Supplementary Information (SI) for ChemComm.

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Effect of Protonating Single-Moiety Sulphonic Acid-Based Dopants on the Mechanical Properties of Electroconductive Polyaniline/Poly(2-acrylamido-2-methyl-1-propanesulfonic Acid) Complexes

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Materials

A 10 wt.% poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA) (average molecular weight: 800,000 g/mol) aqueous solution was purchased from Thermo Scientific Chemicals (Waltham, MA). Aniline (ACS grade) and ammonium persulfate (ACS grade) were purchased from Sigma-Aldrich (St. Louis, MO). Mono-sulfonic acid, (1S)-(+)-10-camphorsulfonic acid (99%) was purchased from Sigma-Aldrich. 4-dodecylbenzene sulfonic acid ($\geq$ 95%) and trifluoromethane sulfonic acid ($\geq$ 99%) were purchased from Millipore Sigma. All chemicals were used as received without further purification/modification.

Preparation of PANI/PAAMSA/SABD

The film preparation began by adding 50 g of 10 wt.% PAAMPSA solution to erlenmeyer flask. Subsequently, 0.5 g of aniline and 1.10 g of deionized water were added into the mixture and stirred thoroughly. The Sulfonic acid–based dopants (SABDs) were then incorporated according to the molar ratio approach described by Lu et al.[1]. The corresponding dopant quantities were as follows: trifluoromethane sulfonic acid- 0.2842 g, 4-dodecyl benzene sulfonic acid- 0.6183 , (1S)-(+)-10-camphorsulfonic acid- 0.4397 g. An initiator solution was prepared separately by dissolving 0.685 g of ammonium persulfate (APS) and 1.25 g of deionized water. The initiator solution was then slowly added to the reaction mixture, which was stirred for 3 h in an ice bath to control exothermic polymerization and then at room temperature for 21 h. After 24 h, the resulting solution was cast into a teflon petridish and and left in a fume hood for at least 48 h to remove residual water. The film was then subsequently conditioned in a humidity chamber at 50% relative humidity for a minimum of 2 days prior to testing.

Characterization of PANI/PAAMSA/SABD

Fourier transform infrared (FTIR) spectra was collected with a range between 400 and 4000 cm^{-1} using a Nicolet iS20 (Thermo Fischer Scientific Inc.). FTIR spectrometry in the attenuated total reflectance (ATR) mode with 28 scans and 0.25 cm^{-1} resolution.Zeta (ζ)-potential values and particle size measurements of the polymer dispersions were collected using a Malvern Nanoseries Zetasizer. The solid films were dissolved in deionized water at concentrations of 1.5 w/v% (0.3 g/20ml), 0.3 w/v% (0.06g/20ml), and 0.05 w/v% (0.01 g/20 ml) for the measurements of ζ-potential. Particle size measurements were performed using a 0.3 w/v % dispersion. The solutions were sonicated using Misonix Inc. Microson ultrasonic cell disruptor at 0.07 watts for 10 minutes prior to each measurement, to ensure uniform dispersion. The elongation and mechanical self-healing studies were performed using the INSTRON 68TM-5 universal testing machine. The gauge length was set at 20 mm, while the strain rate was set at 10 mmmin. The sample was cut into a rectangular strip measuring 40 mm X 10 mm for testing. TGA analysis was performed using a TGA Q500 model (TA Instruments) by heating the sample from 30 to 850 °C in an N_2 atmosphere. The heating rate was set to 10 $^\circ C$min. For the analysis of water content, the sample was dried in an oven at a temperature of 50 °C prior to the testing. The water content is determined from the weight percentage difference in TGA thermograms of the ambient and dried samples at 150 °C. UV-Vis spectrometry measurements were performed using a GENESYS 10S spectrophotometer (Thermo Scientific). A 0.8 mg mL^{-1} dispersion was prepared by dissolving the sample in 5.0 mL of deionized water for UV–Vis measurements. The electrical properties of the conducting film were measured using a Keithley 2450 source meter by the four-probe method. The sample for this study was fabricated using commercial transparent double-sided adhesive tape (3M VHB-4910 tape) with wires attached at both ends on a 40 mm X 10 mm sample.

Self-healing Studies: Electrical self-healing studies were conducted on a 40 mm X 10 mm sample. The sample was fabricated using commercial transparent double-sided adhesive tape (3M VHB-4910 tape) with wires attached at both ends, then connected to a Keithley 2450 source meter for resistance measurement before and after the cut-heal process. The mechanical self-healing tests were performed with a tensile testing apparatus on a 40mm X 10mm sample. The maximum elongation before and after the cut-heal process is noted to calculate the mechanical self-healing efficiency.

