Supporting Information

Polyrhodamine: A redox stable conducting polyelectrolyte

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pH Measurements: For the UV-Vis and fluorescence studies in different pH solutions, 10.0 mg of solid PRho was dissolved in 10.0 mL of HPLC grade methanol. 100 µL aliquots of the stock solution were then dissolved in 2.9 mL portions of a series of different pH citrate-phosphate-borate-tris (CPBT) buffer solutions (pH 1-12). The samples were left overnight (18 h) before the UV-Vis and fluorescence spectra were collected.

Solvent Studies: UV-Vis spectra of PRho were taken in different solvents. For each sample, 10.0 mg of PRho was dissolved in 10.0 mL of DMSO. A 10 µL aliquot of the DMSO solution was dissolved in 2.99 mL of each solvent (DMSO, acetonitrile, EtOAc, THF, Mili-Q water, and MeOH) and the UV-Vis-NIR spectra were collected. Then polymer solutions (MeOH and Mili-Q water) were acidified with 2.5 µL of 37% HCl. All the other polymer solutions (DMSO, acetonitrile, EtOAc, and THF) were acidified with 1 µL of trifluoroacetic acid (TFA**)**. The samples were allowed to equilibrate overnight before the UV-Vis spectra were recorded.

EPR study

After purification, 100.0 mg of PRho was dissolved in 20.0 mL of methanol. Methanol was removed by rotary evaporation and the sample thoroughly degrassed prior to the collection of solid-state EPR spectrum.

Four-point probe studies

The polymer conductivity was determined from the measured sheet resistivity of the polymer film (**Figure S10**). 3.0 mg of PRho was dissolved in 1.0 mL of MeOH, and the solution was concentrated under reduced pressure. This PRho solution was spin-coated on soda-lime glass slides (2.5 cm × 1 cm) and oven-dried (50 °C under low pressure) overnight before performing the 4-point probe analysis. For acidified PRho samples, a 3.0 mg/mL PRho solution was used. The number of repeating units per 3.0 mg of PRho was calculated (6.668 mmol). Approximately 5%, 10%, 20%, 30%, and 40% HCl (per repeating unit) was added to separate PRho samples, which were left overnight for equilibration. After equilibration, each PRho sample was concentrated under reduced pressure, spin-coated on soda-lime glass slides (2.5 cm × 1 cm), and oven-dried (50 °C under low pressure) overnight before conductivity measurements. The sheet resistivity of the polymer was recorded, and the conductivity was calculated according to the literature.[1] The sheet resistivity values were corrected by a geometric correctional factor to account for the film dimension (i.e. 2.3532). The corrected sheet resistivity was used to calculate the conductivity using the equation below, where t is the sample thickness, and R_s is the sheet resistivity

$$Conductivity = \frac{1}{R_S\, t}$$

The measurements were made in triplicate, and the average conductivity value is reported.

Zeta potential

Zeta potential (ζ-potential) measurements were conducted on a Zetasizer Nano ZS (Malvern Instrument). The solid PRho was dissolved in HPLC grade methanol to yield a concentration of 5 mg/mL. A small stir bar was placed inside the vial, and the solution was stirred for 4 h. Subsequently, ten samples were prepared with pH values 1-10 using a citrate-phosphate-borate-tris (CPBT) buffer solution. The samples were prepared by diluting the stock solutions to a final concentration of 1 mg mL^{-1} using the buffers. Each sample had a total volume of 1.5 mL, and the samples were allowed to equilibrate overnight. Prior to obtaining the Zeta potential measurements, each sample was shaken by hand to resuspend the sample in solution. Each Zeta potential measurement was taken in triplicate and then averaged to obtain the values shown in Table S1.

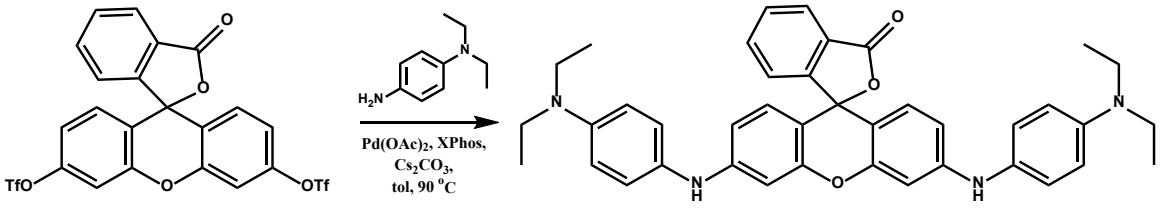
Molecular weight with MALS

The MALS analysis was perform without the separation column because the polymer adheres to the column preventing the correct concentration to be obtained for the dn/dc calculation. A series of PRho samples with different concentrations varying from 0.02 to 0.035 mg/mL were prepared in MeOH. 50 µL of each sample was injected into the GPC to avoid saturating the RI detector of the GPC, and the *d*n/*d*c value was calculated using the RI detector of the GPC. The calculated *d*n/*d*c value was applied to calculate the molecular weight from the light scattering. The study was repeated 3 times for accuracy.

