

Supporting Information for

Impact of the Addition of Redox-Active Salts on the Charge Transport Ability of Radical Polymer Thin Films

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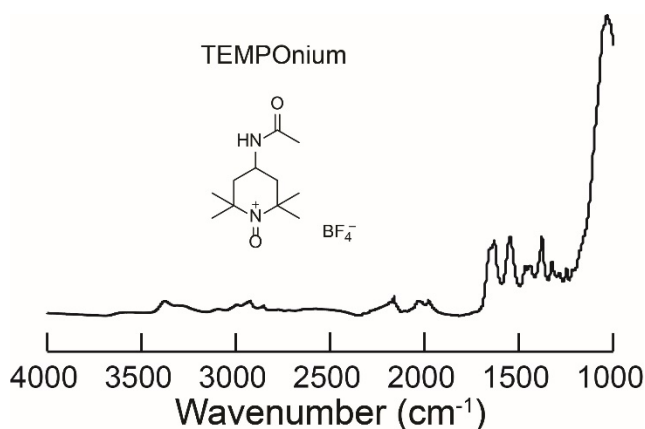


Figure S1. FTIR spectrum of a pristine TEMPOonium thin film. A strong oxoammonium cation peak is observed at $\nu \approx 1540 \text{ cm}^{-1}$. All peaks in the above spectrum are associated with either the TEMPOonium molecule itself, the BF_4^- counter ion, or the glass substrate.

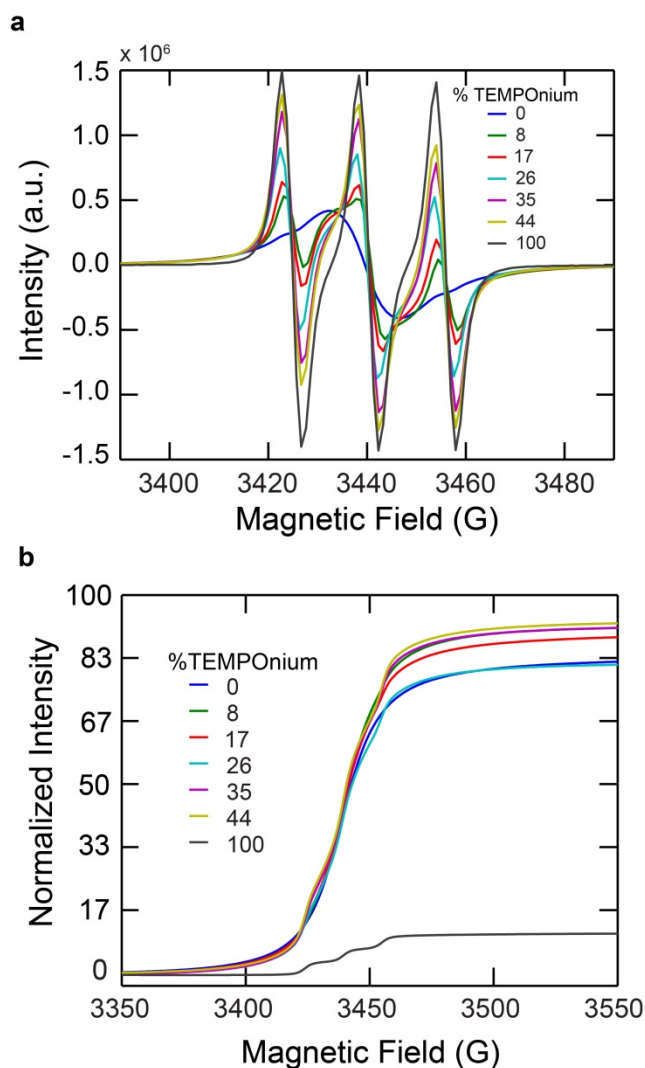


Figure S2. (a) The EPR spectra of varying loadings of TEMPOonium with PTMA in a mixture of DMF (2%, by volume) and benzene (98%, by volume) with a concentration of 0.2 mg of solids per 1 mL of solvent. The change in peak behavior and location is a result of the increasing amount of small molecule TEMPOonium being added to the polymer. (b) The integrated EPR signals illustrating the radical density of various loadings of TEMPOonium blended with PTMA. The intensity values are within the experimental error for pristine PTMA as well as for loadings up to 44%, on a molar basis. This indicates that the radical density remains nearly unchanged for these loadings. The intensity of the 100% TEMPOonium sample demonstrates that the radical density of this material is very low, but still not completely negligible.

