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Electronic Supplementary Information for

Water-coupled Monovalent and Divalent Ion Transport in Polyviologen Networks

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Figure S1. Cyclic voltammograms normalized (by maximum current) at 5 mV/s for poly(1,3,5-tris(4-cyanopyridinio)mesitylene) (PTMP) thin films in 0.5 M NaCl or 0.25 M Na₂SO₄ aqueous electrolyte. PTMP on a Au/Ti EQCM-D crystal was the working electrode, and a Ag/AgCl reference electrode and platinum plate counter electrode were used.



Figure S2. First derivative of mass change vs. potential for the poly(1,3,5-tris(4-cyanopyridinio)mesitylene) (PTMP) film in in a) 0.5 M NaCl or b) 0.25 M Na₂SO₄ aqueous electrolyte. Zoomed in view of the reduction for c) 0.5 M NaCl and d) 0.25 M Na₂SO₄ electrolytes, where the purple boxes highlight the observed additional small peaks. PTMP on a Au/Ti EQCM-D crystal was the working electrode, and a Ag/AgCl reference electrode and platinum plate counter electrode were used. The legend in a) applies to b). The arrows indicate the potential scan direction.



Figure S3. Cyclic voltammograms at 25 mV/s with overlaid charge profiles (a-b) and mass profiles (c-d). The supporting electrolyte was a) and c) 0.5 M NaCl or b) and d) 0.25 M Na₂SO₄. PTMP on a Au/Ti EQCM-D crystal was the working electrode, and Ag/AgCl reference electrode and platinum plate counter electrode were used. The legend in c) applies to all panels. The cyclic voltammogram is the solid curve, and the charge or mass profiles are presented as data points.



Figure S4. Mass change *vs.* charge transferred plots during cyclic voltammetry at 25 mV/s with a) 0.5 M NaCl and b) 0.25 M Na₂SO₄ supporting electrolyte. The mass change and charge transferred as a function of potential in **Figure S3**. PTPM electropolymerized on the Au/Ti EQCM-D crystal was the working electrode with a Ag/AgCl reference electrode and platinum plate counter electrode. The legend in d) applies to all panels.



Figure S5. Bode plots for poly(1,3,5-tris(4-cyanopyridinio)mesitylene) (PTMP) film in 0.5 M NaCl at -0.45 V and -0.90 V *vs.* Ag/AgCl. PTPM electropolymerized on the Au/Ti EQCM-D crystal was the working electrode with a Ag/AgCl reference electrode and platinum plate counter electrode. The legend in d) applies to all panels.



Figure S6. Bode plots for poly(1,3,5-tris(4-cyanopyridinio)mesitylene) (PTMP) film in 0.25 M Na_2SO_4 at -0.45 V and -0.90 V *vs.* Ag/AgCl. PTPM electropolymerized on the Au/Ti EQCM-D crystal was the working electrode with a Ag/AgCl reference electrode and platinum plate counter electrode. The legend in d) applies to all panels.