Reduction of PRho film with $NaBH_4$

PRho (5 mg) was dissolved in DMSO (0.5 mL). The solution was drop-casted as a thin film on a soda lime glass slide and placed inside a quartz cuvette. The cuvette was filled with acetonitrile (2 mL) and the absorption spectrum was collected. $NaBH_4$ (5 mg) was added to the acetonitrile and carefully mixed with a disposable pipette. Absorption spectra were collected after the 4, 8, and 10 minutes.

Figure S1. Synthesis of PRho small molecule via Buchwald/Hartwig cross-coupling reaction



Fgure S2. Partial ^{1}H NMR of A: PRho; B: representative small molecule; C: fluorescein ditriflate; D: *p*-phenylenediamine in DMSO-d_6

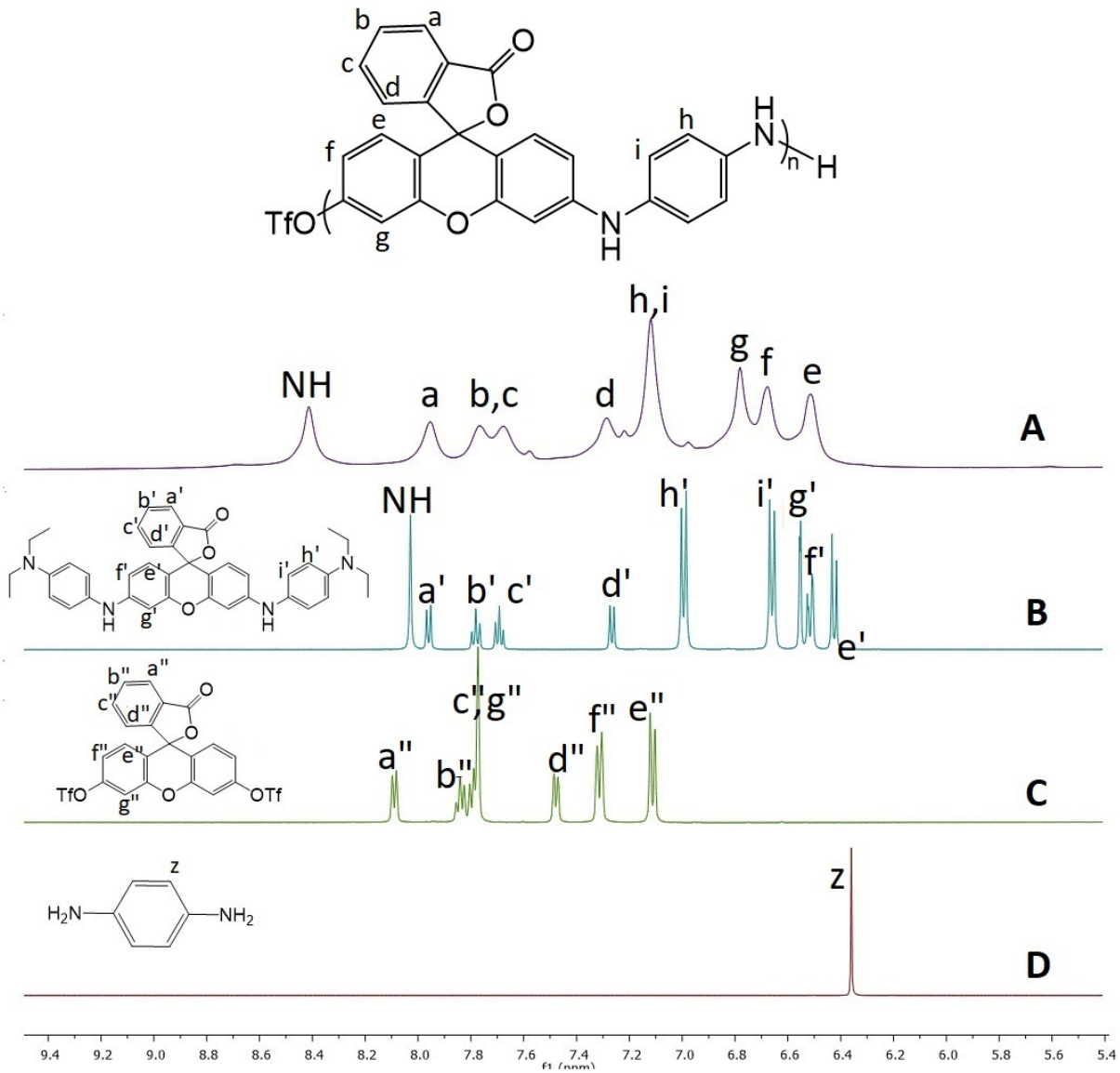


Table S1. *Zeta Potential values of PRho at different pH in CPBT buffer solutions*

pH of buffer	Zeta Potential (mV)
1	+6.11
2	+8.13
3	+4.26
4	-1.50
5	-5.12
6	-9.80
7	-12.73
8	-14.07
9	-13.80
10	-14.80

