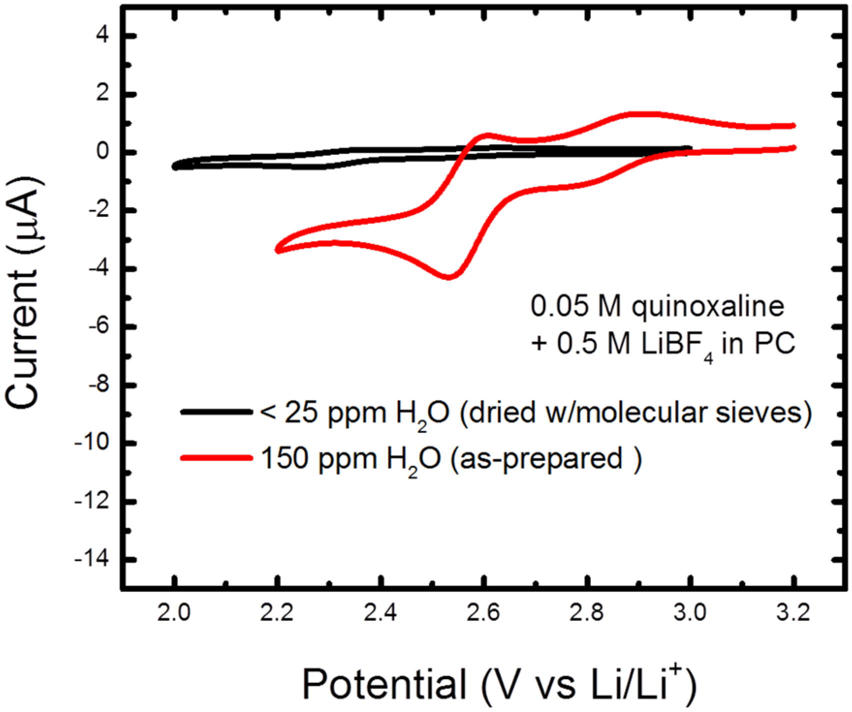


Figure S7. Cyclic voltammetry of 0.05 M quinoxaline in dried 0.5 M $LiBF_4$ / PC electrolyte (black line) and as-prepared 0.5 M Li triflate / PC electrolyte (red line). The data were recorded at a sweep rate of 20 mV/s using a glassy carbon working electrode, a fritted Li/Li^+ reference electrode, and an Au wire counter electrode.

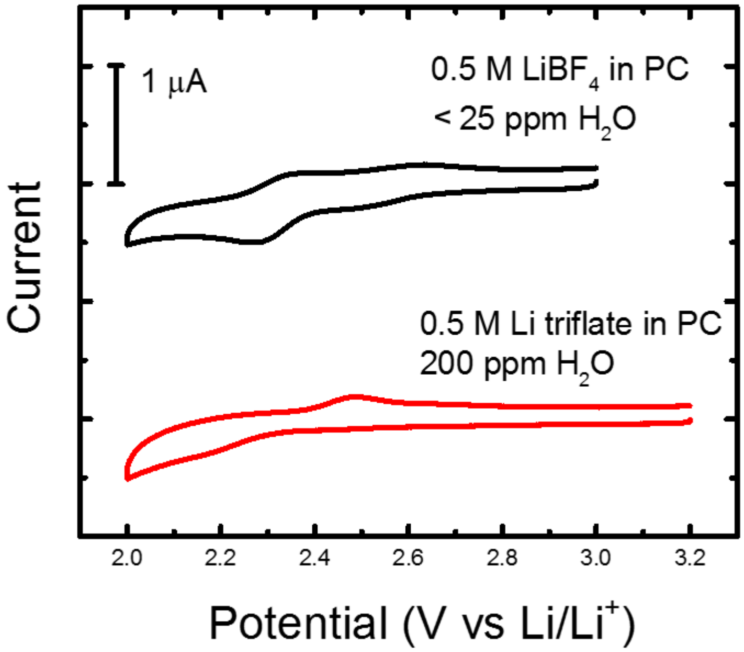


Figure S8. Voltammetry of quinoxaline in $LiBF_4$ (a) and Li triflate (b) supporting electrolyte before and after adding 100 uL of water. The starting volume, prior to water addition, was 10 mL. The data were recorded at a sweep rate of 20 mV/s using a glassy carbon working electrode, a fritted Li/Li$^+$ reference electrode, and an Au wire counter electrode.

