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## **Electronic Supplementary Information for**

## Metal-free Polypeptide Redox Flow Batteries

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**Fig. S1** Molecular structures of the viologen and biTEMPO small molecule analogs to the polypeptide materials.



**Fig. S2** Photographs of 20 mM active materials in 0.5 M TEATFSI/ACN stationary H-cells for crossover testing using Daramic 175 separators and FAPQ 375 PP membranes in the presence of (**A**) viologen-TFSI and (**B**) biTEMPO polypeptides. The left side of the H-cell originally contained 20 mM of active material in 0.5 M TEATFSI/ACN, and the right side originally contained 0.5 M TEATFSI/ACN. The images were taken at 6, 12, 24, 48, 72, and 96 h after the solutions were added to H-cells.



**Fig. S3** Photographs of 20 mM active materials in 0.5 M TEATFSI/ACN stationary H-cells for crossover testing using Daramic 175 separators and FAPQ 375 PP membranes in the presence of (**A**) viologen-TFSI and (**B**) biTEMPO analogs. The left side of the H-cell originally contained 20 mM of active material in 0.5 M TEATFSI/ACN, and the right side originally contained 0.5 M TEATFSI/ACN. The images were taken at 6, 12, 24, 48, 72, and 96 h after the solutions were added to H-cells.



**Fig. S4** Time-dependent crossover studies of (A) the redox-active polypeptides and (B) small-molecule analogs using Daramic 175 separator.



**Fig. S5** Bode plot of the EIS data before galvanostatic cycling for the redox flow cell with a BiTEMPO polypeptide catholyte and viologen polypeptide anolyte. EIS was conducted with circulating electrolytes at open circuit potential with an amplitude of 10 mV in a frequency range of 200 kHz to 0.4 Hz (5 steps per decade).



**Fig. S6** Normalized CD spectra of (A) viologen polypeptide and (B) biTEMPO polypeptide without TEATFSI, before cycling, and after 500 cycles. The spectra were normalized to a wavelength of 222 nm. The "no salt" curve indicates electrolytes without supporting salt that had not been cycled. The other curves included supporting salt.



Fig. S7 ATR-FTIR spectra of (A) 0.5 M TEATFSI/ACN, (B) 50 mM viologen-TFSI polypeptide/ACN, and 50 mM viologen-TFSI polypeptide in 0.5 M TEATFSI/ACN (C) before cycling, (D) after rate study and (E) after 500 cycles at 10 mA  $\cdot$  cm<sup>-2</sup>. The y-axes of the spectra are transmittance (%).



Fig. S8 ATR-FTIR spectra of (A) 0.5 M TEATFSI/ACN, (B) 25 mM biTEMPO polypeptide/ACN, and 25 mM biTEMPO polypeptide in 0.5 M TEATFSI/ACN (C) before cycling, (D) after rate study and (E) after 500 cycles at 10 mA $\cdot$ cm<sup>-2</sup>. The y-axes of the spectra are transmittance (%).