

**Supporting Information (SI)**

**Mixed ionic-electronic conductance across naphthalenediimide-functionalized  
biopolymer**

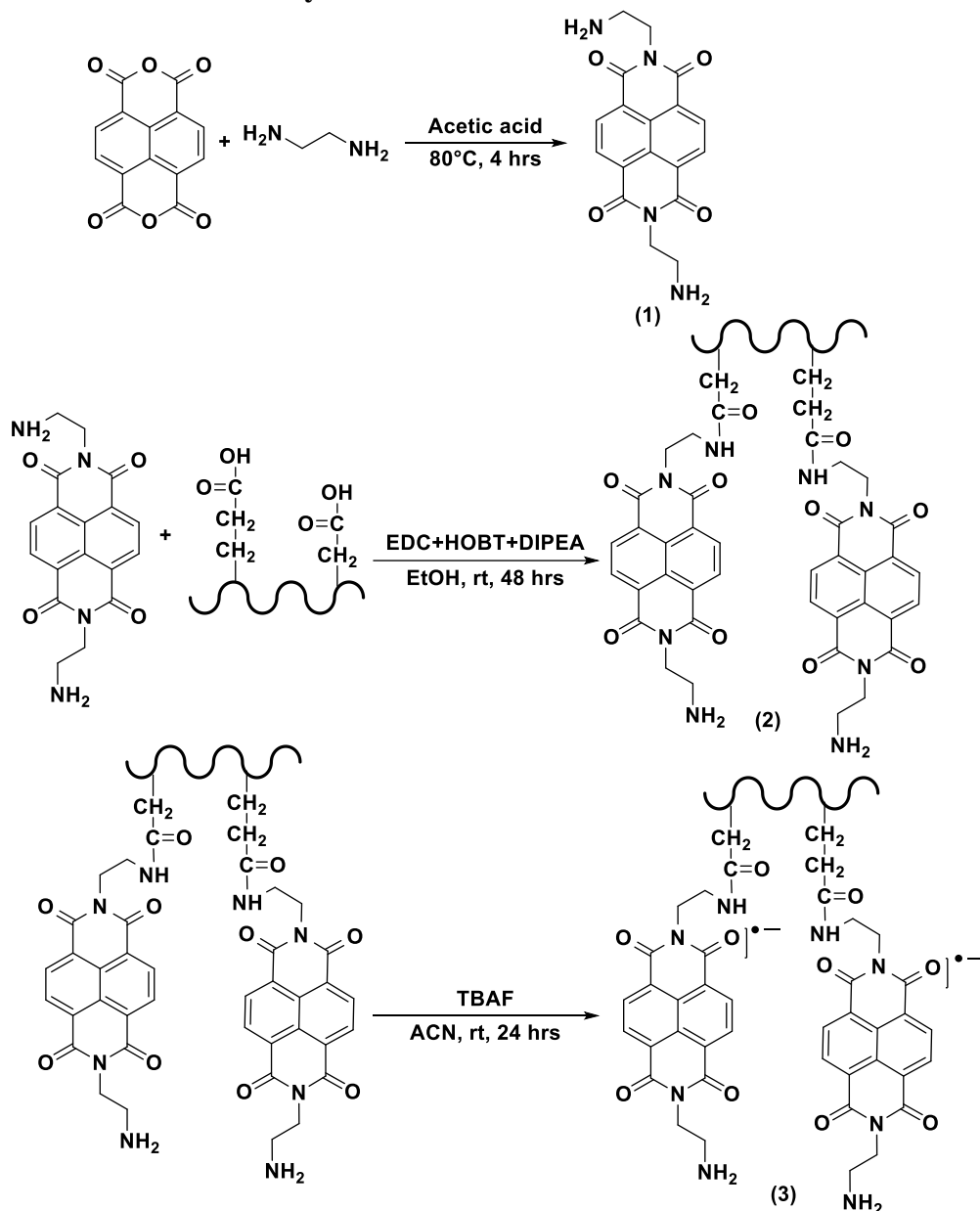
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## Synthesis and Characterization



