

Supporting Information

Impact of Open-Shell Loading on Mass Transport and Doping in Conjugated Radical Polymers

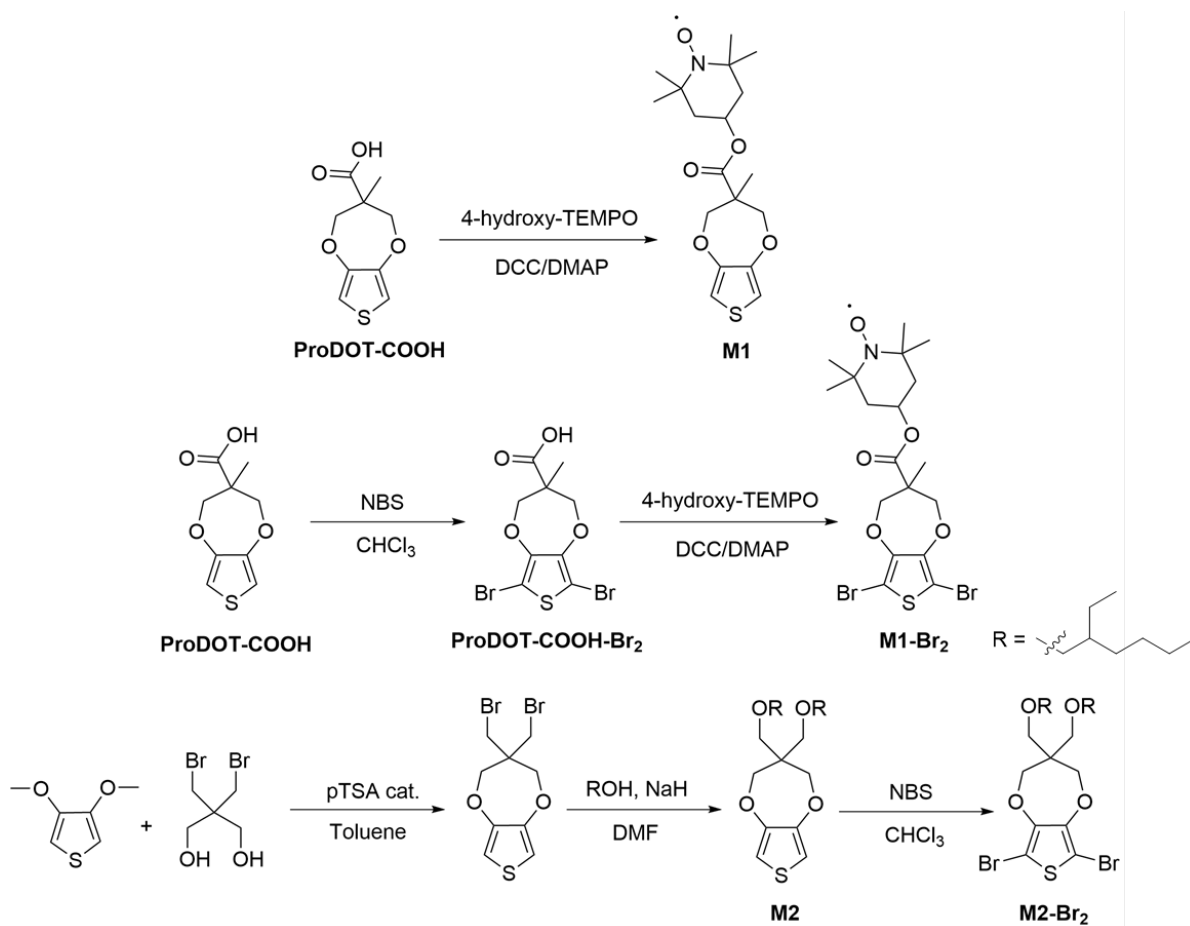
Kangying Liu,¹ Kuluni Perera,¹ Zhiyang Wang,¹ Jianguo Mei,¹ and Bryan W. Boudouris^{1,2,*}

¹ Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907, USA

² Charles D. Davidson School of Chemical Engineering, Purdue University, 480 W Stadium Avenue, West Lafayette, Indiana 47907, USA

* To whom correspondence should be addressed: boudouris@purdue.edu

Scheme S1. Monomer Synthesis Scheme.



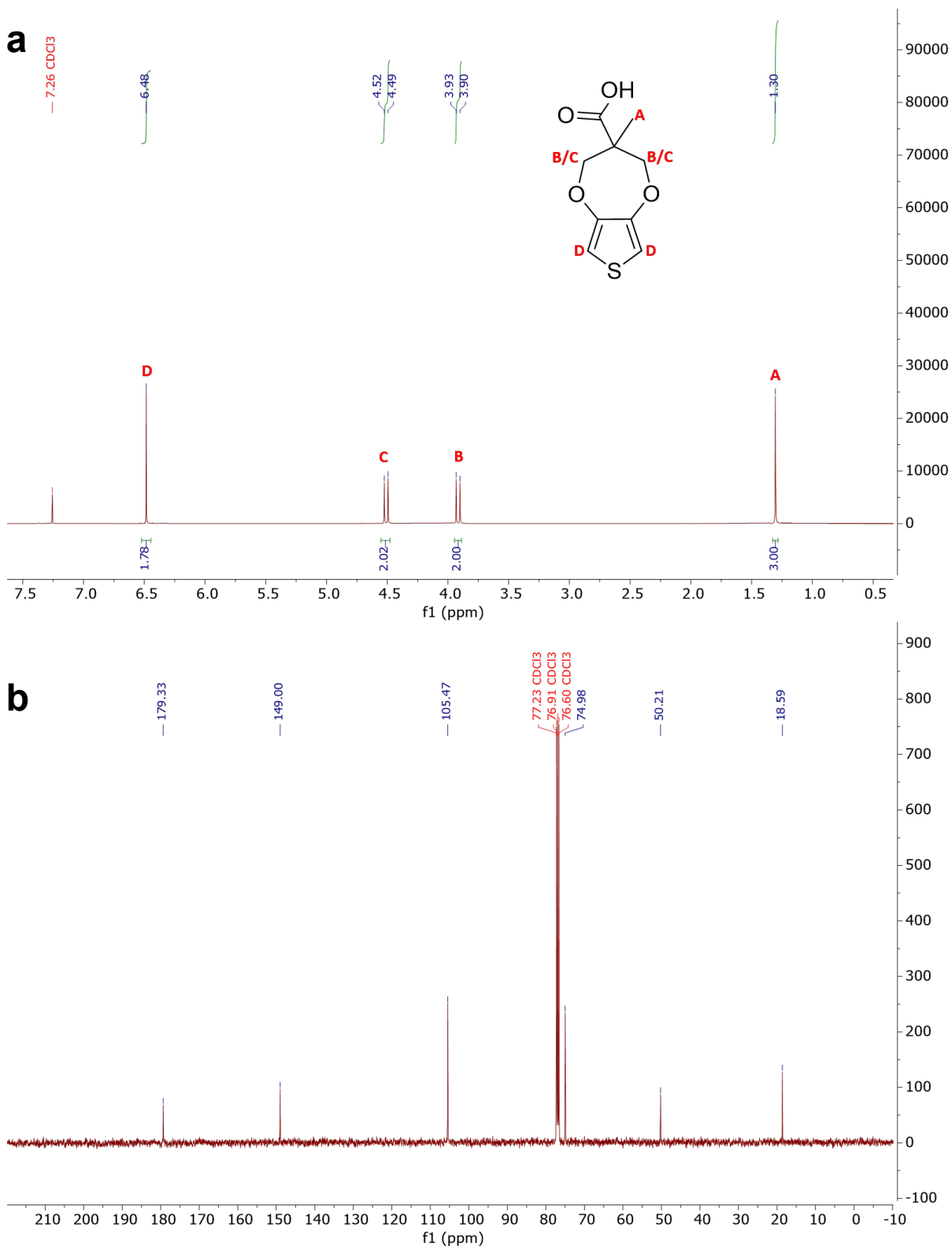


Figure S1. (a) ¹H NMR and (b) ¹³C NMR spectra of 3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-carboxylic acid (**ProDOT-COOH**), prepared based on a previously reported method.¹

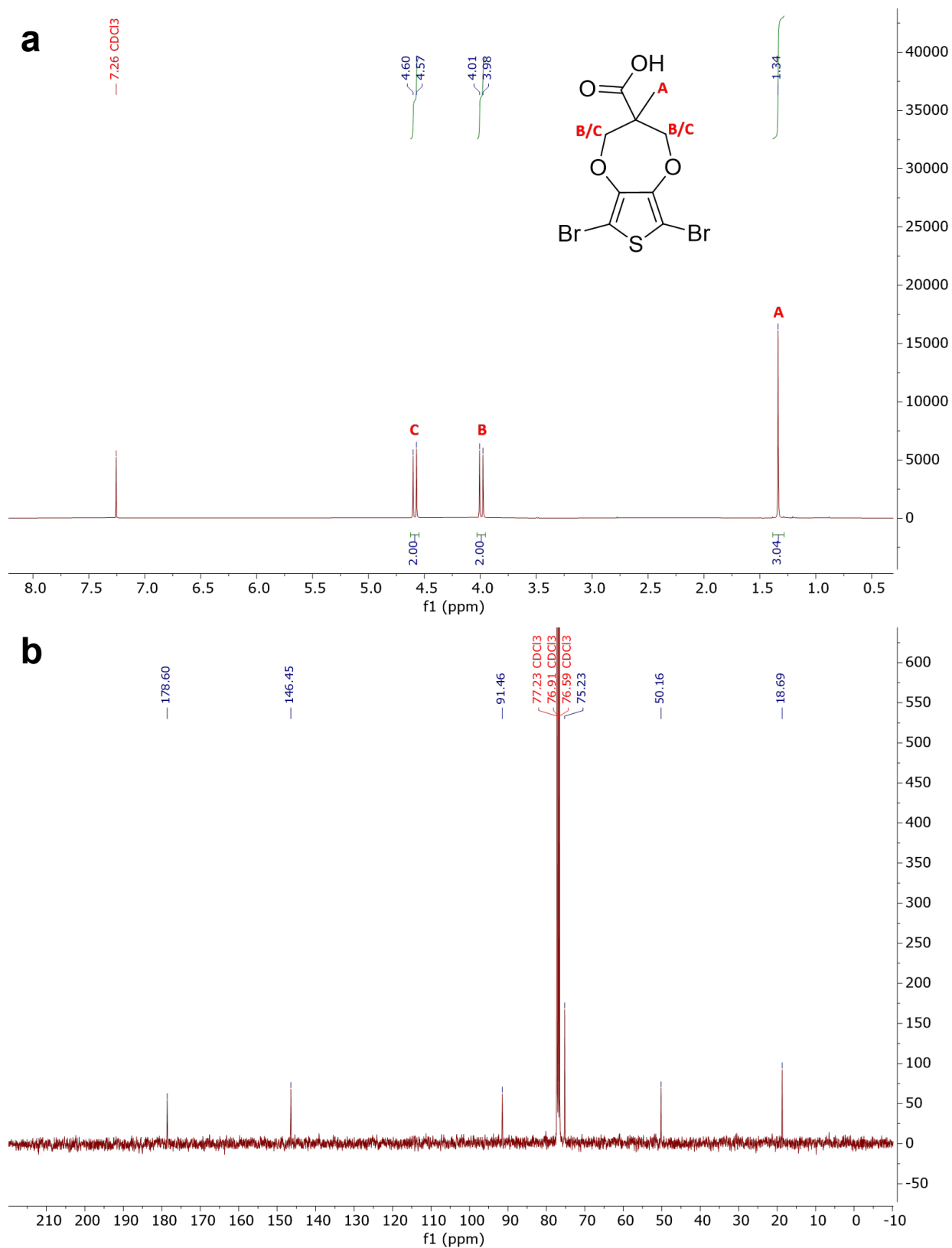


Figure S2. (a) ¹H NMR and (b) ¹³C NMR spectra of 6,8-dibromo-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-carboxylic acid (**ProDOT-COOH-Br₂**).