Figure S3. *FTIR spectra of PRho under acidic (top) and basic (bottom) forms*

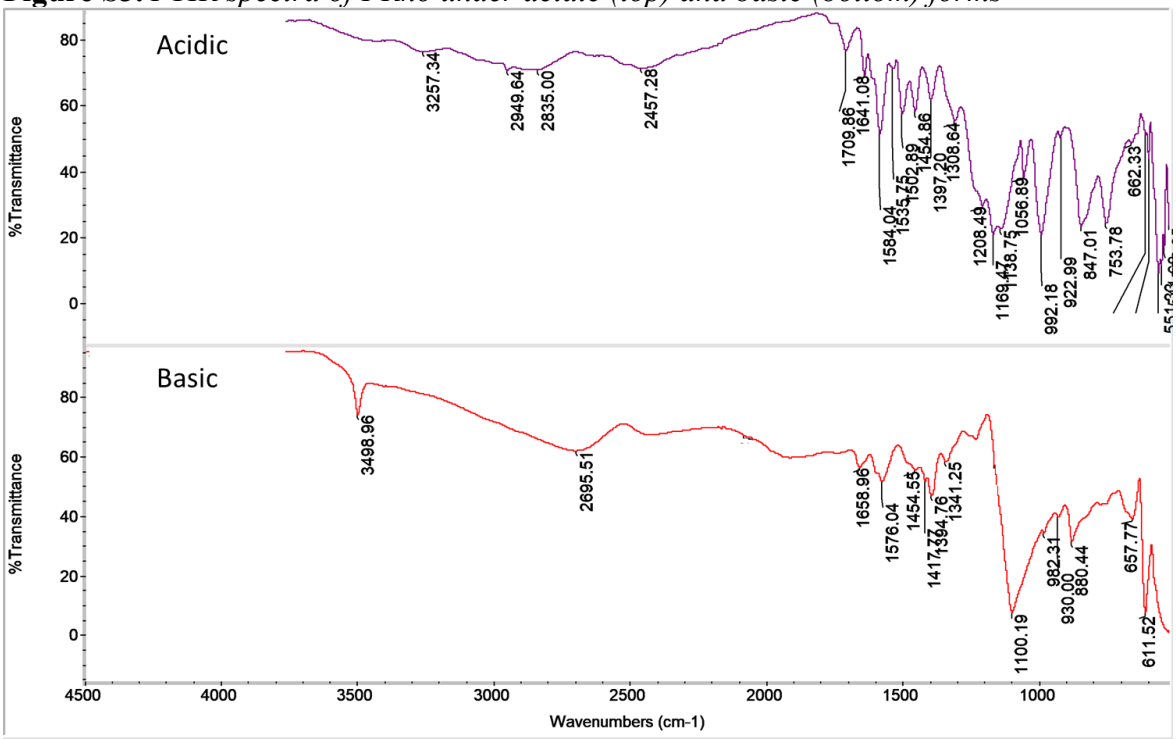


Figure S4: *Solvatochromic effect of PRho in different solvents under acidic (A) and basic conditions (B).*

