Supplementary Material

Redox-State Dependent Spectral Properties of Porous Organic Polymers Containing Furan, Thiophene, and Selenophene

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Figure S1. TGA of a) **POP-O**, **POP-O1** and **ox-POP-O**, b) **POP-S**, **POP-S1**, and **ox-POP-S**, c) **POP-Se**, **POP-Se1**, and **ox-POP-Se** from 25 – 700 °C under nitrogen, d) **POP-S** and **POP-Se** measured under air. The origin of the mass increase in POP-S and POP-Se is unknown, but appears regardless of whether the TGA was measured in air or nitrogen.



Figure S2. Solid state cyclic voltammograms of a) **POP-O**, b) **POP-S** and c) **POP-Se** in $[(n-C_4H_9)_4N]PF_6/CH_3CN$ electrolyte where the arrow indicates the direction of the forward scan.



Figure S3. Solid state cyclic voltammograms of a) **POP-O1**, b) **POP-S1** and **POP-Se1** at scan rates of c) 10 - 100 mV/s and d) 100 - 1000 mV/s in $[(n-C_4H_9)_4N]PF_6/CH_3CN$ where the arrow indicates the direction of the forward scan.





Figure S4. Solid state Vis/NIR spectroelectrochemical experiment in $[(n-C_4H_9)_4N]PF_6/CH_3CN$ electrolyte of **POP-Se** with oxidation from 0-2.5 V a) over the range 5000-25000 cm⁻¹ and b) photos of the polymer during the course of the experiment.



Figure S5. X-band solid-state EPR spectra of the polymers a) POP-O, POP-S, POP-Se, ox-POP-O, ox-POP-S and ox-POP-Se at room temperature at where the sharp peaks 2-2.0025 are due to impurities in the sample tube used.

 Table S1. Simulation Parameters for the EPR signal of POP-S.

g⊥	2.0068
g_	2.0045
A(mT)	0.1
Line broadening	0.15
Experimental MW phase	-30*π/180



Figure S6. Solid state spectra from the EPR spectroelectrochemical experiment for **POP-S** over three oxidation and reduction cycles in $[(n-C_4H_9)_4N]PF_6/CH_3CN$ electrolyte at X-band at room temperature.



Figure S7. a) Signal intensity as a function of the scan number, with the potential applied indicated for the most positive point of the signal at 3517 G and the most negative point of the signal at 3522 G and b) simulation of the EPR signal.