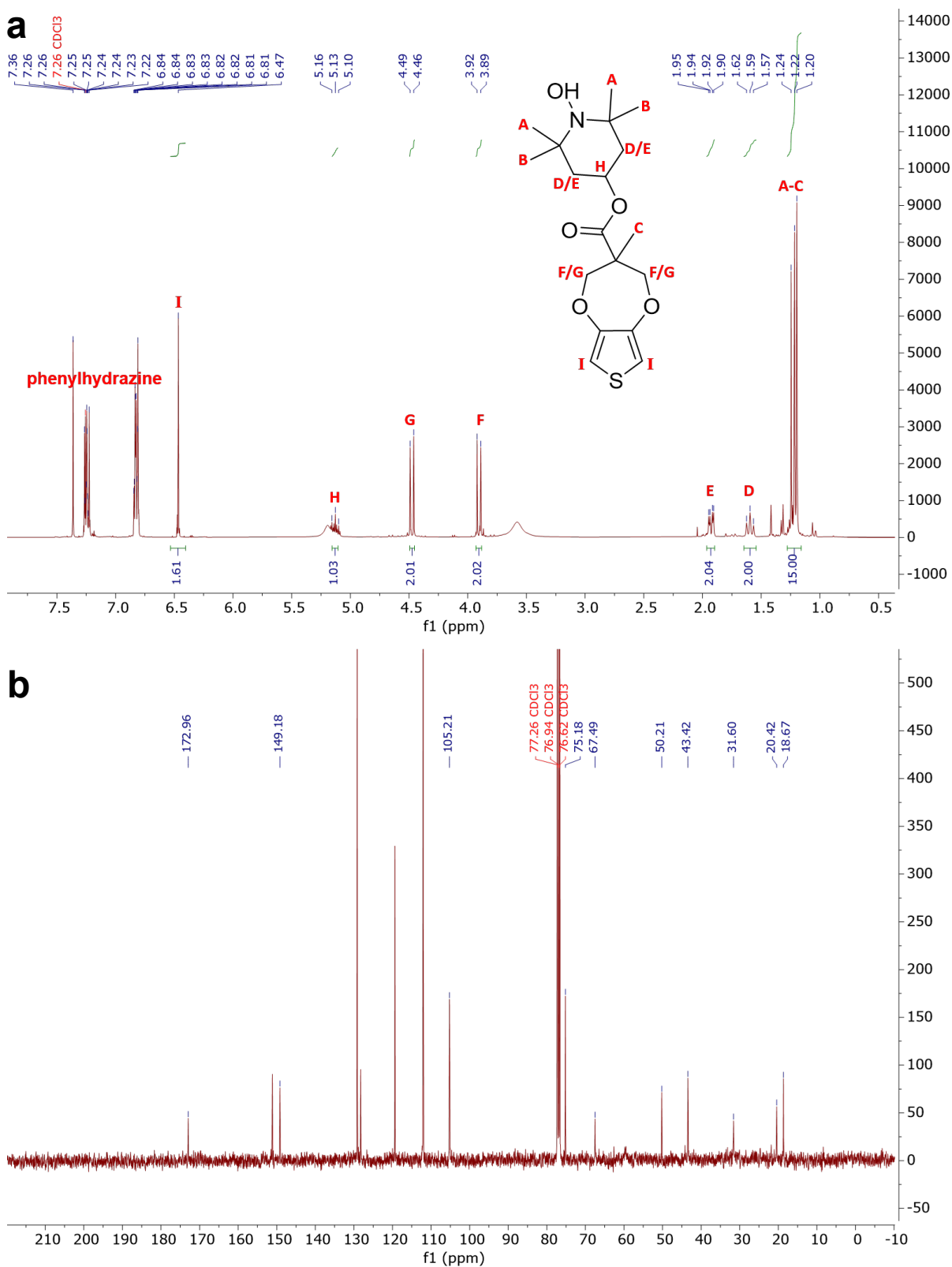


Figure S3. (a) ^1H NMR and (b) ^{13}C NMR spectra of 2,2,6,6-tetramethylpiperidiny-N-oxyl 3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-carboxylate (**M1**) quenched with phenylhydrazine.

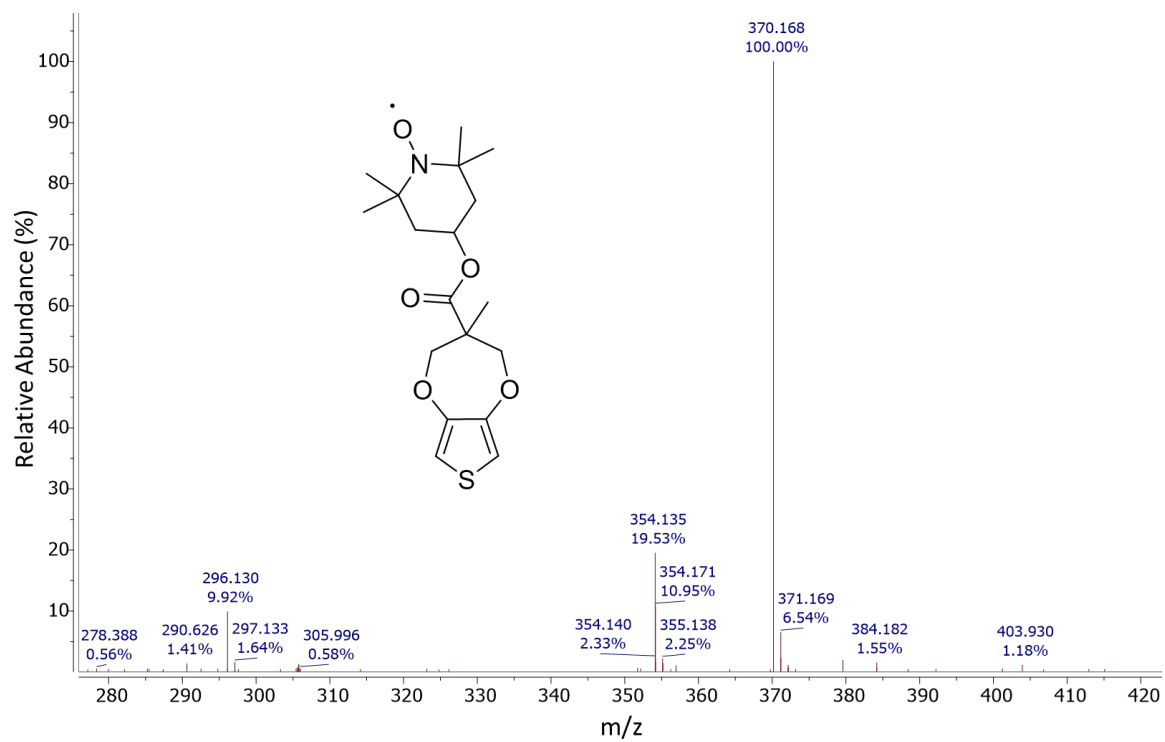


Figure S4. Atmospheric pressure chemical ionization (APCI) mass spectra of **M1**.

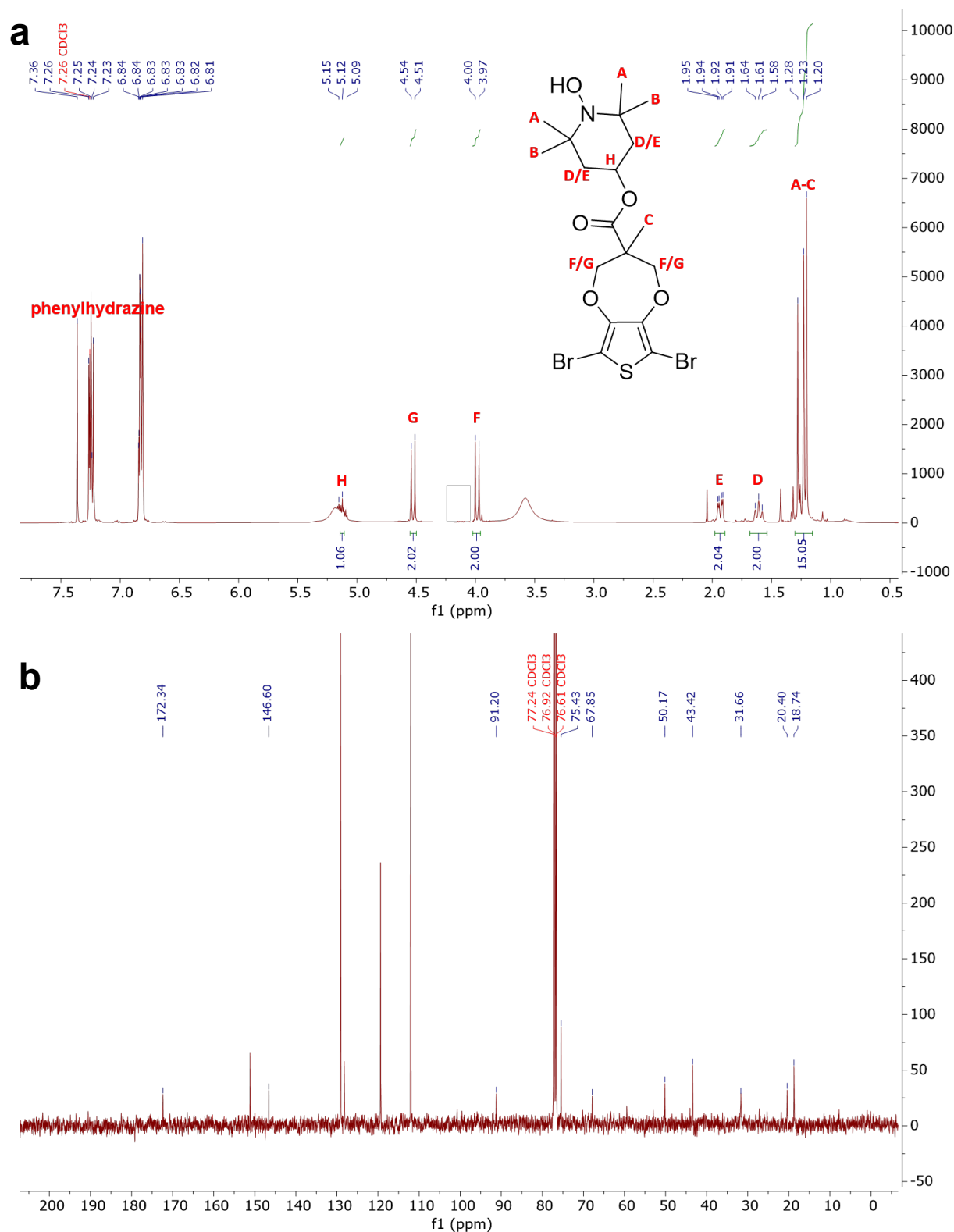


Figure S5. (a) ^1H NMR and (b) ^{13}C NMR spectra of 6,8-dibromo-2,2,6,6-tetramethylpiperidinyln-oxyl 3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-3-carboxylate (**M1-Br₂**) quenched with phenylhydrazine.

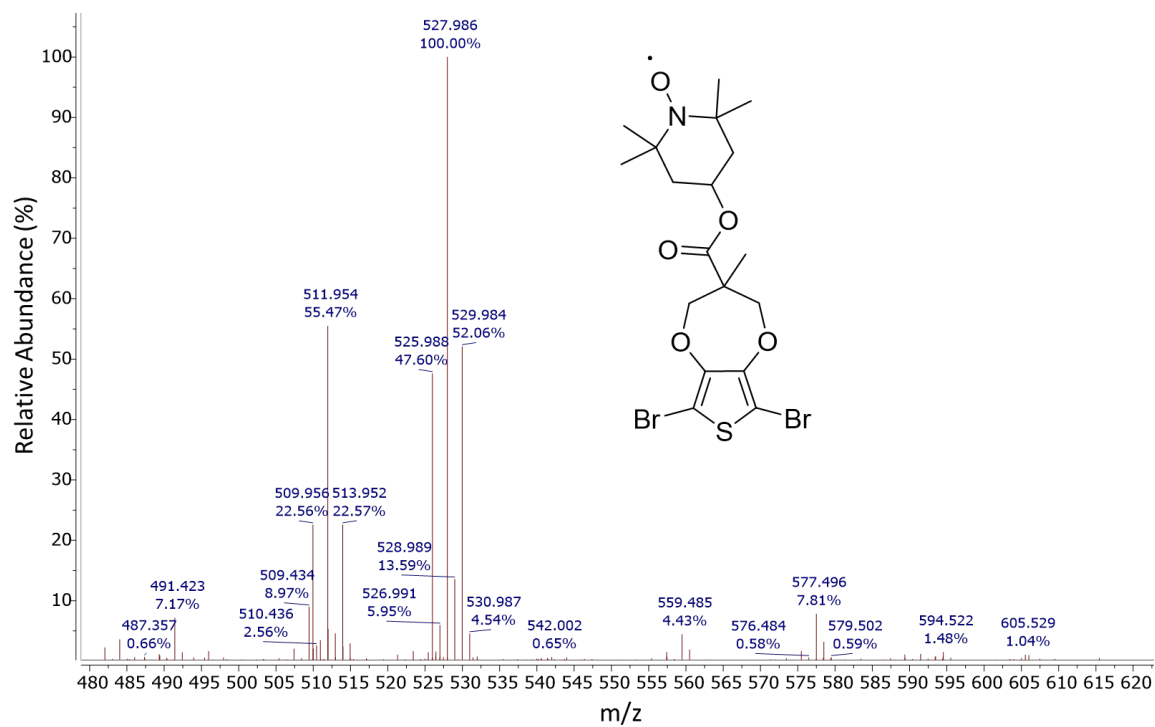


Figure S6. Atmospheric pressure chemical ionization (APCI) mass spectra of **M1-Br₂**.