Supporting figures and tables

Zeta-potential

ζ-potential determination was carried out at three different concentrations and is shown in Figure S1. A high ζ-potential values of more than -74mV were observed for all three dopants, indicating stable dispersions. However, the magnitude of ζ-potential varies with different dopant type. PANI/PAAMPSA/TFMSA showed highest ζ-potential values, indicating enhanced electrostatic stabilization and homogeneous dispersion. While, PANI/PAAMPSS/DBSA showed least negative potential, consistent with phase-separated morphology arising from its hydrophobic alkyl chain. The moderate potential of PANI/PAAMPSA/CSA suggests balanced electrostatic and steric stabilization. These results highlight that compact, highly acidic dopants such as TFMSA promote uniform charge distribution and improved dispersion stability, which directly correlates with the enhanced mechanical and self-healing performance observed.

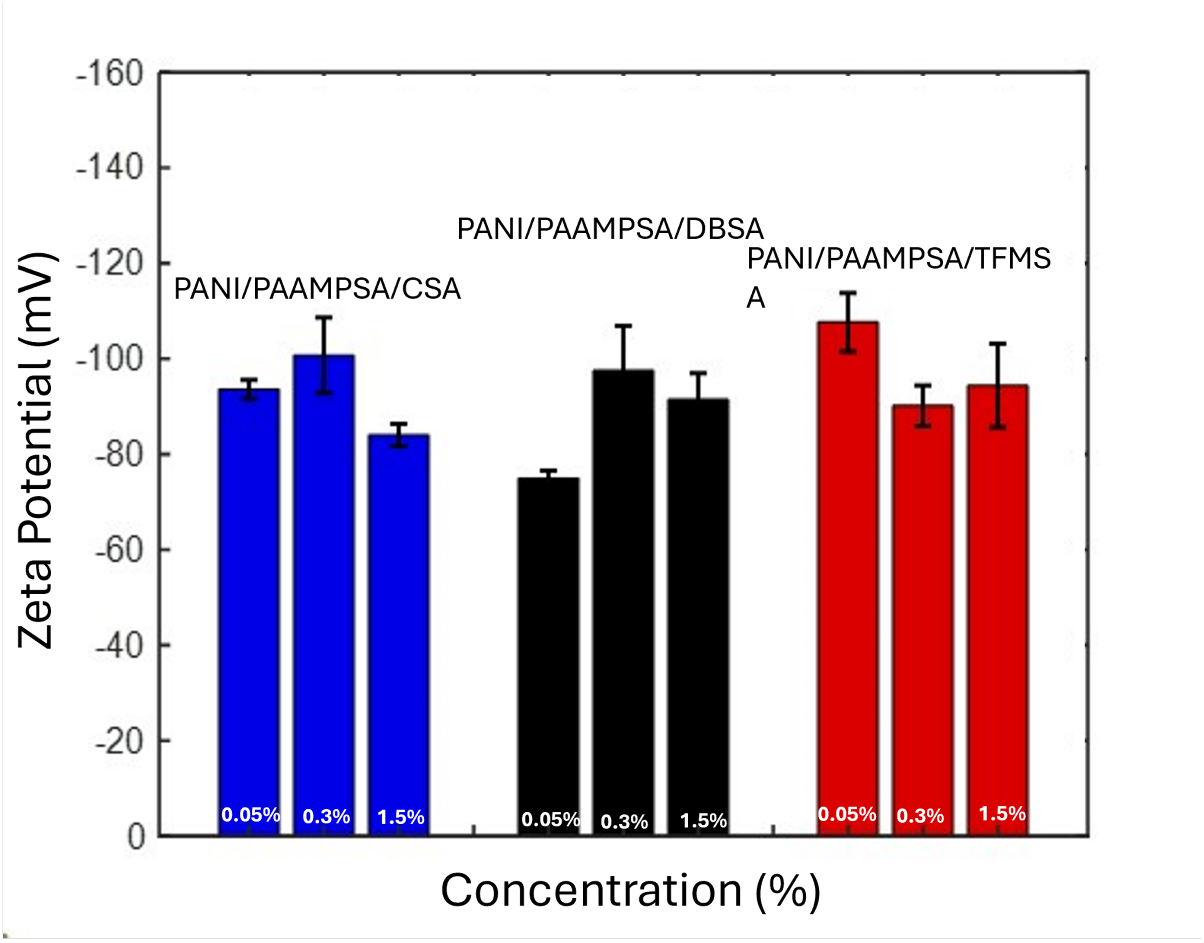

Figure S1: The change of zeta potential versus the concentration of PANI/PAAMPSA/MSAs. The data plotted represents the mean and standard deviation (n=3, n means number of independent experiments)