**Scheme S1.** Synthesis scheme of NDI (1), BSA-NDI (2), and reduction of BSA-NDI (3).

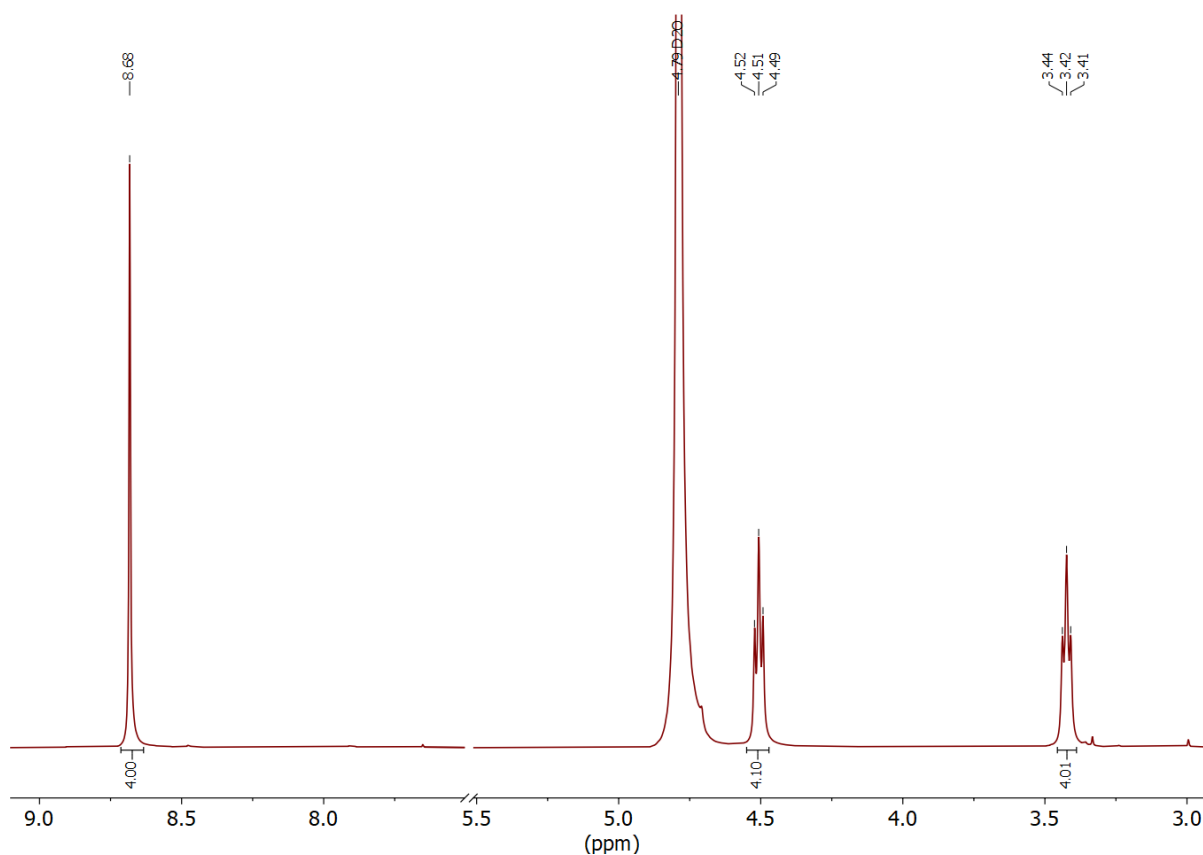
### Synthesis of (1):

A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA, 1.4 mmol, Apollo Scientific) and ethylenediamine (4.4 mmol, Sigma-Aldrich) was refluxed in acetic acid (30 ml) in a 100 ml round bottom flask. The reaction mixture was stirred for 4 hours at  $80^\circ\text{C}$ . After cooling and washing with water, the resulting brown precipitate was filtered. The crude product was dissolved in ethyl acetate and washed with water for several times. Further purification was carried out by silica gel column chromatography (ethylacetate:hexane, 7:3). An orange-brown solid was obtained as product in 48% yield and the product formation was confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectroscopy techniques.