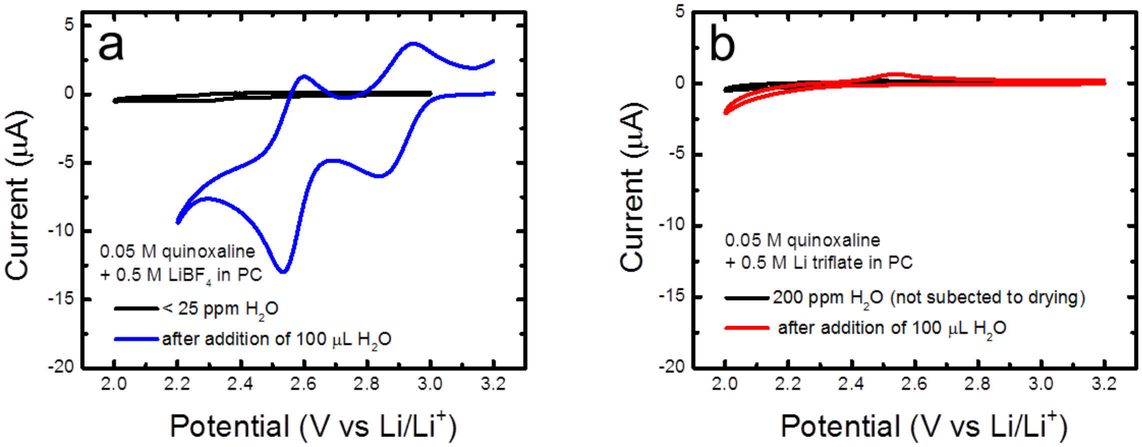


Figure S9. Cyclic voltammetry of the as-prepared solution of quinoxaline in $LiBF_4$ / PC electrolyte, recorded immediately after mixing the dry electrolyte with quinoxaline (fresh solution, red line) and 1 h later (blue line). The data were recorded at a sweep rate of 20 mV/s using a glassy carbon working electrode, a fritted Li/Li$^+$ reference electrode, and an Au wire counter electrode.

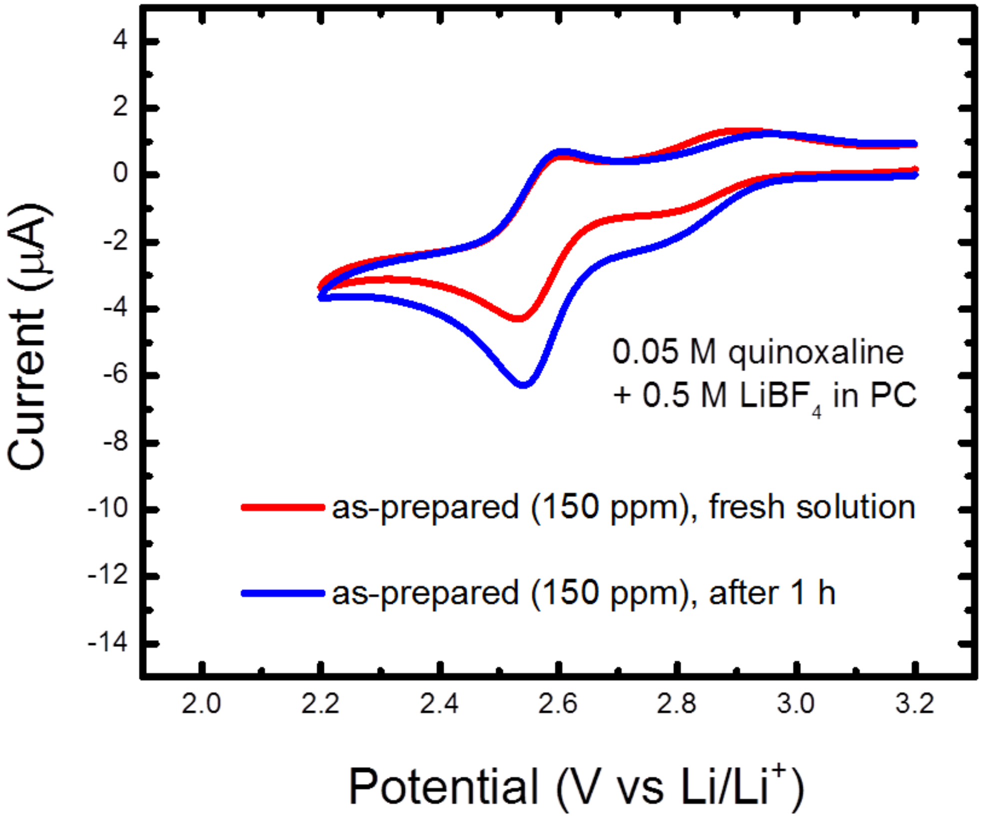


Figure S10. Cyclic voltammetry of a dried solution of quinoxaline in $NaBF_4$ / PC electrolyte. The data were recorded at a sweep rate of 20 mV/s using a glassy carbon working electrode, a fritted Li/Li^+ reference electrode, and an Au wire counter electrode.