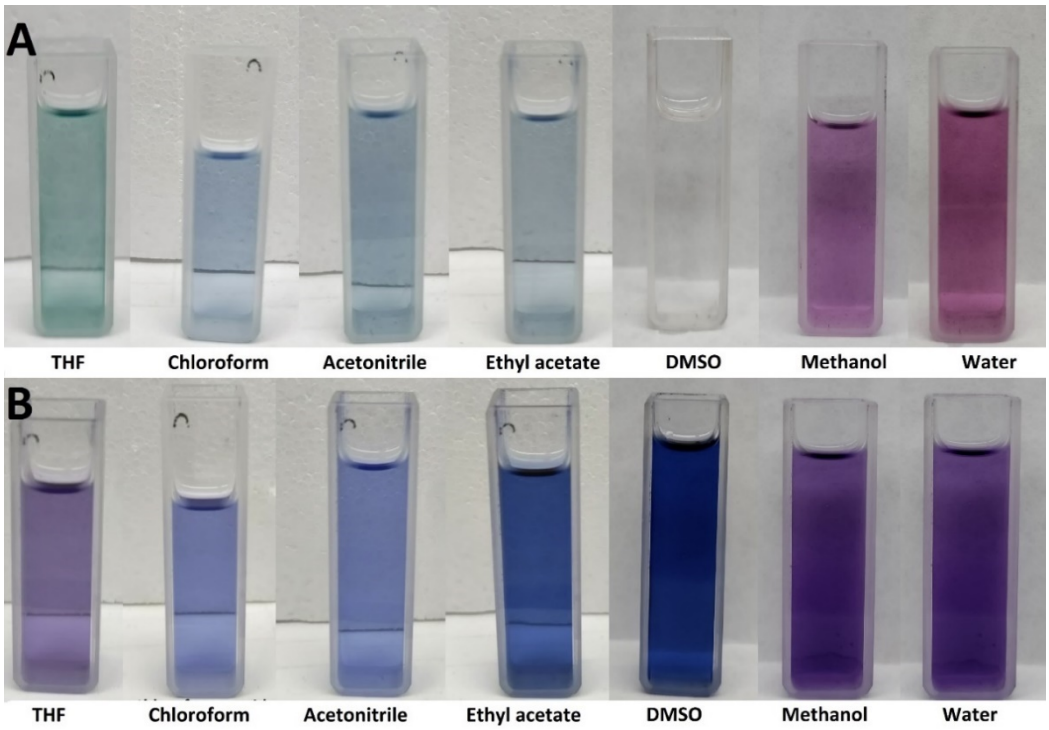


Figure S5*: Cyclic voltammograms of the polymer film for 1000 CV cycles (scan rate 500 mV/sec). First 100 CV cycles (A); CV cycle 101-200 (B); CV cycle 201-300 (C); CV cycle 301-400 (D) CV cycle 401-500 (E); Cv cycle 500-1000 (F)*

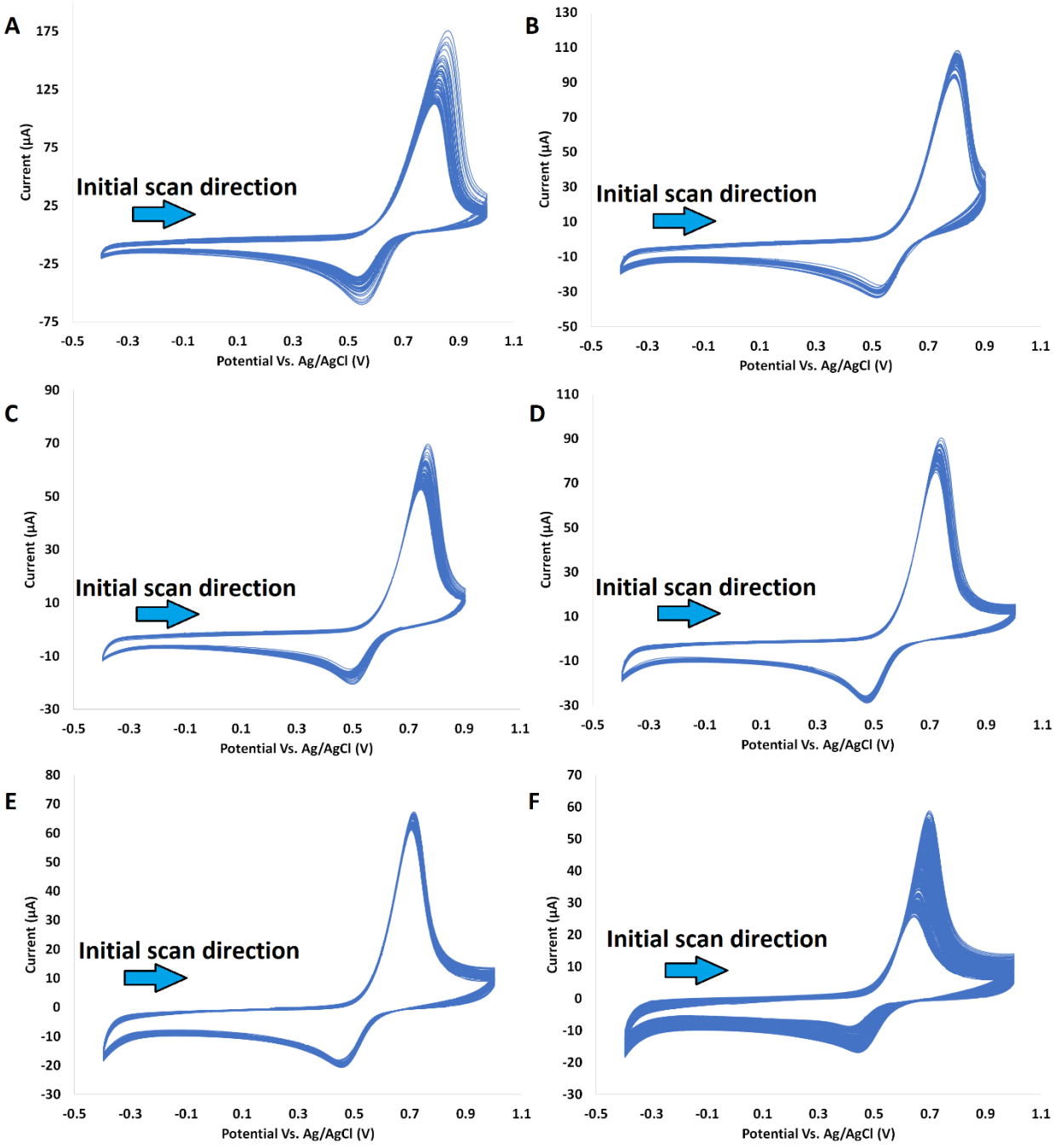


Figure S6: *Cyclic voltammograms of the polymer films(scan rate 100 mV/sec.) (A); forward sweep (B) reverse sweep*