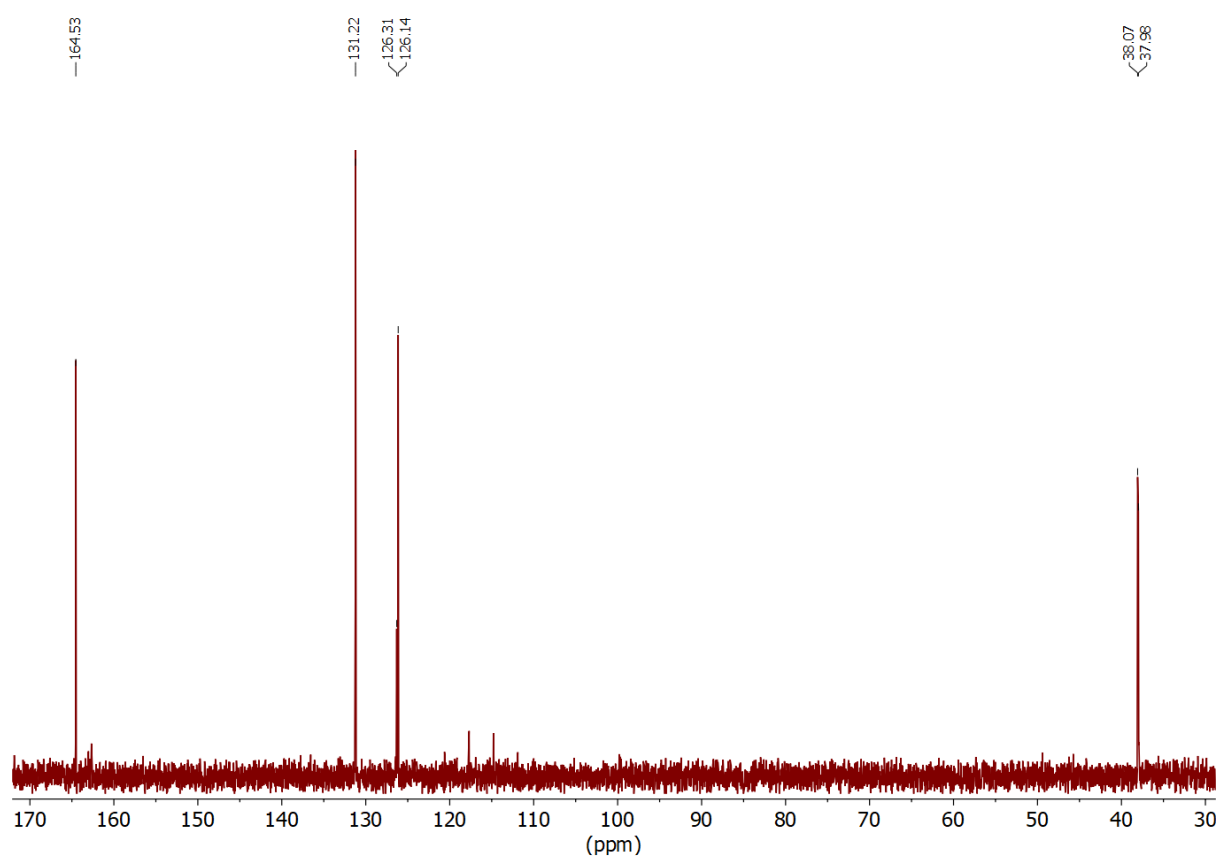
$^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.68 (s, 4H), 4.51 (t, 3H,  $J=6.12$  Hz), 3.42 (t, 3H,  $J=5.88$  Hz);  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  164.53, 131.22, 126.31, 126.14, 38.07, 37.98; HR-MS  $m/z$  353.0968 ( $\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_4$ ,  $\text{M}^+\text{H}$ ).

**Synthesis of (2):** BSA mat ( $3 \times 10^{-5}$  mmol) was placed in a petri dish containing ethyl(dimethylaminopropyl) carbodiimide (EDC, 0.003 mmol, Apollo Scientific), hydroxybenzotriazole (HOBt, 0.003 mmol, J&K) and *N,N*-diisopropylethylamine (DIPEA, 0.006 mmol, Alfa Aesar) in ethanol (2 ml). After agitating for one hour at room temperature, (1) (0.01 mmol) was dissolved in the reaction mixture and kept agitating for another 48 hours. The obtained light brown mat was washed with both ethanol and water for several times. Successful NDI attachment on BSA mat was confirmed by UV-Vis absorption, FTIR and electrochemical impedance measurements. The amount of (1) attached to BSA mat is  $1.05 \pm 0.12$  mg, calculated by doping-density evaluation which was performed by measuring the absorption spectra before and after placing the mats in dopant solution.