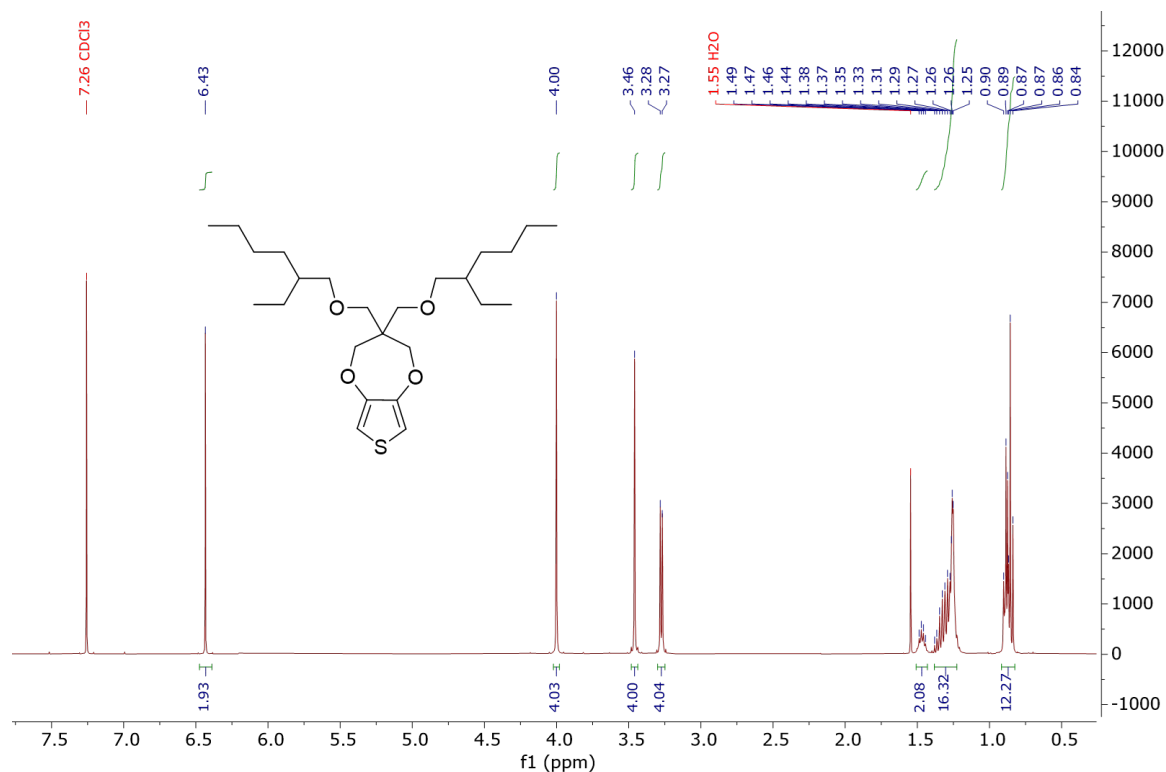


Figure S7. ¹H NMR spectra of 3,3-bis(2-ethylhexyloxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (**M2**), prepared based on a previously reported method.²

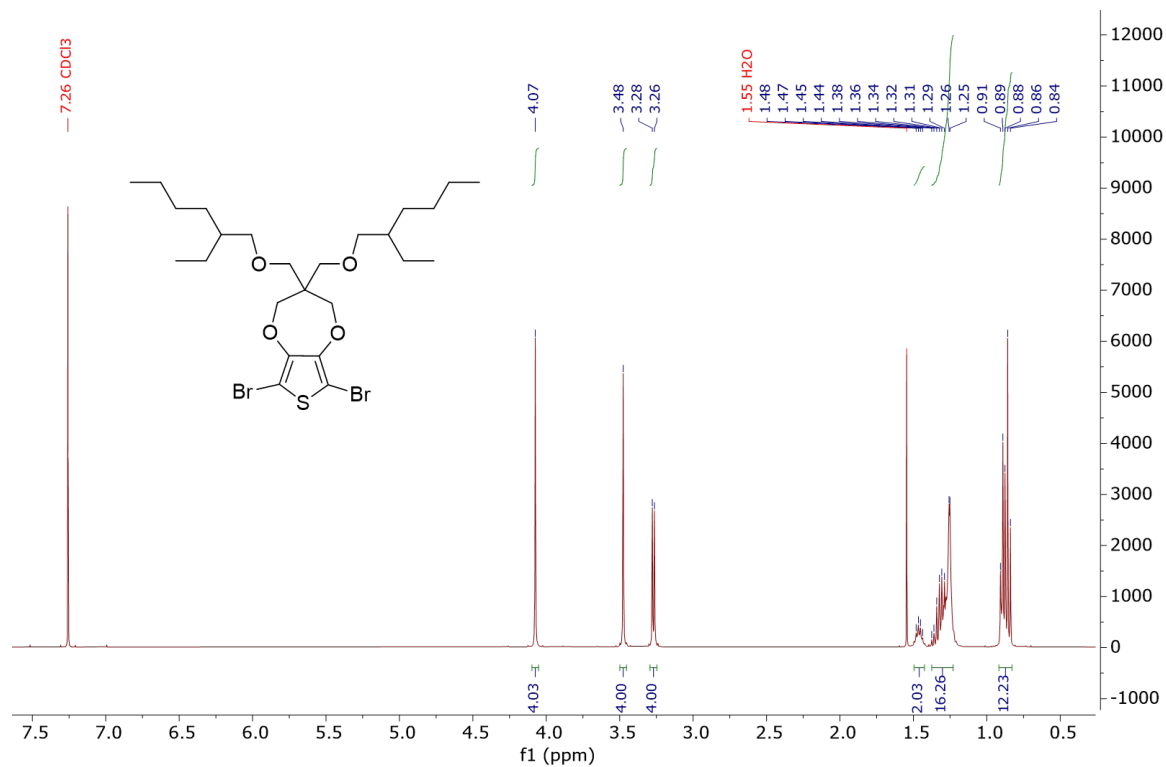


Figure S8. ¹H NMR spectra of 6,8-dibromo-3,3-bis(2-ethylhexyloxymethyl)-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (**M2-Br₂**), prepared based on a previously reported method.²

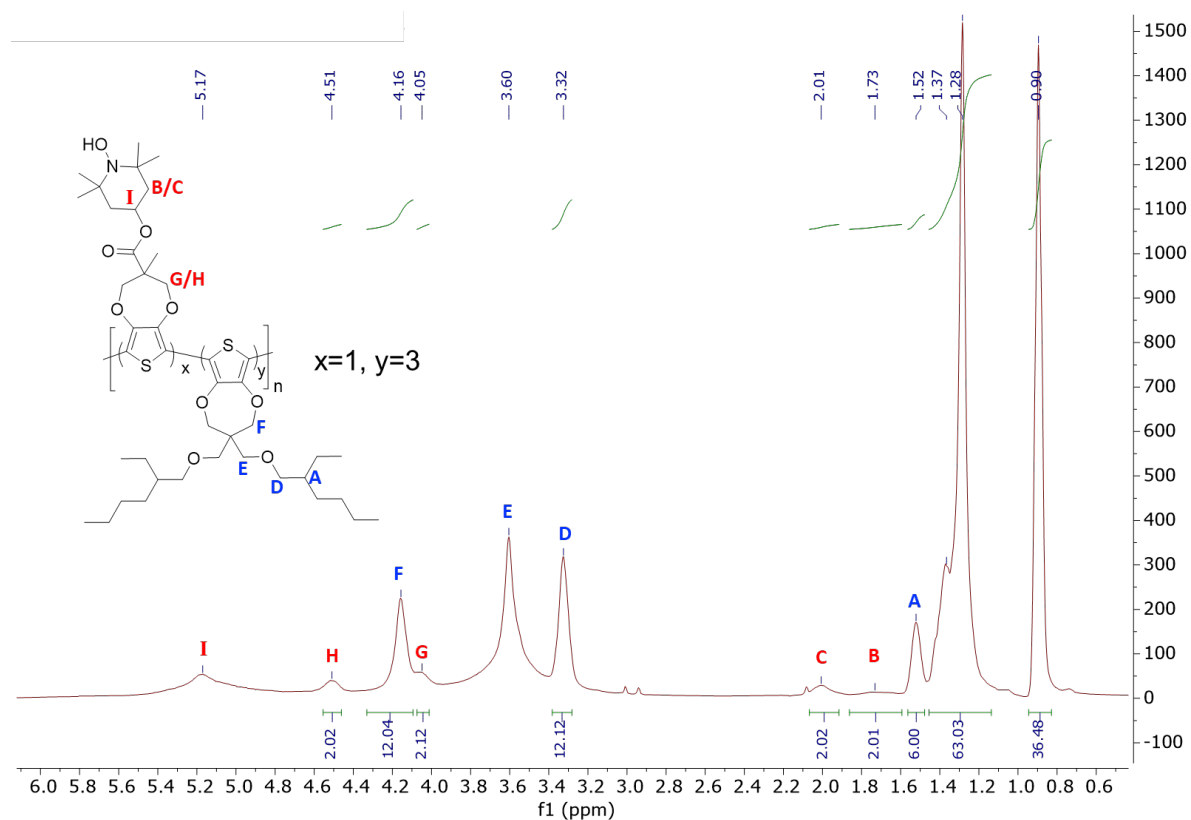


Figure S9. ^1H NMR spectra of PProDOT-TEMPO-24 quenched with phenylhydrazine in CDCl₃.

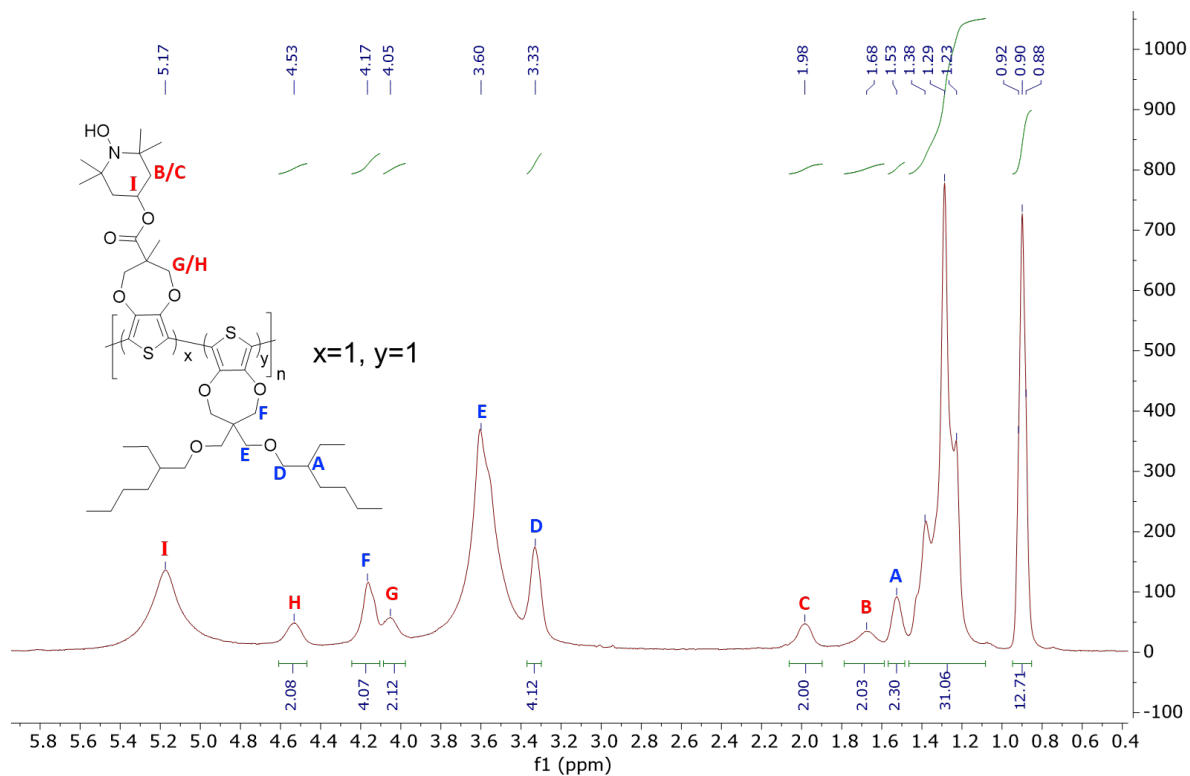


Figure S10. ^1H NMR spectra of PProDOT-TEMPO-46 quenched with phenylhydrazine in CDCl₃.

