Supporting Information for:

ELECTRON AND MASS TRANSPORT IN HYBRID REDOX POLYETHER MELTS CONTACTED WITH CARBON DIOXIDE

Dongil Lee, John C. Hutchison, Anthony M. Leone,
Joseph M. DeSimone,* and Royce W. Murray*

Kenan Laboratories of Chemistry and NSF Center for Environmentally Responsible Solvents and Processes, University of North Carolina, Chapel Hill, NC 27599

Figure S1. Argon pressure dependencies of D_{PHYS} (●) and D_E (■) in $[Co(bpy(CO_2MePEG\text{-}350)_2)_3](ClO_4)_2$ melt at 23 °C.

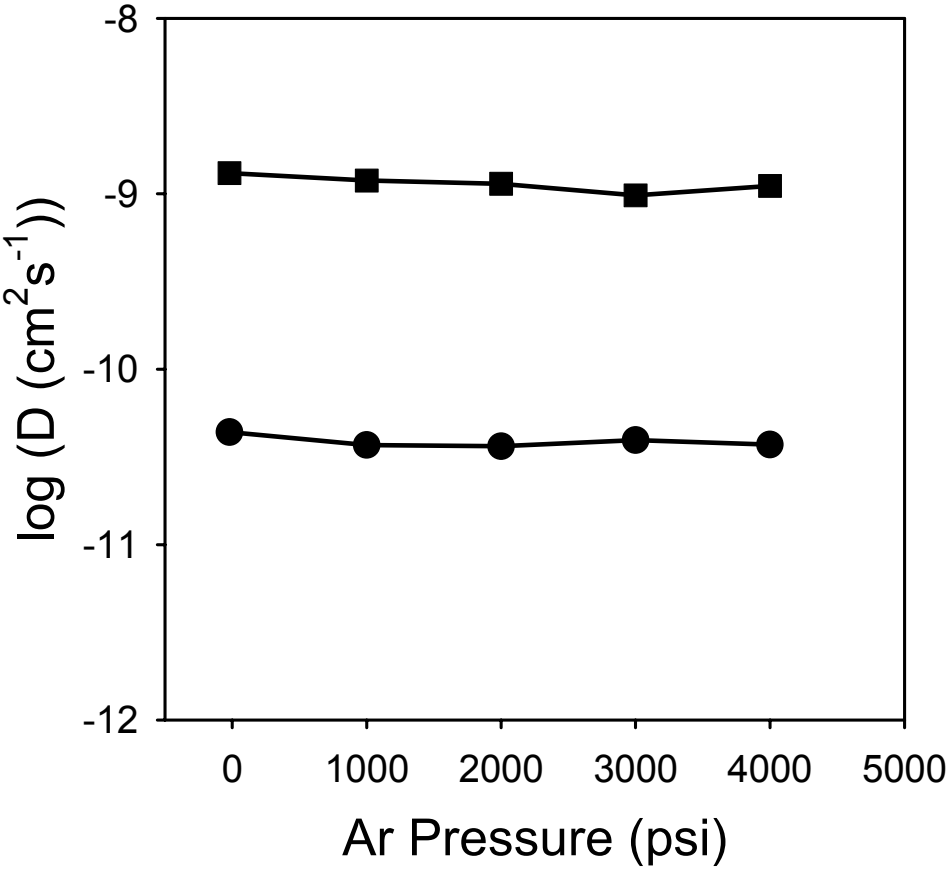

Table S1. Concentration (C), average center-to-center distance (δ), and fractional free volume (FFV) for CO_2-swollen $[Co(bpy(CO_2MePEG\text{-}350)_2)_3](ClO_4)_2$ melt at indicated CO_2 pressures.

CO_2 Pressure (psi) at 23 °C	Vacuum	200	500	800	1000	2000
Swelling Volume (mL/mol) [a]	0	45	141	234	288	295
Molar Volume, V_m(mL/mol) [b]	2248	2293	2389	2482	2536	2543
Concentration of Co (M)	0.445	0.436	0.419	0.403	0.394	0.393
δ(Å) [c]	15.5	15.6	15.8	16.0	16.2	16.2
FFV [d]	0.361	0.374	0.399	0.421	0.434	0.435

(a) From CO_2-induced swelling volume measurements.

(b) Molar volume at vacuum from density measurement (1.301 g/mL). Molar volume at a given CO_2-pressure was taken as the summation of the swelling volume and molar volume at vacuum.

(c) From molar volume assuming face-centered cubic packing.

(d) Calculated via Eq. 4 using V_w=1436 mL/mol and molar volume (V_m) at an indicated pressure.

Table S2. Electron and Mass Transport Data for $[Co(bpy(CO_2MePEG\text{-}350)_2)_3](ClO_4)_2$ melt plotted in Figures 4 and 6.

Temperature (°C)	CO_2 Pressure (psi)	Conc. of Co (M)	D_{PHYS} Co(III/II) (cm^2/s)	σ_{ION} (S/cm)	D_E Co(II/I) (cm^2/s)	k_{EX} ($M^{-1}s^{-1}$)
22.5	vacuum	0.445	2.4×10^{-11}	1.4×10^{-6}	1.2×10^{-9}	6.8×10^{5}
30.9	vacuum	0.445	$(1.3\times10^{-10})^a$	2.3×10^{-6}	1.8×10^{-9}	1.0×10^{6}
38.9	vacuum	0.445	$(2.5\times10^{-10})^b$	3.6×10^{-6}	2.6×10^{-9}	1.5×10^{6}
47.4	vacuum	0.445	$(4.4\times10^{-10})^c$	5.5×10^{-6}	3.7×10^{-9}	2.1×10^{6}
22.9	203	0.436	8.3×10^{-11}	3.3×10^{-6}	1.9×10^{-9}	1.1×10^{6}
34.9	212	0.436	1.8×10^{-10}	5.9×10^{-6}	3.2×10^{-9}	1.8×10^{6}
49.3	222	0.436	4.0×10^{-10}	1.1×10^{-5}	5.7×10^{-9}	3.2×10^{6}
22.9	506	0.419	2.4×10^{-10}	8.3×10^{-6}	3.3×10^{-9}	1.9×10^{6}
30.9	525	0.419	3.4×10^{-10}	1.0×10^{-5}	4.4×10^{-9}	2.5×10^{6}
39.4	545	0.419	4.8×10^{-10}	1.3×10^{-5}	5.9×10^{-9}	3.4×10^{6}
48.5	564	0.419	7.4×10^{-10}	1.7×10^{-5}	7.7×10^{-9}	4.4×10^{6}
22.8	800	0.403	5.8×10^{-10}	1.5×10^{-5}	5.6×10^{-9}	3.3×10^{6}
31.0	853	0.403	7.3×10^{-10}	1.8×10^{-5}	7.0×10^{-9}	4.0×10^{6}
38.9	895	0.403	9.4×10^{-10}	2.2×10^{-5}	8.7×10^{-9}	5.0×10^{6}
47.6	933	0.403	1.3×10^{-9}	2.8×10^{-5}	1.1×10^{-8}	6.3×10^{6}

(a) Measured at 45.0 °C

(b) Measured at 53.9 °C

(c) Measured at 64.4 °C