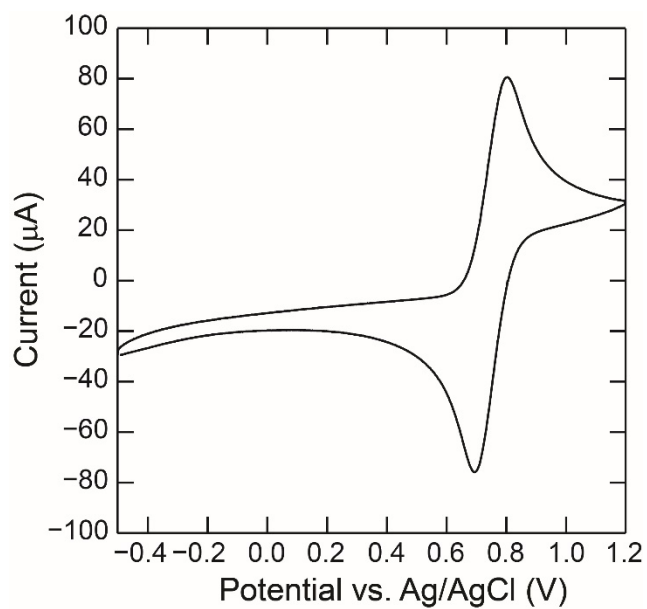


Figure S3. Cyclic voltammetry data of 25 mg of TEMPOonium in 300 mL of acetonitrile and 0.05 M tetrabutylammonium tetrafluoroborate electrolyte salt. The onset oxidation and reduction peaks differ minimally from PTMA/TEMPOonium mixtures, and the peaks present could occur due to a non-trivial amount of open-shell TEMPO being present in the purchased TEMPOonium salt.

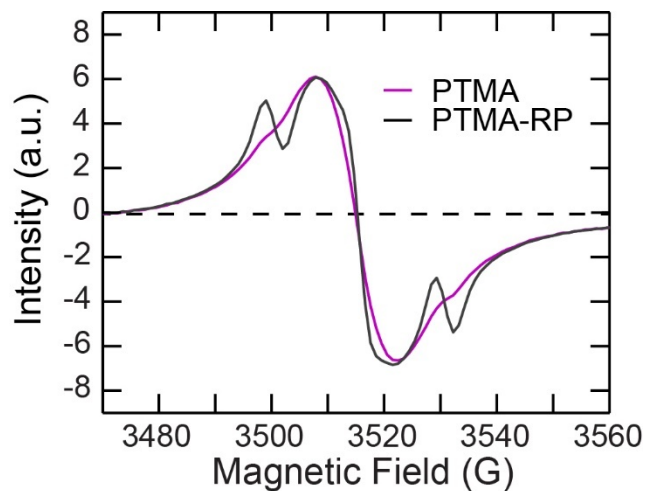


Figure S4. EPR data comparing a pristine PTMA powder to PTMA that had been selectively precipitated from a PTMA/TEMPO⁺ mixture. Both polymers were dissolved in DMF (2%, by volume) and benzene (98%, by volume) in order to acquire the two spectra of the figure. The precipitated PTMA shows hyperfine splitting due to decreased spin exchange interactions from redox reactions occurring between the TEMPO⁺ and PTMA while the PTMA and TEMPO⁺ salts were dissolved in solution. That is, there is an oxidation conversion of some of the PTMA units from radical moieties to positively-charged moieties.

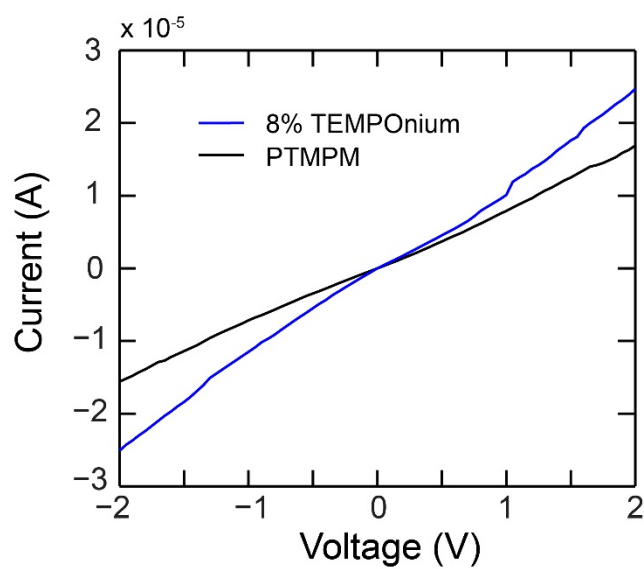


Figure S5. Representative current-voltage curves of ITO / PTMPM / Au and ITO / PTMPM + 8% TEMPOonium / Au devices. The difference in conductivity of the two systems is almost insignificant, indicating that the TEMPOonium itself cannot act as a dopant for this poor conducting system.