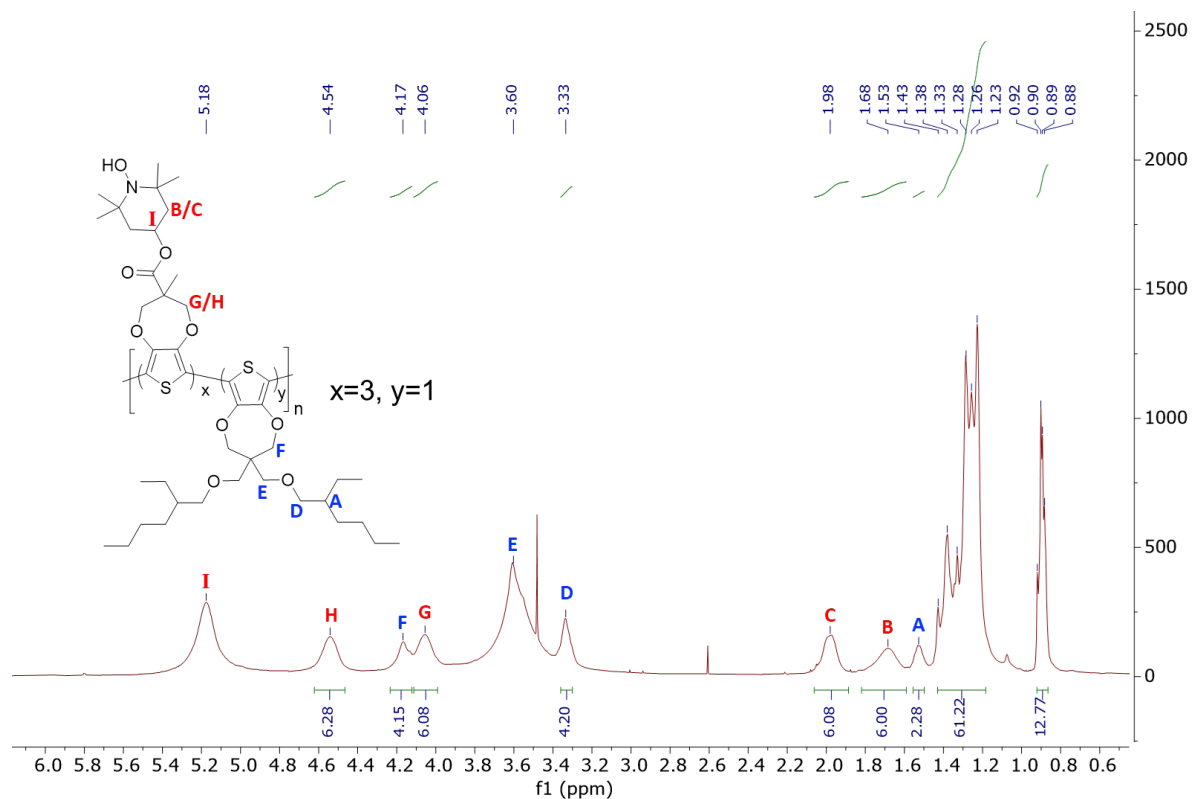


Figure S11. ¹H NMR spectra of PProDOT-TEMPO-63 quenched with phenylhydrazine in CDCl₃.

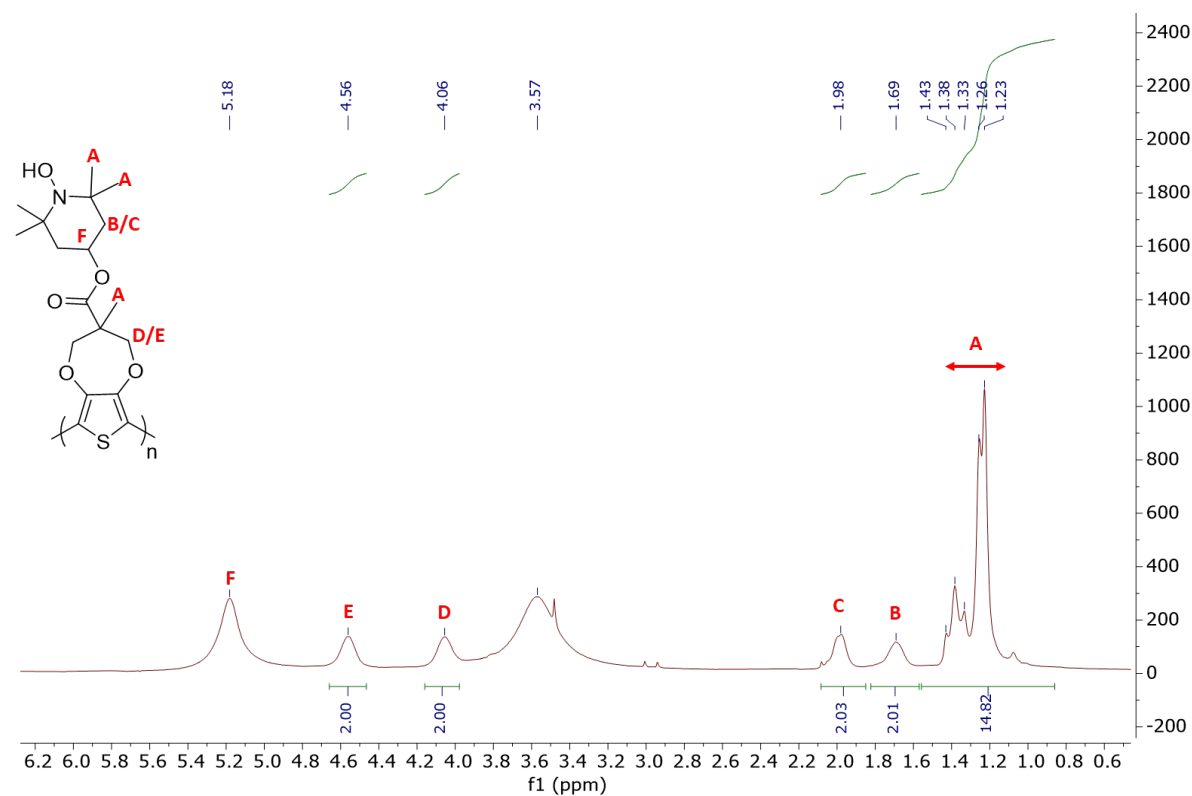


Figure S12. ¹H NMR spectra of PProDOT-TEMPO-82 quenched with phenylhydrazine in CDCl₃.

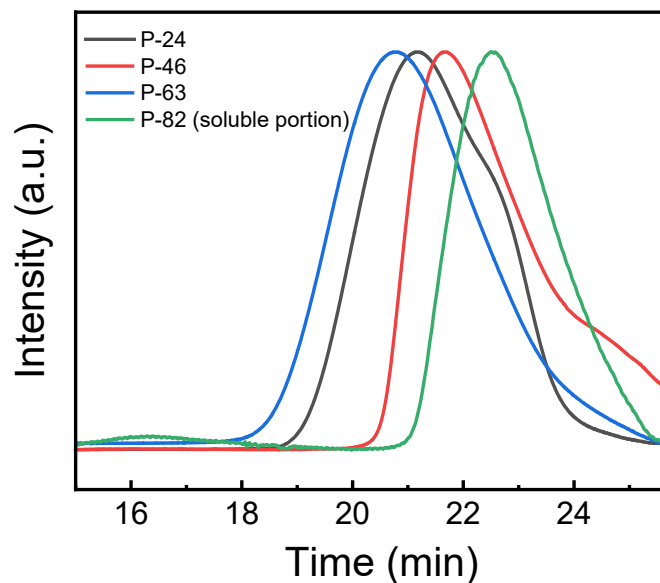


Figure S13. SEC chromatograms of PProDOT-TEMPO polymers with tetrahydrofuran (THF) serving as the mobile phase at room temperature.

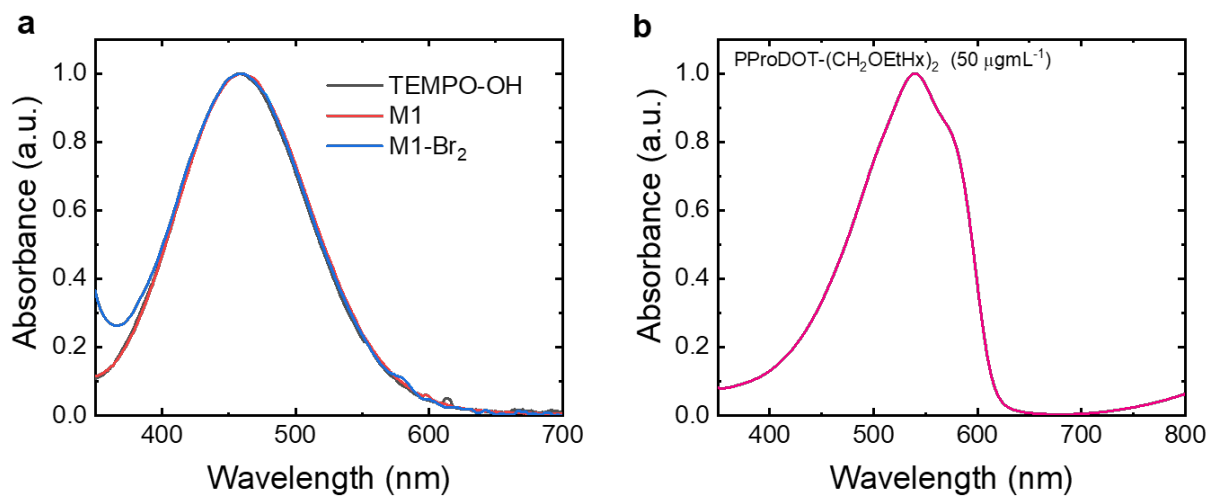


Figure S14. The normalized UV-Vis absorption spectra of (a) the TEMPO-containing small molecules used in this work, including TEMPO-OH, ProDOT-TEMPO (**M1**), and dibromo-ProDOT-TEMPO (**M1-Br₂**), and (b) the PProDOT-(CH₂OEtHx)₂ polymer in a chloroform solution.

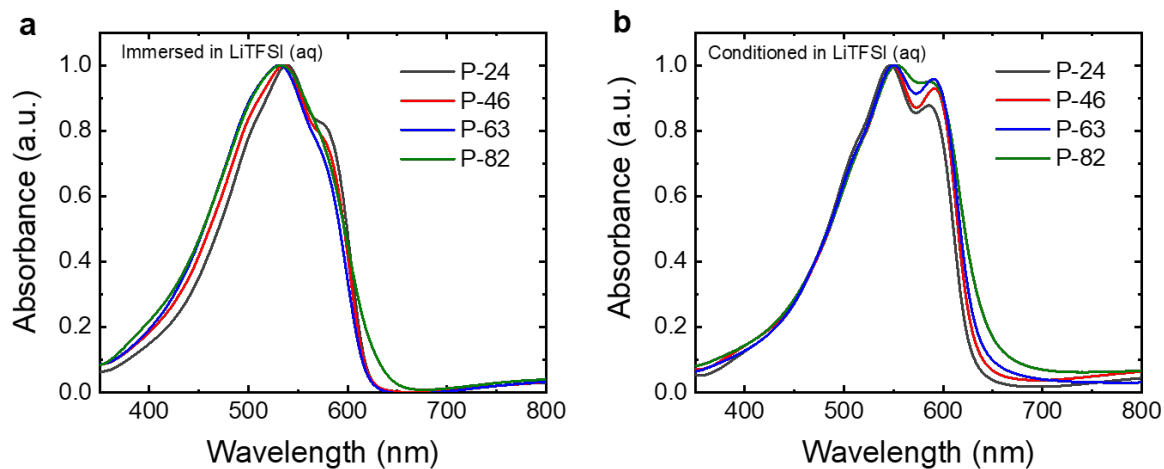


Figure S15. The normalized UV-Vis absorption spectra of PProDOT-TEMPO polymers as (a) thin films immersed in a 0.2 M LiTFSI (aq) and (b) thin films electrochemically conditioned in LiTFSI (aq).