Self-Healing Efficiency

The self-healing efficiencies of the films were evaluated in terms of both electrical conductivity and mechanical stretchability as shown in Equation S1 & S2

$$S.H\%_c = \left(\frac{\sigma_c}{\sigma_{c_\circ}}\right) \times 100 \tag{S1}$$

$$S.H\%_s = \left(\frac{\varepsilon}{\varepsilon_\circ}\right) \times 100 \tag{S2}$$

S.H$\%_c$ and S.H$\%_s$ are the self-healing efficiencies with respect to electrical conductivity and mechanical stretchability. where the parameters $\sigma_{c_\circ}$, $\varepsilon_\circ$, and σ_c, ε represent the initial conductivity, initial elongation at break, conductivity post-self-healing, and elongation at break post-self-healing, respectively.[2;3]

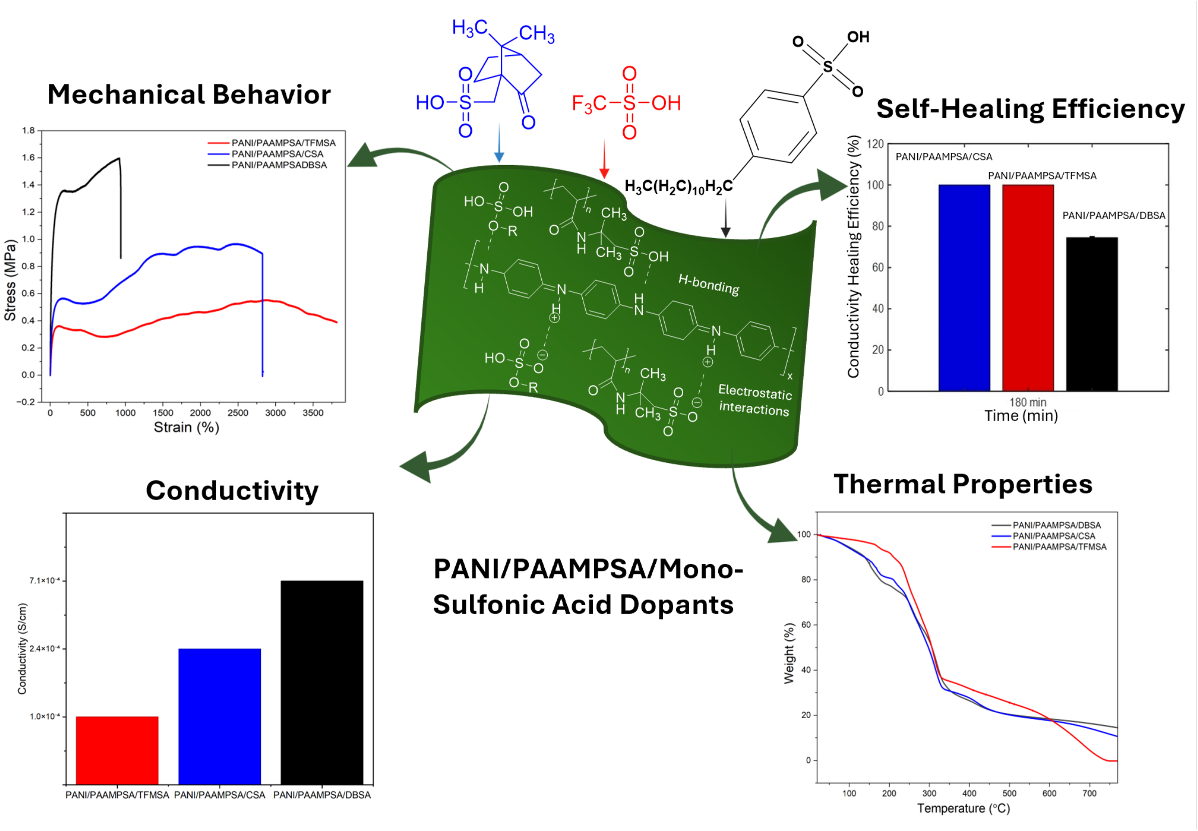

Figure S2: TOC Figure

References

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2. H. Yu, Y. Feng, L. Gao, C. Chen, Z. Zhang and W. Feng, *Macromolecules*, 2020, **53**, 7161–7170.

3. A. Ajeev, C. Duprey and E. K. Wujcik, *ACS Appl. Polym. Mater*, 2025.