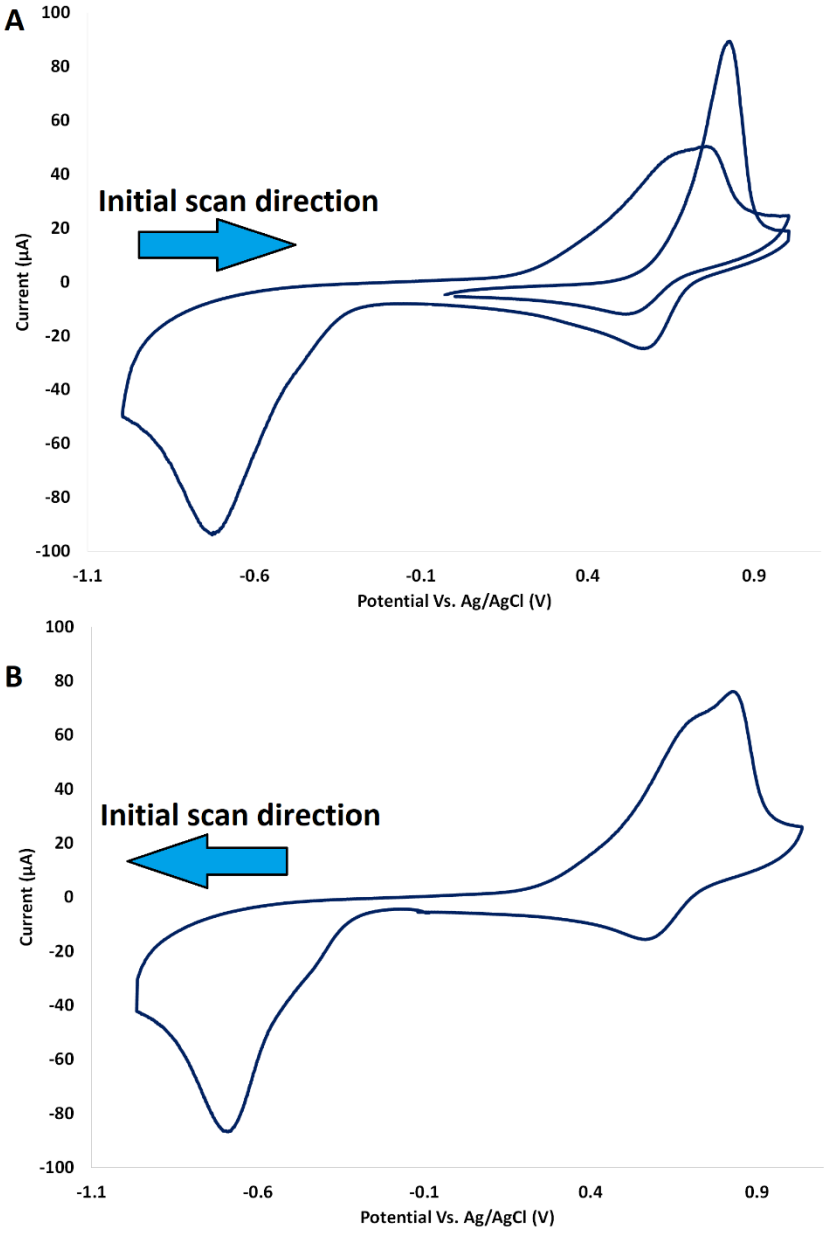


Figure S7: *PRho structures in different oxidization states.*

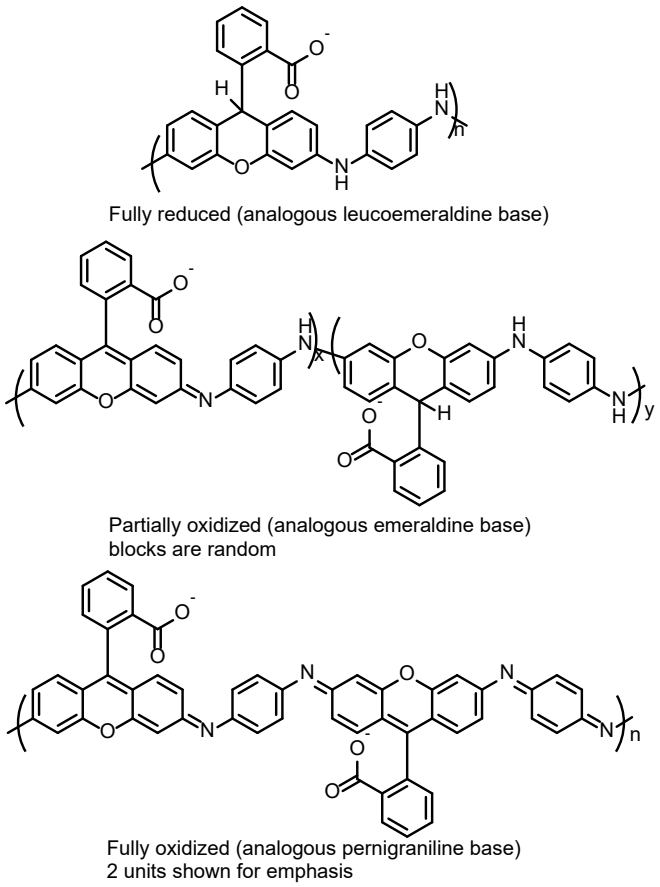


Figure S8. *Reduction of PRho by Electochemcial (A) and Chemical (B) methods.*