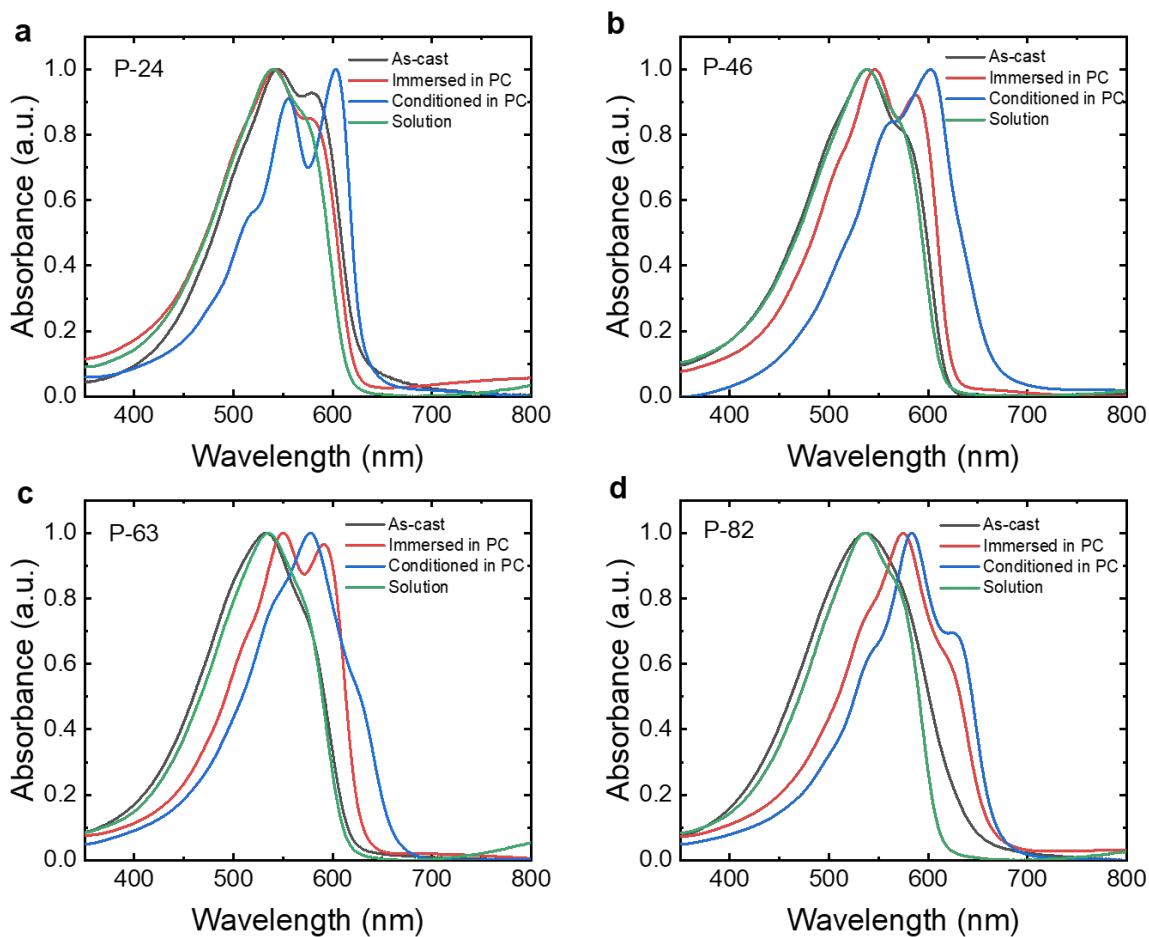


Figure S16. Evolution of the UV-Vis absorbance spectra for (a) PProDOT-TEMPO-24, (b) PProDOT-TEMPO-46, (c) PProDOT-TEMPO-63, and (d) PProDOT-TEMPO-82 from solution to solid state, thin films immersed in LiTFSI (PC) electrolyte and electrochemically conditioned thin films in LiTFSI (PC).

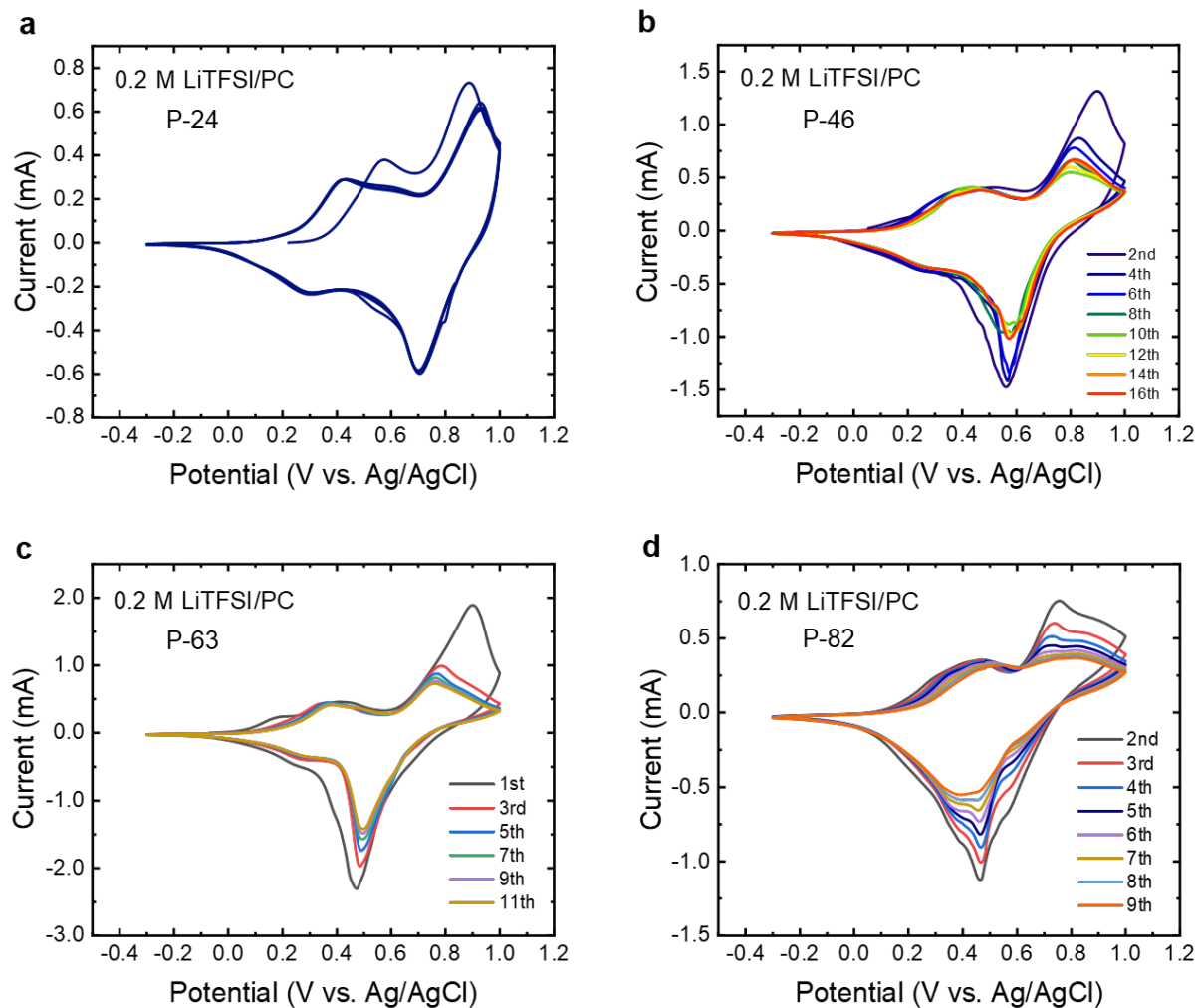


Figure S17. Cyclic voltammetry of (a) P-24, (b) P-46, (c) P-63 and (d) P-82 in a 0.2 M LiTFSI solution where propylene carbonate (PC) served as the solvent. These data were recorded at a scan rate of 40 mV s^{-1} .

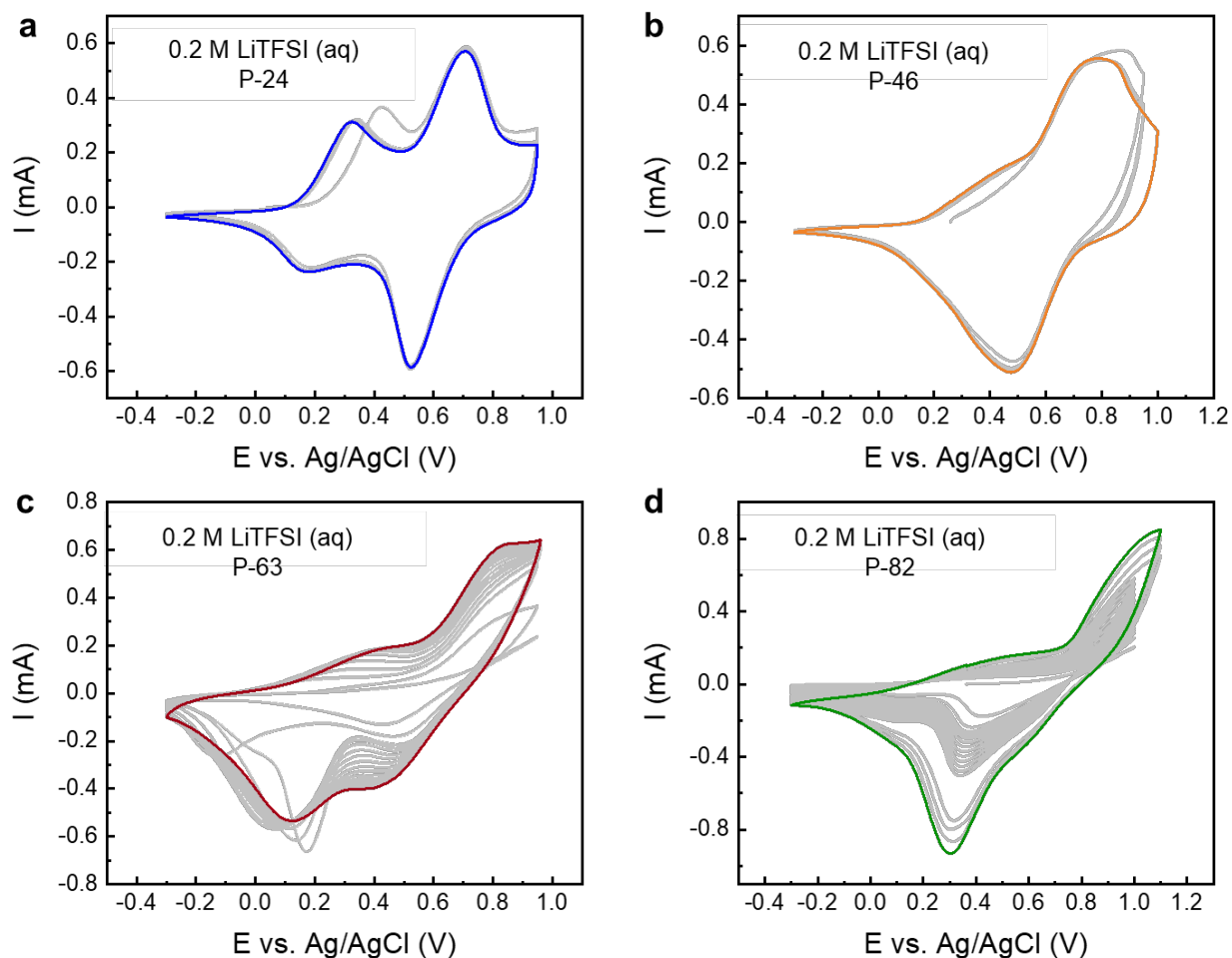


Figure S18. Cyclic voltammetry of (a) P-24, (b) P-46, (c) P-63 and (d) P-82 in a 0.2 M LiTFSI solution where deionized water served as the solvent. These data were recorded at a scan rate of 40 mV s⁻¹. The oxidation peaks are not resolved for P-46, P-63, and P-82. The break-in process takes much longer for P-63 and P-82 relative to P-24 and P-46. The last cycle is colored for each polymer.