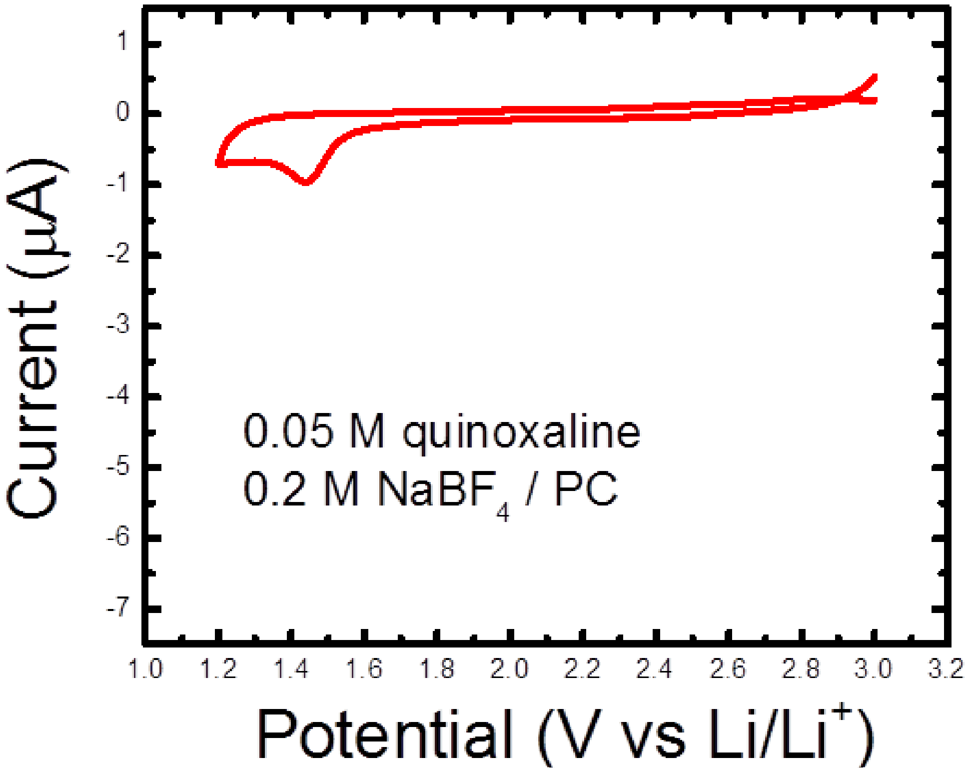
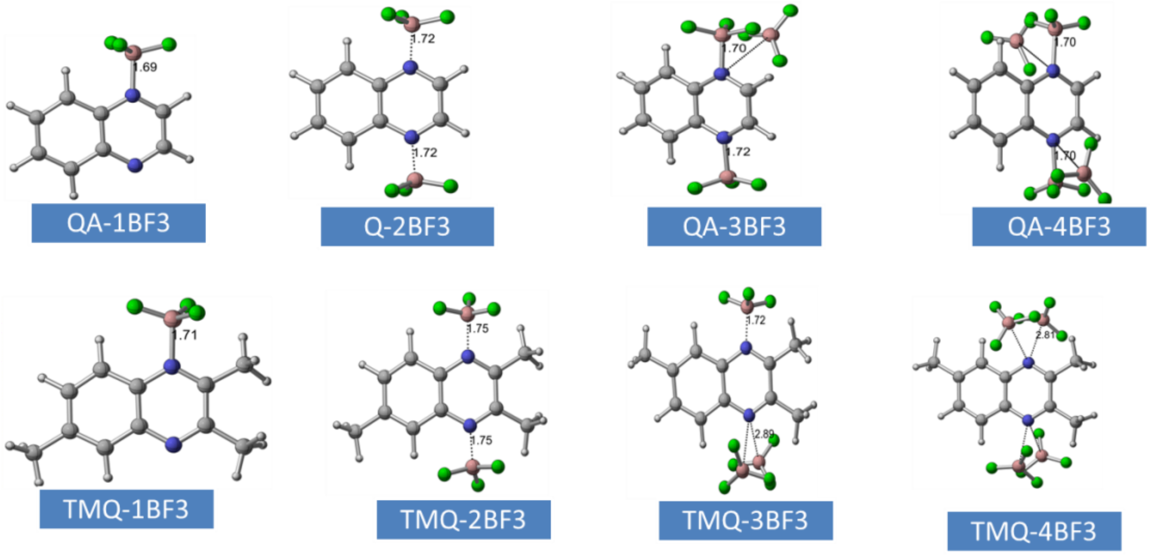


Figure S11. Optimized geometries of quinoxaline (here, QA), and 2,3,6-trimethylquinoxaline (2,3,6-TMQ) when complexed with 1, 2, 3, and 4 BF_3 molecule respectively, computed at the B3LYP/6-31+G(d) level of theory.



QA-1BF3

Q-2BF3

QA-3BF3

QA-4BF3

TMQ-1BF3

TMQ-2BF3

TMQ-3BF3

TMQ-4BF3