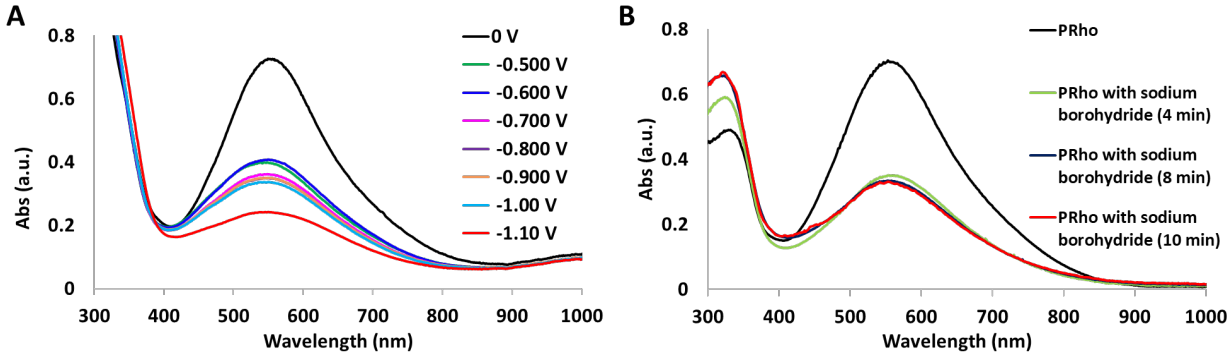


Figure S9. *Proposed polaron formation mechanism of PRho*

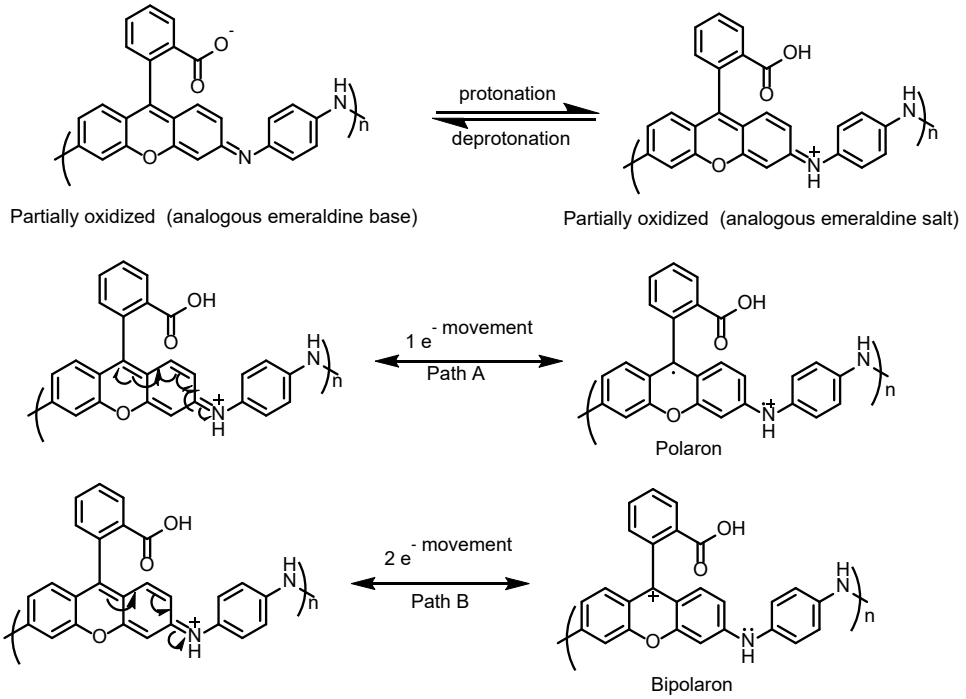
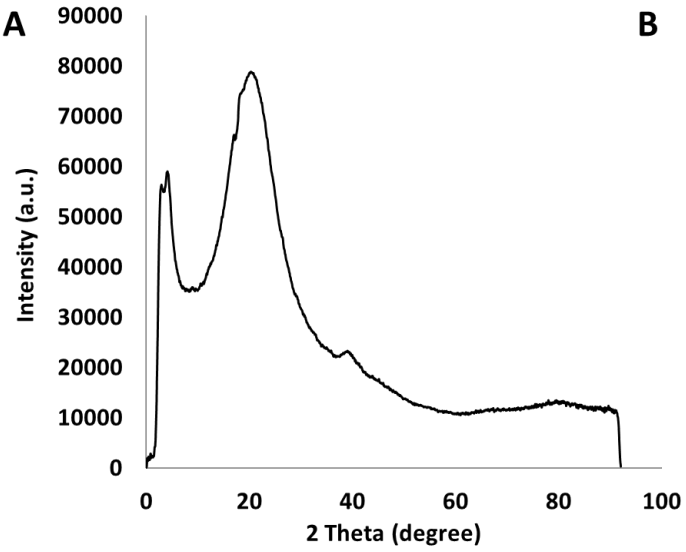