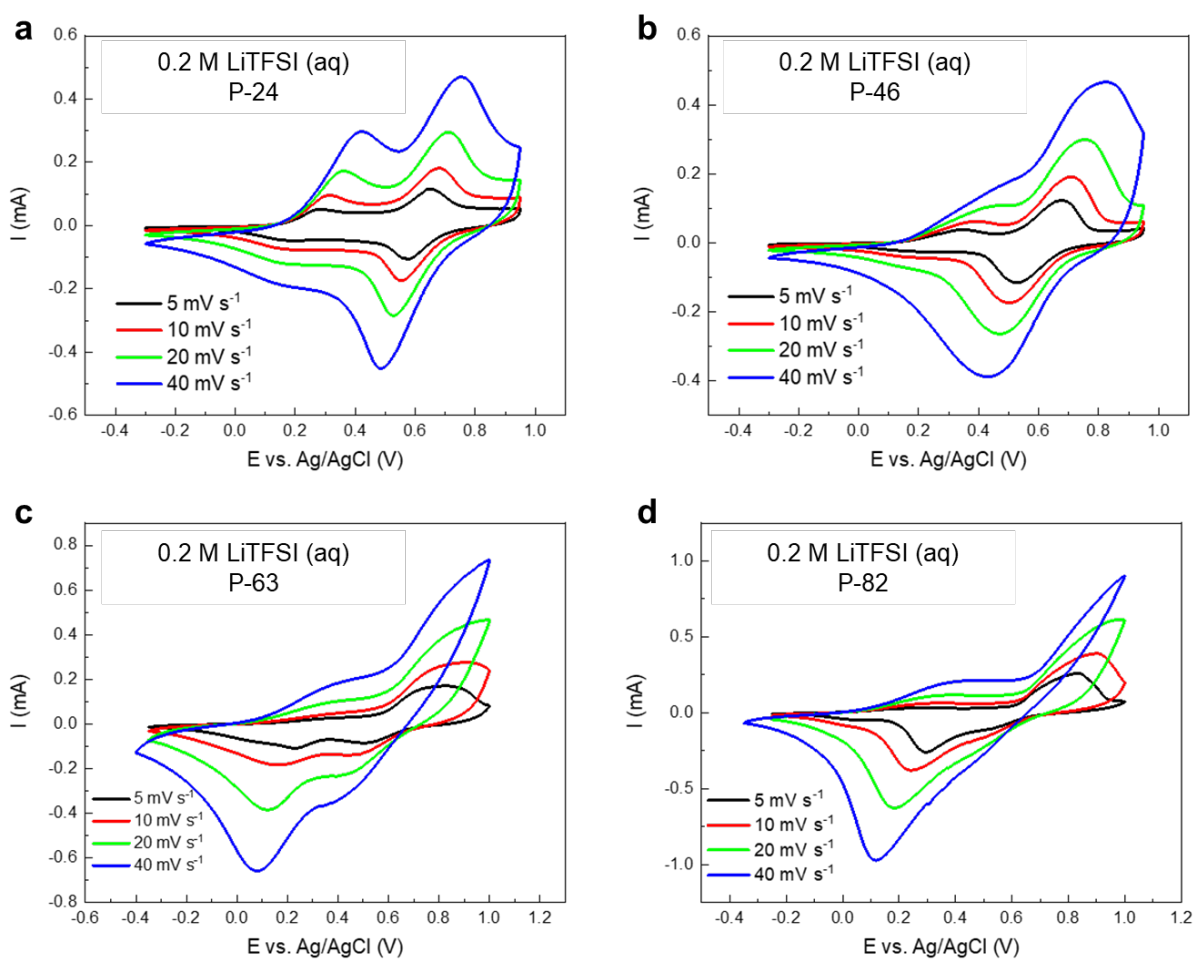


Figure S19. Cyclic voltammetry of (a) P-24, (b) P-46, (c) P-63, and (d) P-82 in a 0.2 M LiTFSI solution where deionized water served as the solvent. These data were recorded at scan rates of 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} and 40 mV s^{-1} for each polymer.

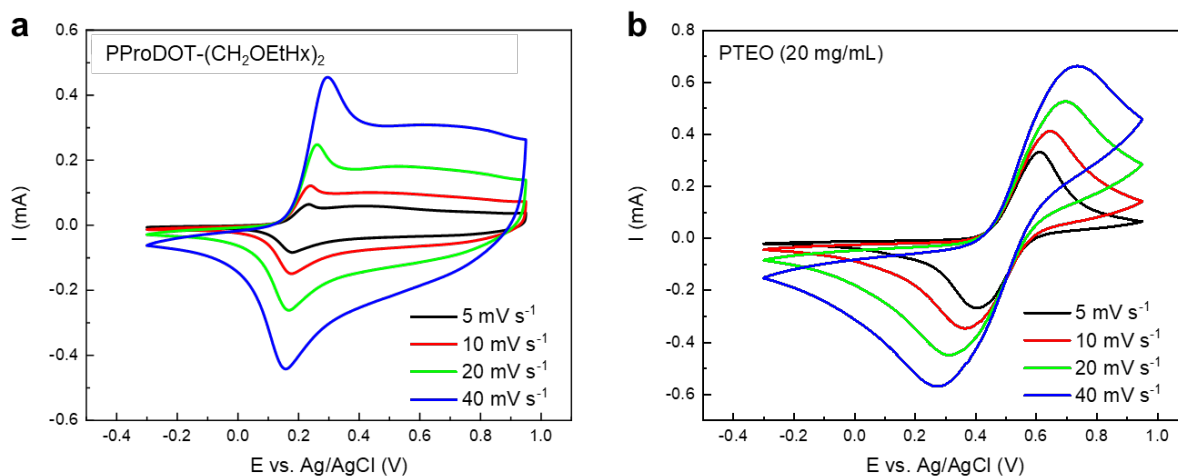


Figure S20. Cyclic voltammetry of (a) PProDOT-(CH₂OEtHx)₂ and (b) PTEO in a 0.2 M LiTFSI solution where deionized water served as the solvent. These data were recorded at scan rates of 5 mV s⁻¹, 10 mV s⁻¹, 20 mV s⁻¹ and 40 mV s⁻¹ for each polymer.

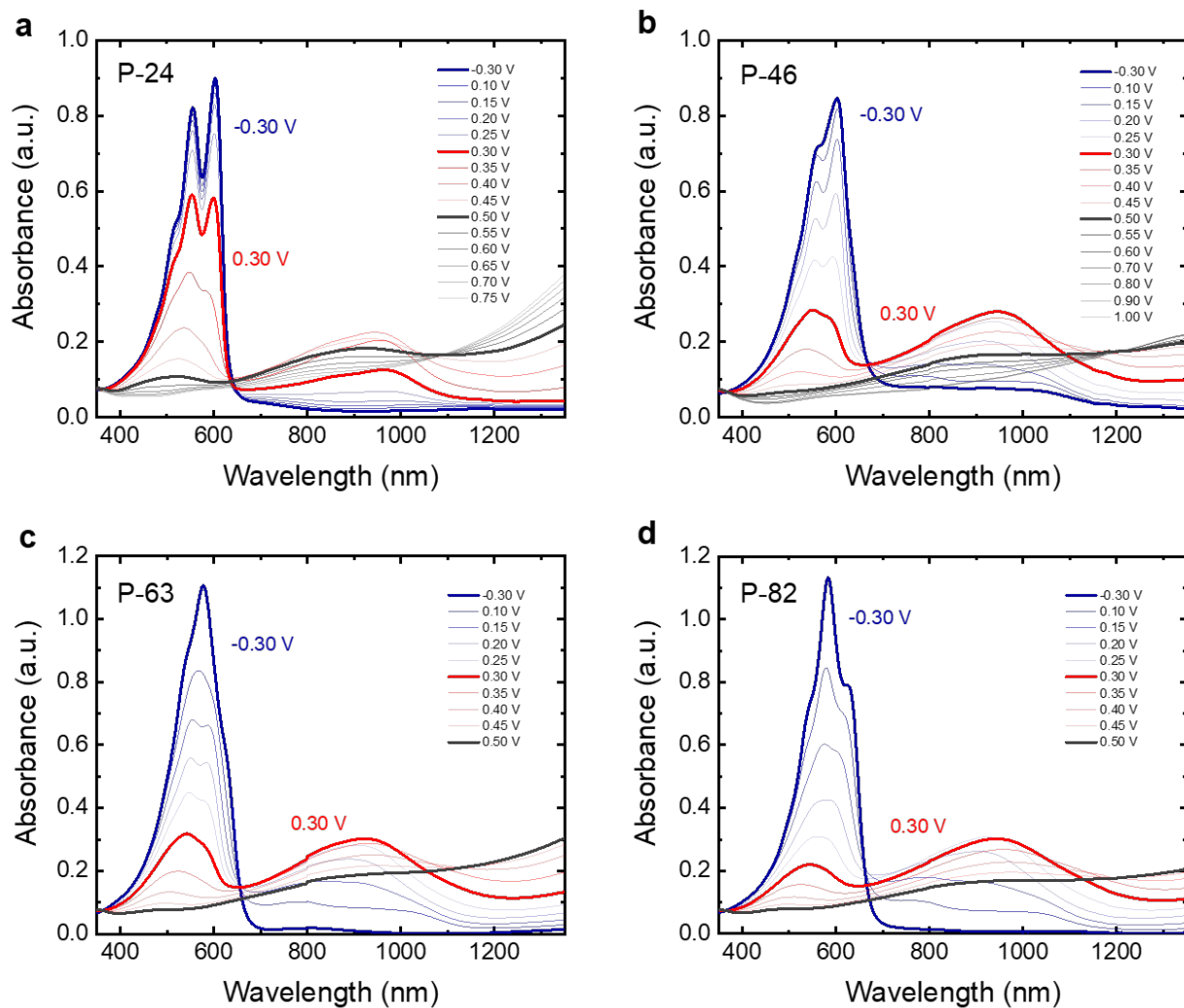


Figure S21. Spectroelectrochemical analysis of the PProDOT-TEMPO radical polymers in a 0.2 M LiTFSI solution where propylene carbonate (PC) served as the solvent. (a) P-24 recorded from -0.30 V to $+0.75$ V vs. Ag/AgCl; (b) P-46 recorded from -0.30 V to $+1.00$ V vs. Ag/AgCl; (c) P-63 recorded from -0.30 V to $+0.50$ V vs. Ag/AgCl; and (d) P-82 recorded from -0.30 V to $+0.50$ V vs. Ag/AgCl. The suppressed bipolaron formation is observed for polymers P-46 and onwards.