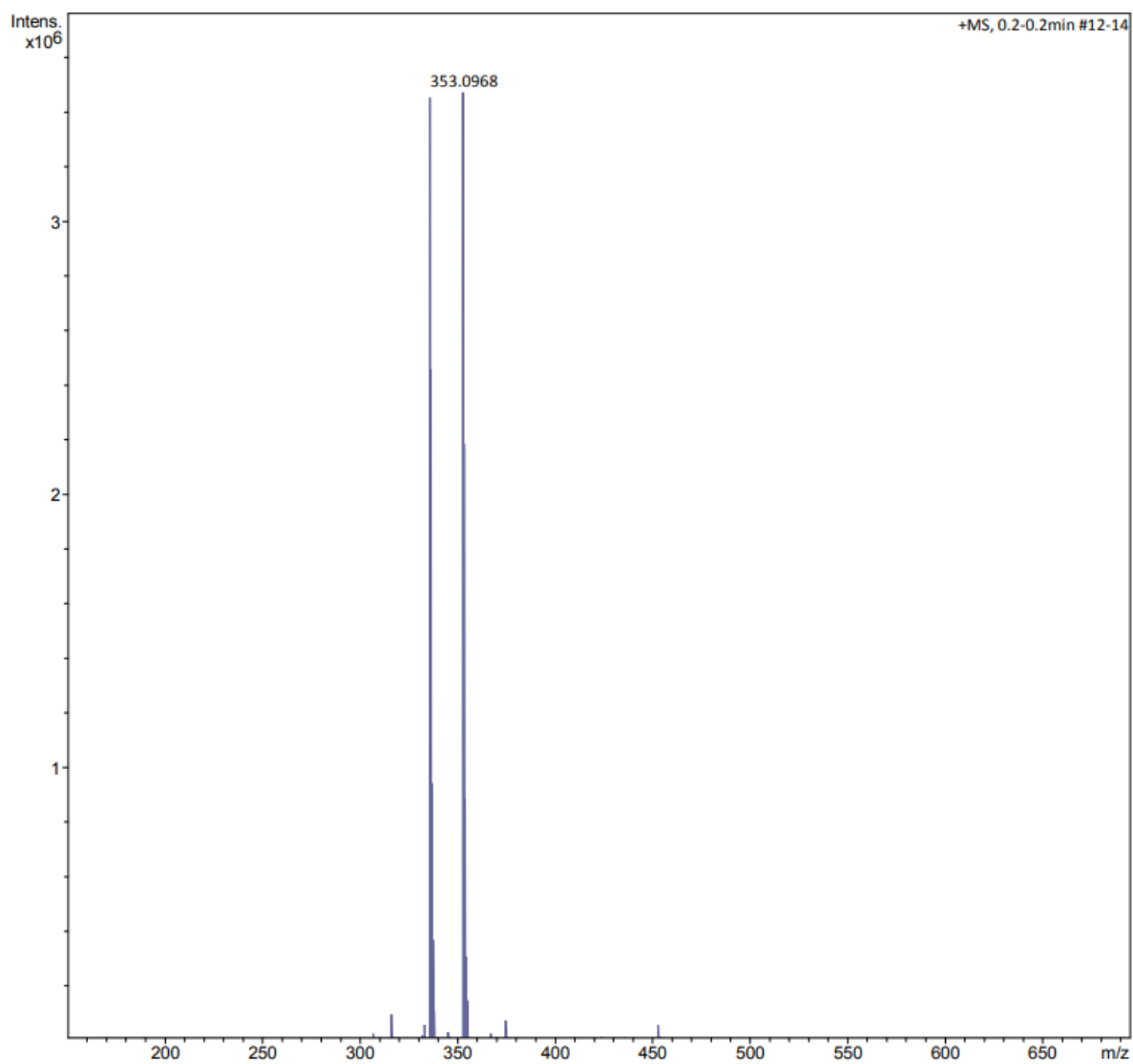
**Synthesis of (3):** BSA-NDI mat was added into a solution of tetra-*n*-butylammonium fluoride (TBAF) in acetonitrile and kept agitating for 24 hours at room temperature. The resulting mat was washed with acetonitrile and formation of NDI radical anions was verified by UV-Vis absorption, FTIR and electrochemical impedance measurements. A maximum of 60% reduction of NDI absorption peak was observed when at least 4 equivalents of TBAF was used.