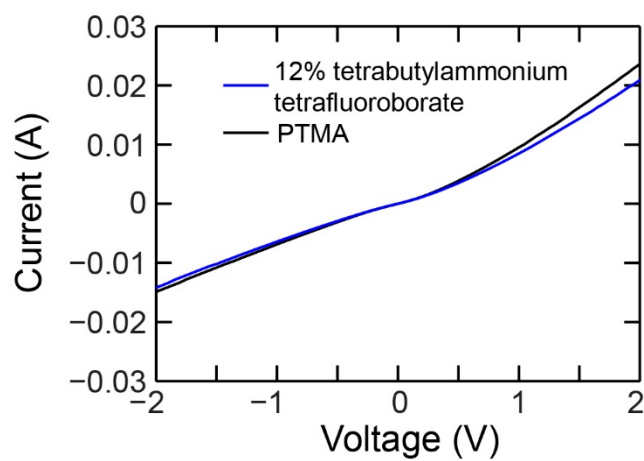


Figure S6. Representative current-voltage curves of ITO / PTMA / Au and ITO / PTMA + tetrafluoroborate salt / Au devices. The difference in current voltage performance is negligible, indicating that any tetrafluoroborate salt cannot act as a dopant for this system.

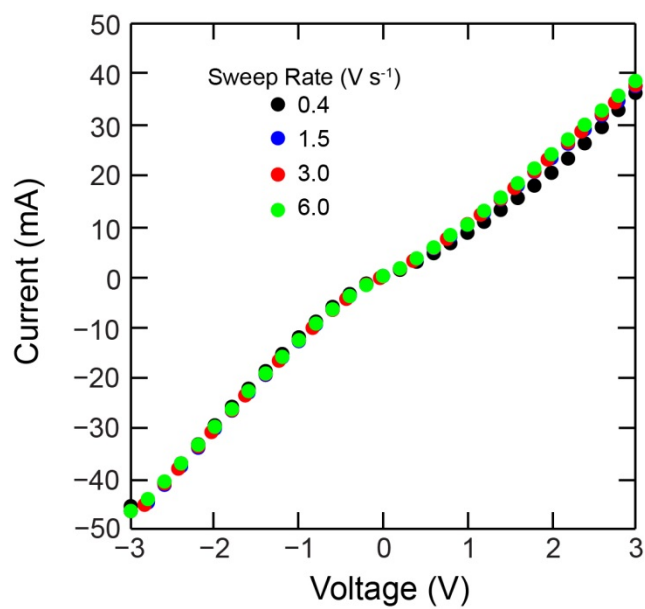


Figure S7. Current-voltage sweeps of an ITO/ PEDOT:PSS / PTMA + TEMPOonium / Au device with a TEMPOonium loading of 8% (molar basis). At these rapid sweep rates, there is no dependence on the sweep rate. This minimizes the contribution of the ionic current to the electrical conductivity calculations.

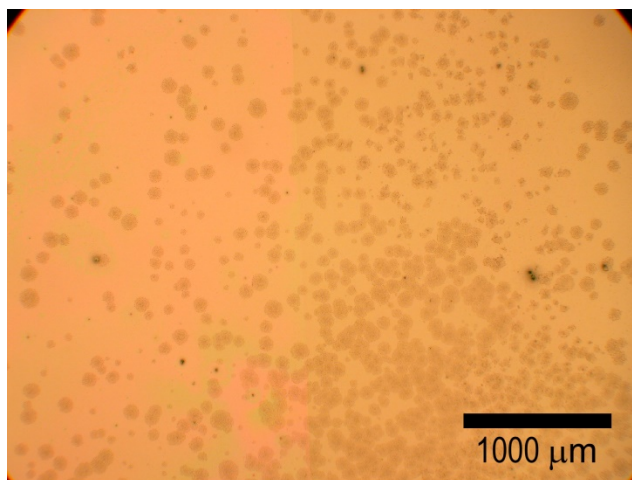


Figure S8. Optical microscopy image of a pristine TEMPOonium thin film on ITO/PEDOT:PSS. The image indicates clear defects in the film due to the inability to cleanly cast the small molecule from solution.