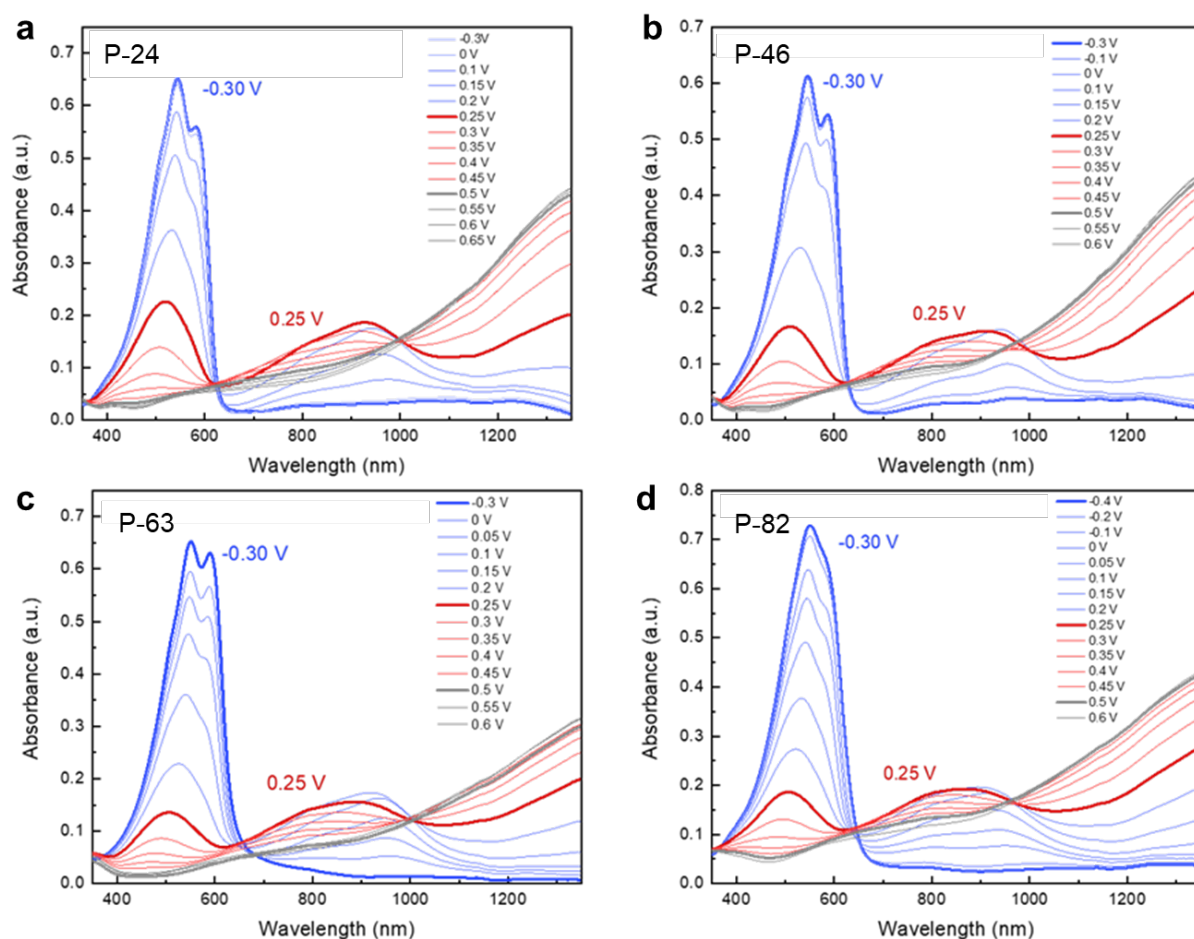


Figure S22. Spectroelectrochemical analysis of the PProDOT-TEMPO radical polymers in a 0.2 M LiTFSI solution where deionized water served as the solvent. (a) P-24 recorded from -0.30 V to +0.65 V vs. Ag/AgCl; (b) P-46 recorded from -0.30 V to +0.60 V vs. Ag/AgCl; (c) P-63 recorded from -0.30 V to +0.60 V vs. Ag/AgCl; and (d) P-82 recorded from -0.40 V to +0.60 V vs. Ag/AgCl. All polymers show bipolaron formation in the NIR region.

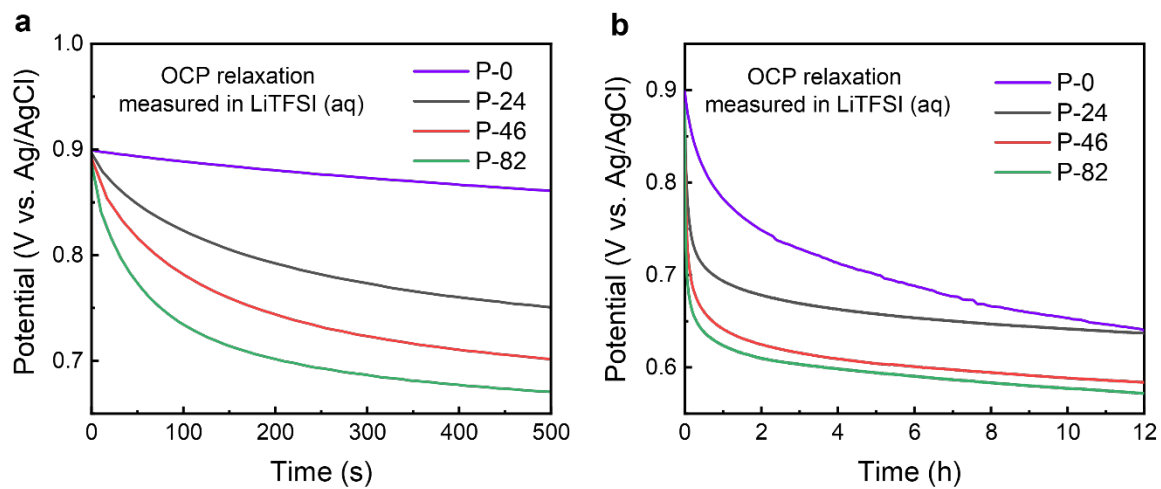


Figure S23. Open-circuit potential decay of the polymers over time measured in 0.2 M LiTFSI (aq) after being oxidized to +0.9 V (vs. Ag/AgCl) (a) in the first 500 s and (b) over the course of 12 h.

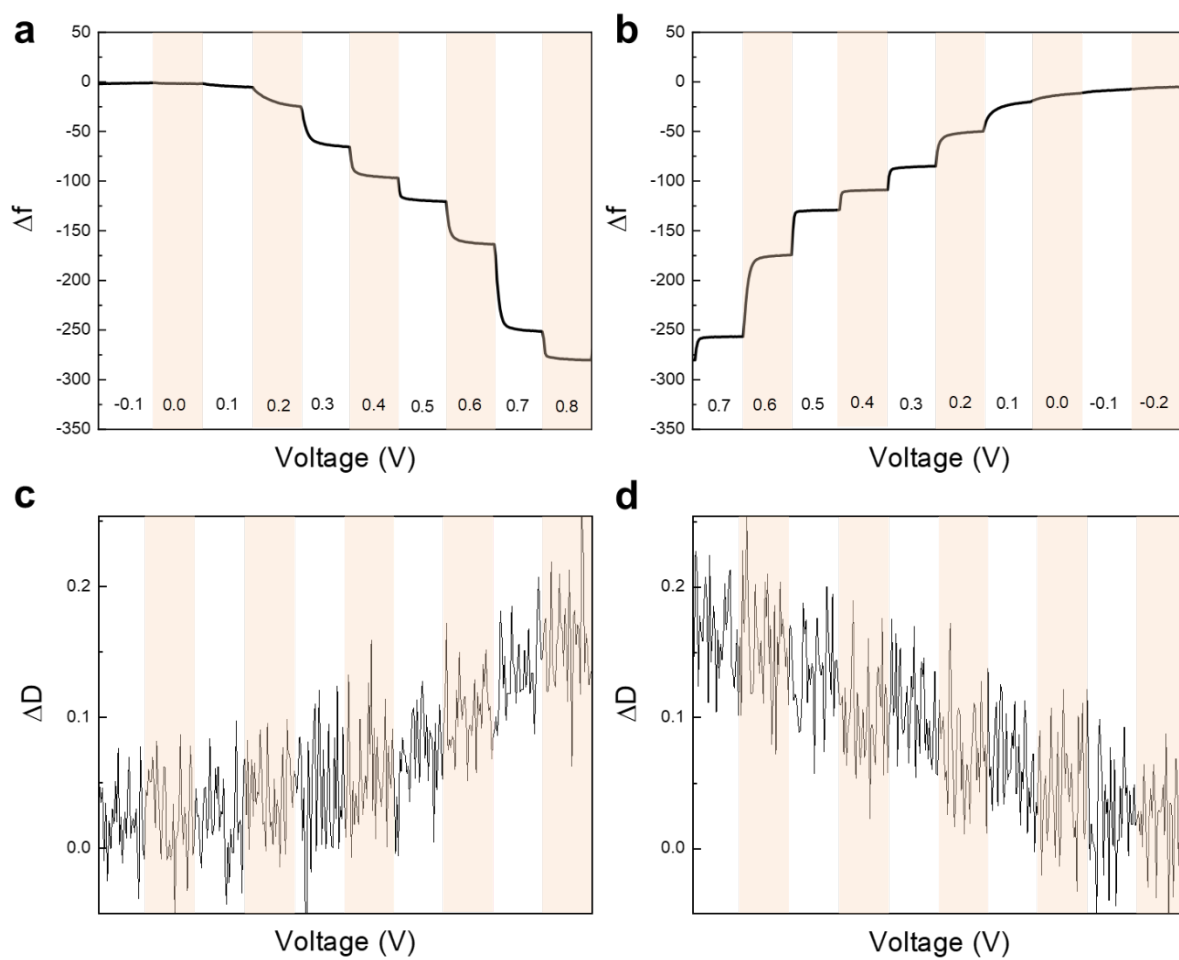


Figure S24. Frequency and dissipation changes recorded during cyclic voltammetry of P-24 in 0.2 M LiTFSI (aq).

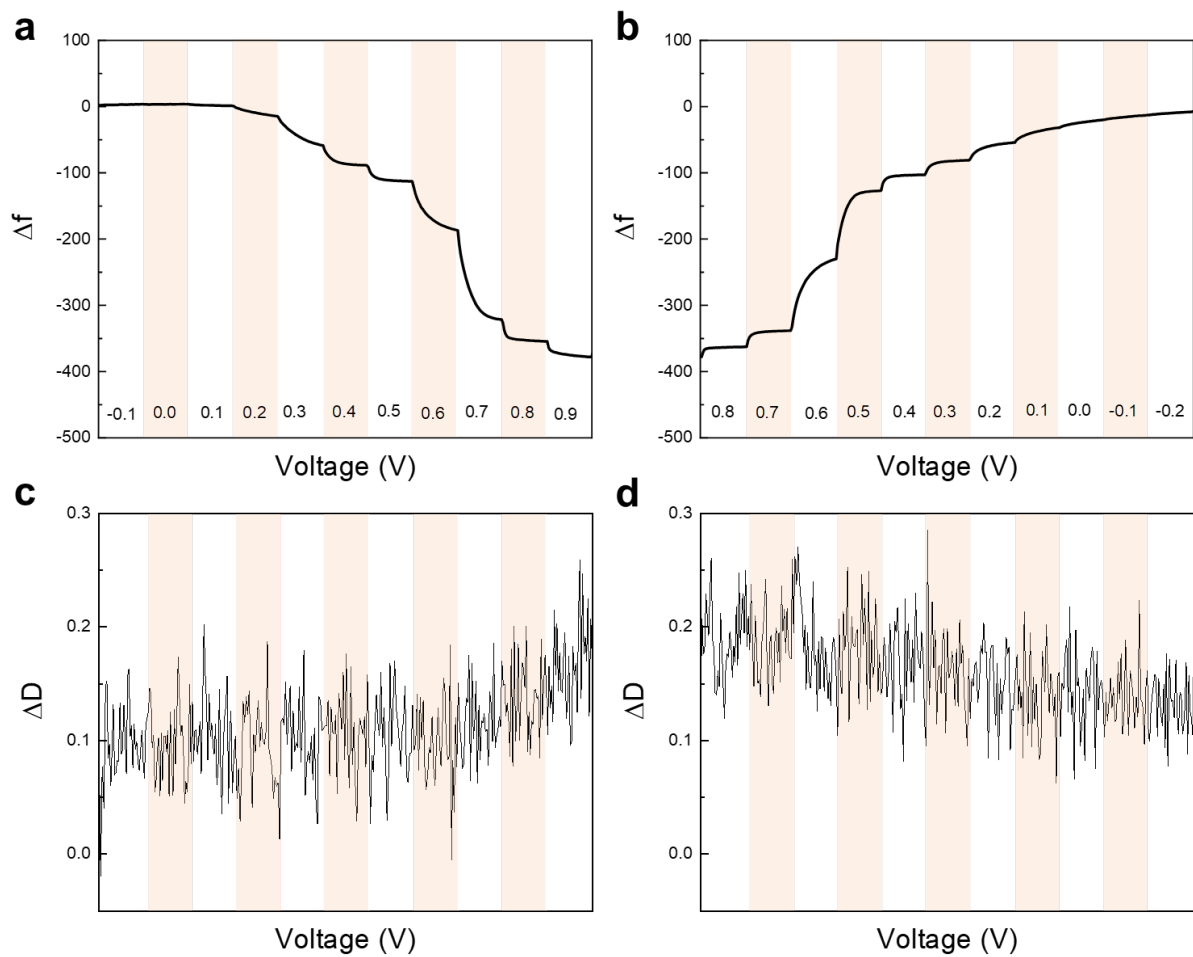


Figure S25. Frequency and dissipation changes recorded during cyclic voltammetry of P-46 in 0.2 M LiTFSI (aq).