Figure S10. *XRD spectrum (A) and list of 2Θ and d-spacings values (B) for the polymer*

A



B

Peak index	2 Theta (deg)	d-spacing (Å)
1	3.10	28.45
2	4.20	21.02
3	16.88	5.25
4	18.37	4.82
5	20.10	4.41
6	39.34	2.29
7	43.86	2.06
8	52.79	1.73
9	66.96	1.40
10	80.06	1.20

Figure S11. *Four-point probe measurements of I/V curves of PRho films A: 0% HCl; B: 5% HCl; C: 10% HCl; D: 20% HCl; E: 30% HCl;F: 40% HCl*

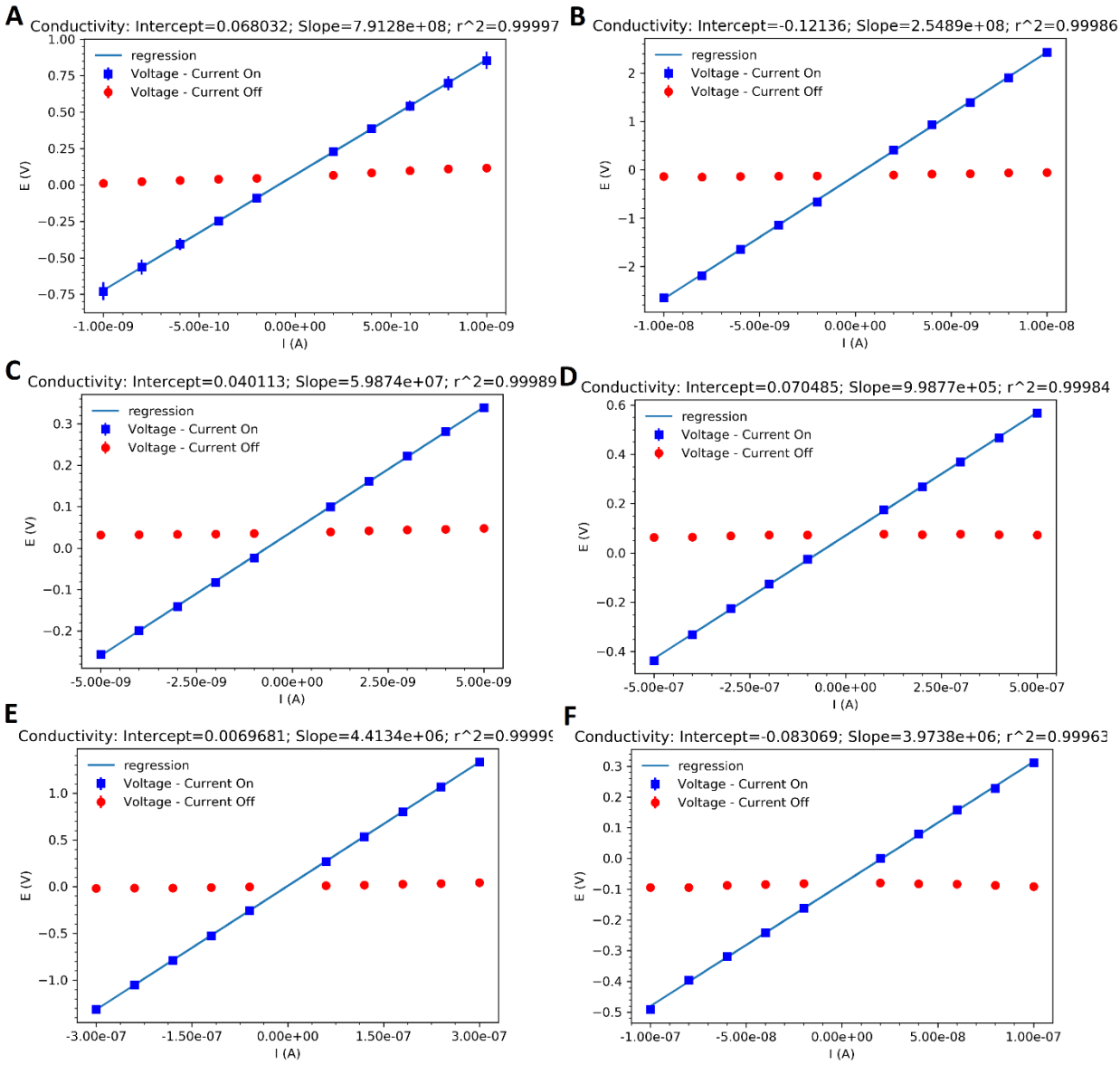
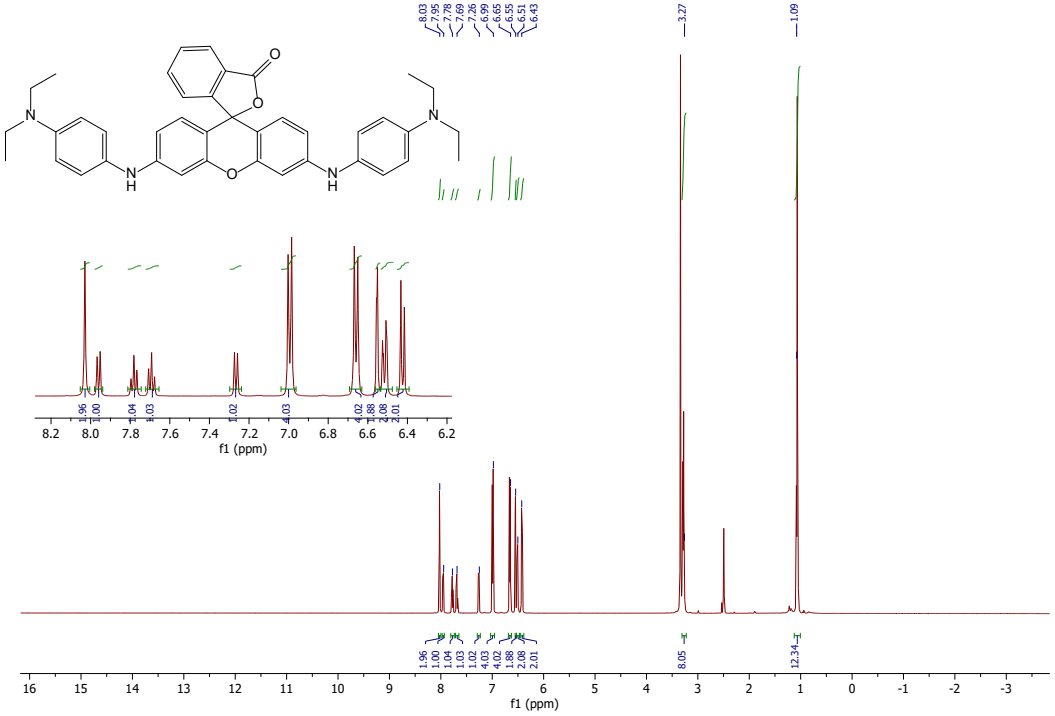
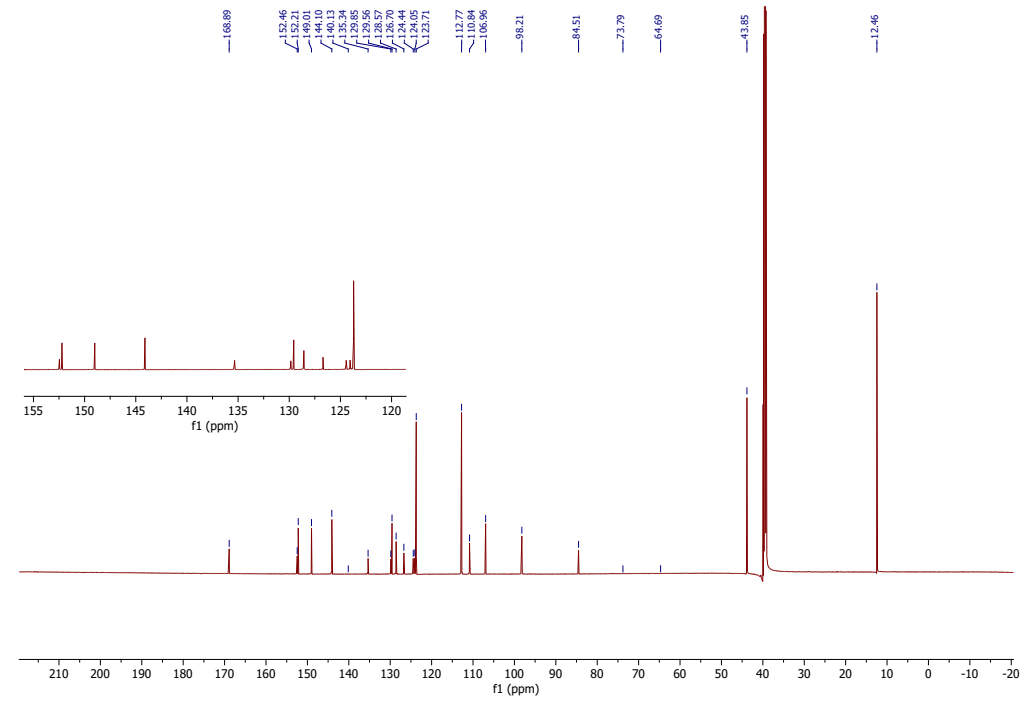


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of small molecule (SM) in DMSO-d_6





References

(1) Smits, F. M. Measurement of Sheet Resistivities with the Four-Point Probe. *Bell Syst. Tech. J.* **1958**, *37* (3), 711–718. https://doi.org/10.1002/j.1538-7305.1958.tb03883.x.