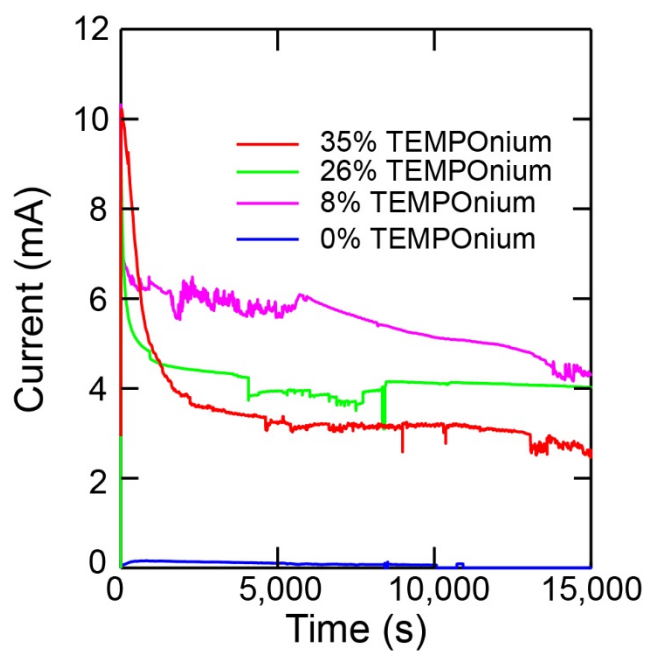


Figure S9. Current as a function of time for ITO / PEDOT:PSS / PTMA+TEMPOonium / Au devices at $V = + 2.0V$. The total time is on the order of hours. The initial decrease in current is from the effect of the motion of the BF_4^- counterion. After the system reaches a steady state value, the current remains approximately constant. The steady-state current of all the TEMPOonium loaded systems is significantly larger than that of the pristine PTMA thin film.

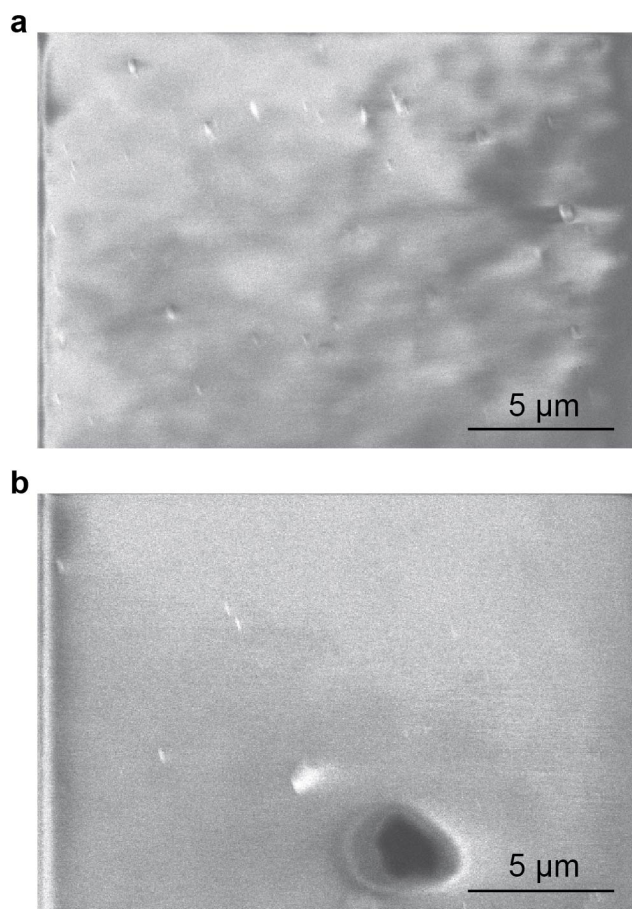


Figure S10. SEM images of (a) a pristine (i.e., 0% TEMPO⁺) PTMA film and (b) a 44% TEMPO⁺-doped PTMA film illustrating a lack of morphological features at this length scale. Due to the defects within the films and the overall roughness of the films, clear morphological characteristics at this length scale were unidentifiable.