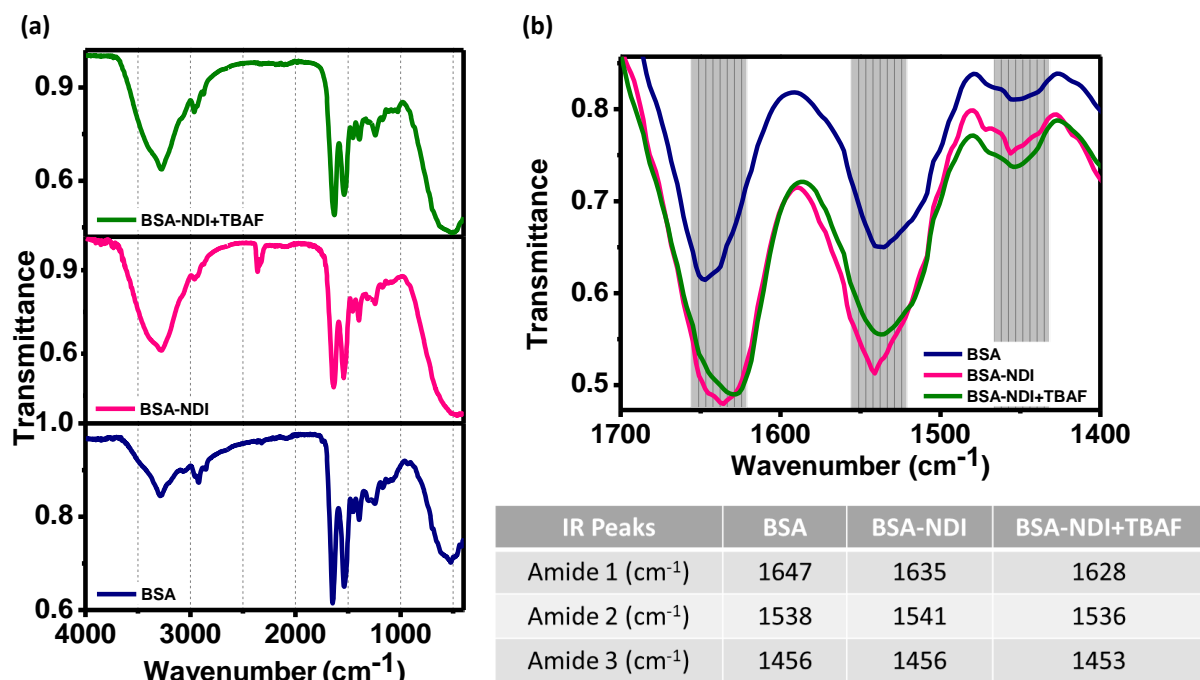
**Figure S1.**  $^1\text{H}$  NMR spectrum of (1) recorded in  $\text{D}_2\text{O}$  solvent.