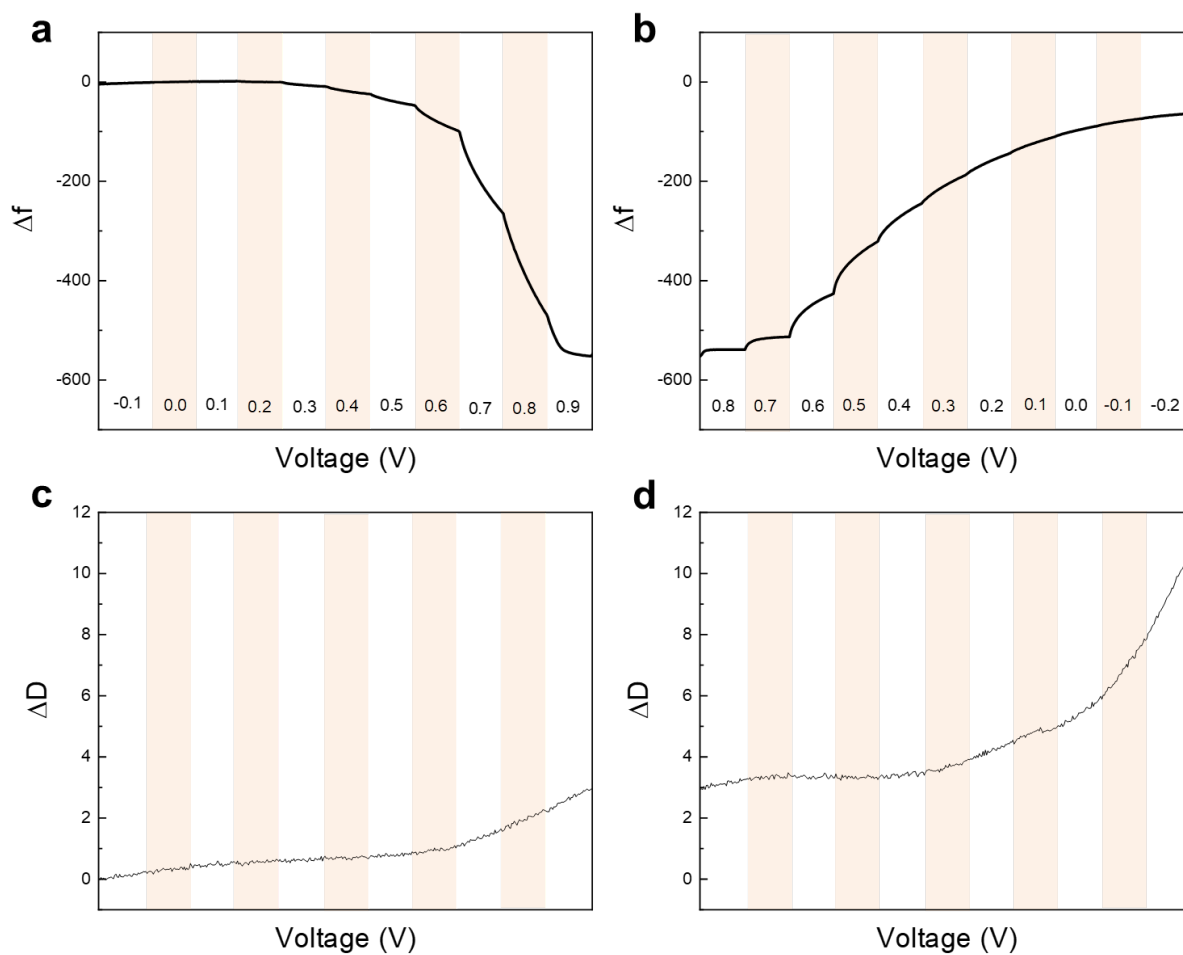


Figure S26. Frequency and dissipation changes recorded during cyclic voltammetry of P-63 in 0.2 M LiTFSI (aq).

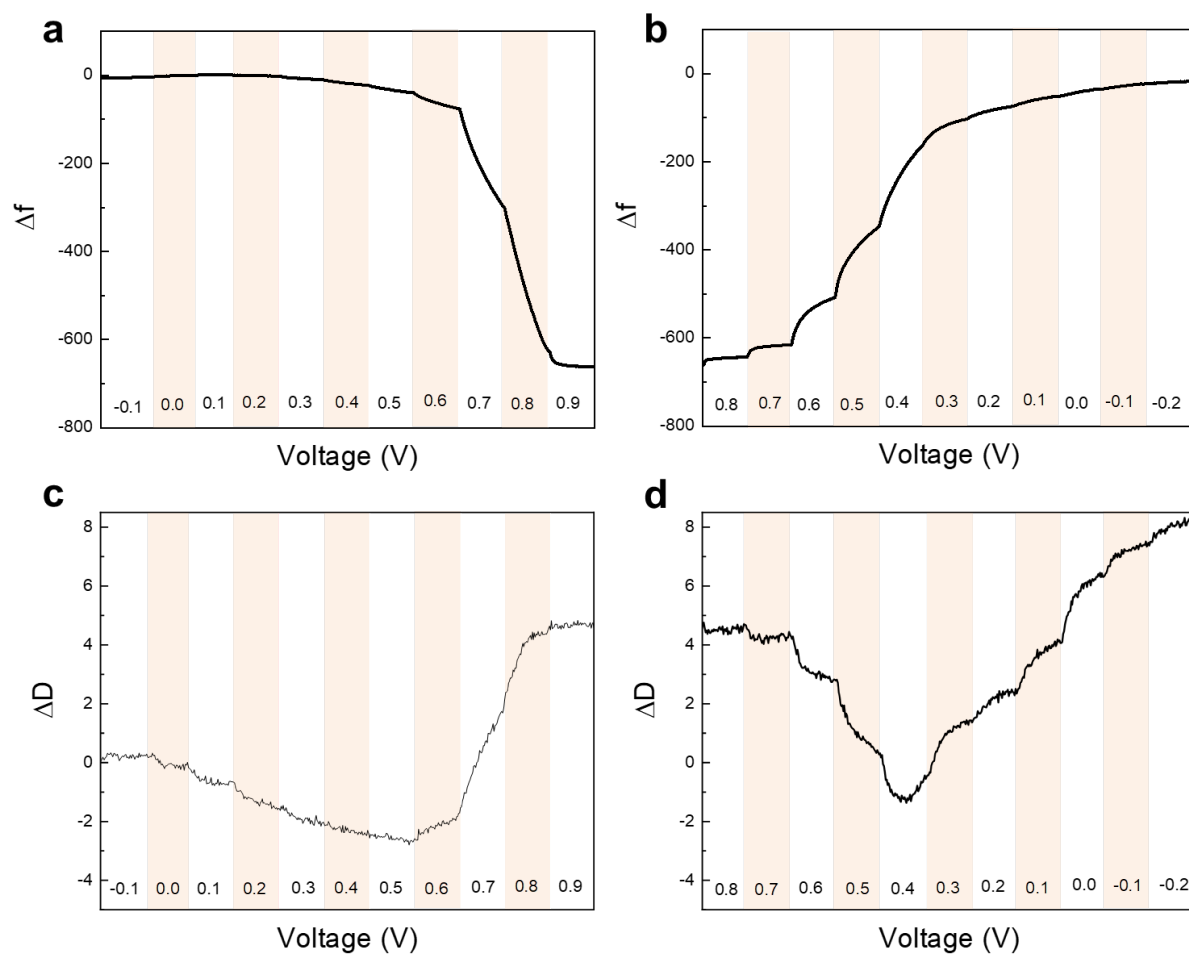


Figure S27. Frequency and dissipation changes recorded during cyclic voltammetry of P-82 in 0.2 M LiTFSI (aq).

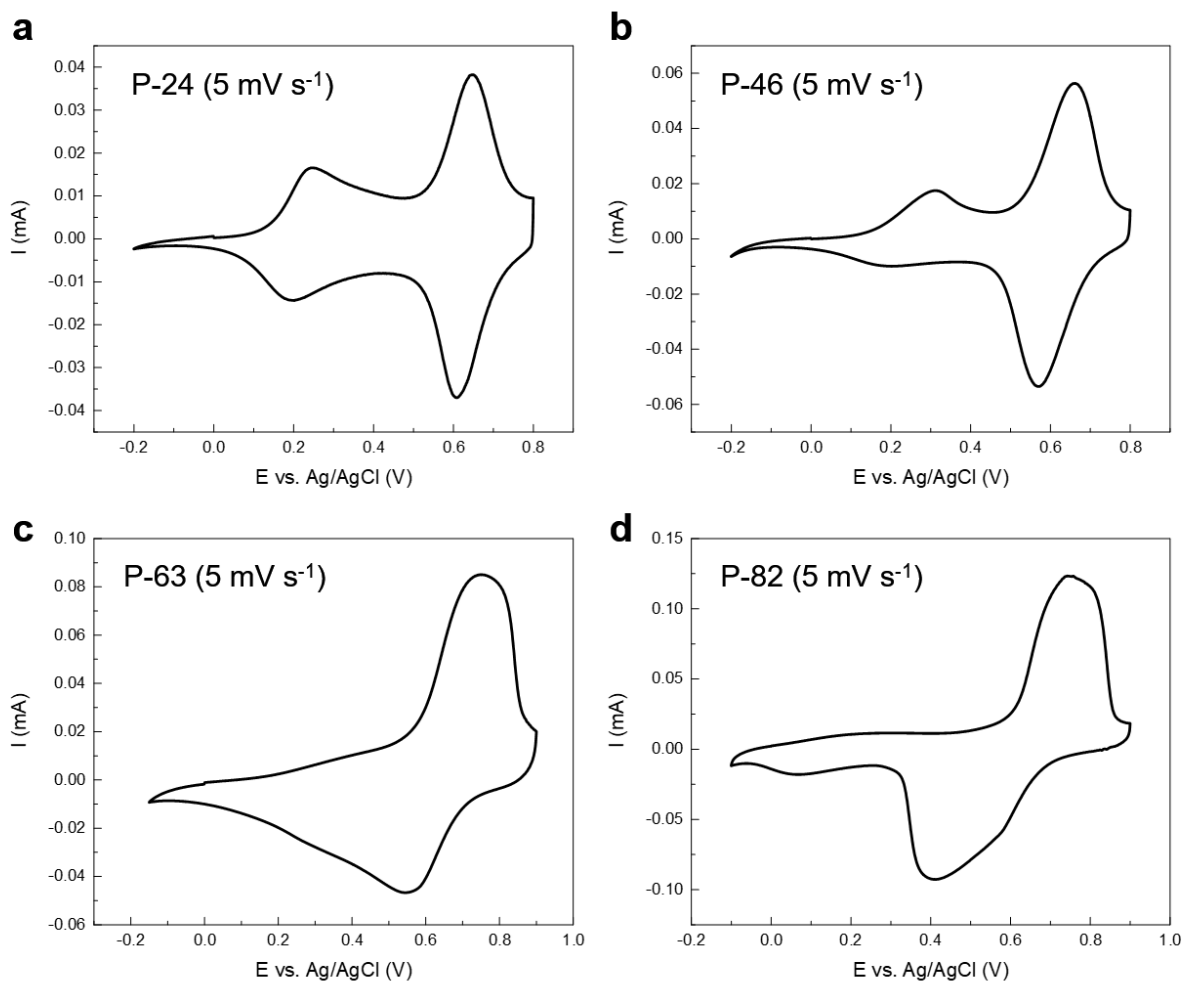


Figure S28. Cyclic voltammetry of (a) P-24, (b) P-46, (c) P-63, and (d) P-82 in a 0.2 M LiTFSI solution where deionized water served as the solvent at a scan rate of 5 mV s^{-1} during EQCM-D.

References

- [1] D. Mantione, N. Casado, A. Sanchez-Sanchez, H. Sardon, D. Mecerreyes, *J. Polym. Sci. Part A: Polym. Chem.* **2017**, 55, 2721.
- [2] B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarley, J. R. Reynolds, *Macromolecules* **2004**, 37, 7559.