**Figure S2:**  $^{13}\text{C}$  NMR spectrum of (1) recorded in  $\text{D}_2\text{O}$  solvent.

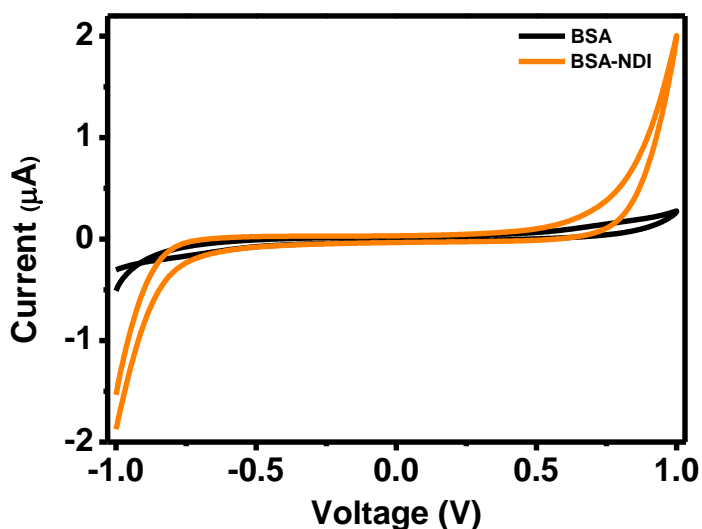


**Figure S3.** Mass spectrum of compound (1).

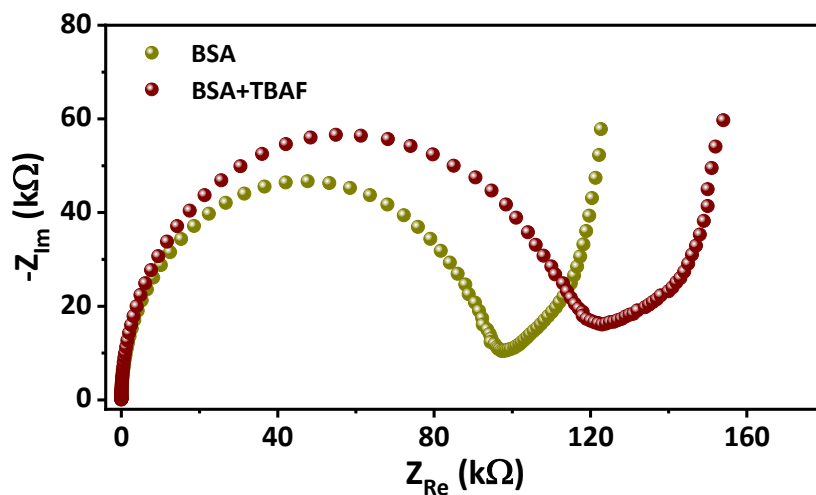


**Figure S4.** (a) Solid state FTIR spectra and (b) zoomed images of amide bands of BSA mat, NDI functionalized BSA mat and reduced BSA-NDI mat.

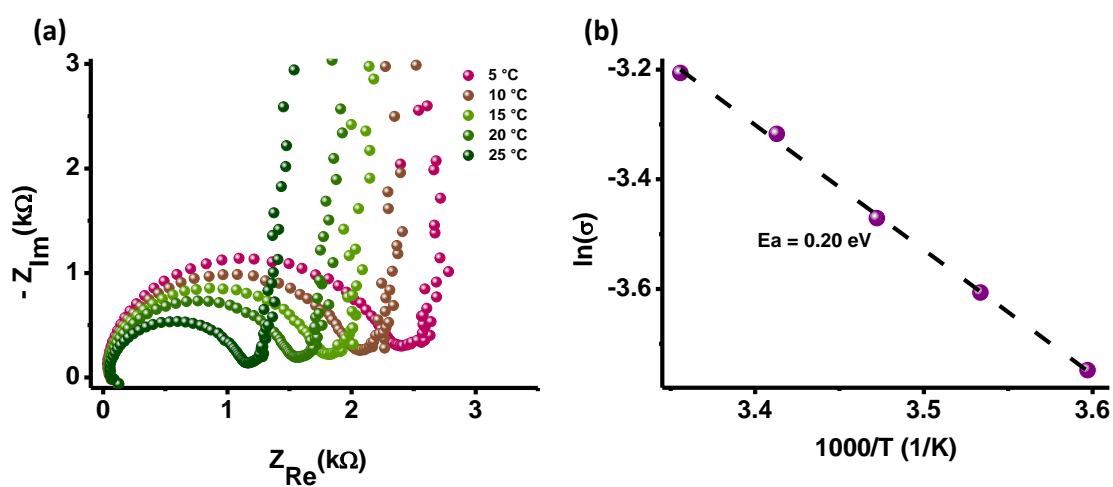
FTIR spectrum of BSA exhibits two important vibration peaks of amide bond at  $1647\text{ cm}^{-1}$  and at  $1538\text{ cm}^{-1}$  which are referred as amide-I ( $-\text{C}=\text{O}$  stretching) and amide-II ( $-\text{C}-\text{N}$  stretching and  $-\text{N}-\text{H}$  bending) respectively. Also, a broad peak around  $3200\text{ cm}^{-1}$  is observed which is attributed to  $-\text{N}-\text{H}$  stretching mode of vibration. Upon binding of NDI with carboxylic acid groups of aspartic acid and glutamic acid residues of BSA, amide-I shifts to lower frequencies, to  $1635\text{ cm}^{-1}$ . In addition, we observed a small change in amide II stretching frequency as well. The amide-I and amide-II peaks were shifted to  $1628\text{ cm}^{-1}$  and  $1536\text{ cm}^{-1}$  respectively upon the reduction of BSA-NDI with TBAF.



**Figure S5.** I-V response of BSA and BSA-NDI for both positive and negative voltage regimes.



**Figure S6.** Impedance measurement of BSA mat before and after the reaction with TBAF, showing no significant change in the resistance of the mat.



**Figure S7.** (a) Temperature dependent impedance measurements of reduced BSA-NDI mat with TBAF and (b) Arrhenius plot of the extracted conductivity and the calculated activation energy.