Supporting information for

Supramolecular Approach for Synthesis of Cross-linked Ionic Polyacetylene Networks Gels

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Contents

Materials and Characterization.

Polyvinyl alcohol, 1,8-dibromooctance and suberic acid were bought from J&K Scientific Ltd.. The microstructure and morphologies were investigated via S4800 scanning electron microscope (SEM) and JEOL 2100F transmission electron microscope (TEM). TEM samples were prepared by drop coating 5 μL of the IPN-gels dispersion (diluted with vast ethanol) onto a copper grid precoated with an ultrathin carbon film (Beijing Zhongjingkeyi Technology Co., Ltd.). ITO glass was knife coated with IPN-gels as the samples (with area of 1 cm^2). The surface of samples was sputtered with gold prior to SEM test. Specific surface area and isotherms pore size distribution curves obtained by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods by nitrogen adsorption specific surface area analyzer 3H-2000. The weight-average (Mw) and the dispersity (Mw/Mn) were determined by Gel Permeation Chromatography (GPC) in DMF with a flow rate of 1 mL/min and calibrated against narrow polydispersity polystyrene standers. The GPC was conducted with a Waters 1515 isocratic HPLC pump and Waters 2414 refractive index detector using PPS columns. X-ray photoelectron spectroscopy (XPS) data was recored with a PHI QUANTERA-II SXM. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV400 with tetramethylsilane (TMS) as the marker. Differential Scanning Calorimetry (DSC) data was recored on DSC-60 plus (Shimadzu corporation) with N_2 protecting and heating rate of 10 °C/min. Thermo Gravimetric Analyzer (TGA) was recorded on PerkinElmer STA8000 with N_2 protecting and heating rate of 10 °C/min. Elecrochemical data were used to charicterize the electrochemistry property of devices. Cyclic voltammetry (CV), chronopotentiometry (CP) and Electrochemical Impedance Spectroscopy (EIS) were conducted via the electrochemical workstation (CHI 660C) at difference scan rate with three-electrode method, respectively.

Preparation and cross-linking degree of IPN-gels.

IPN-1A: A 10 mL Schlenk tube was charged with PPA (300 mg, [repeating unit] = 1.3 mol, 1 equiv) and suberic acid (114 mg, 0.65 mol, 0.5 equiv). Then chlorobenzene (5.1 mL) (the polymer concentration was 5 wt%) was added. The reaction mixture was heated at 80 °C. After 12 h, the solution cooled down to room temperature and formed gel. The measurement of crosslinking degree was calculated from XPS spectra.

All the other cross-linked polymer with different functional groups ratio were prepared following the general procedure given for the preparation of **IPN-1A**.

Preparation of electronic devices.

The PVA/H_2SO_4 electrolyte was prepared as following process: a 150 mL flask was charged with 6 g of PVA and 6 g of concentrated H_2SO_4. Then 60 mL of deionized (DI) water was added. The solution was stirred at 85 °C until the solution became clear. Two ITO glasses were supported IPN-gels by knife coating method and a piece of polypropylene film (used as separator) was soaked in electrolyte solution. Then solvent was removed at 50 °C. Afterward, two ITO glasses and separator membrane filled with electrolyte were stacked together with face-to-face method to fabricate a symmetric device. The structure of the device was shown in Figure S1.

Flexible device. The process almost same with above-mentioned device. PVA/H_2SO_4 was used as the electrolyte and ITO-PET membrane was used as support material instead of ITO glass. Two ITO-PET were supported IPN-gels by knife coating method and a piece of polypropylene film (used as separator) were soaked in electrolyte solution. Then extra moisture was removed at 50°C. Afterward, two ITO-PET and separator membrane filled with electrolyte were stacked together with face-to-face method. It was encapsulated by flexible PET film to carry out a symmetric device.

Calculation of capacitance.

The capacitance values were calculated from the CV data according to the following equation (1):

$$\mathrm{C} = \frac{1}{v \times \Delta V} \int_{V_1}^{V_2} I(V)dV \tag{1}$$

Where C is capacitance from electrodes, v is the scan rate (V/s), *ΔV* is the difference of voltage of CV curve (V_2-V_1). *I(V)* is the discharge current (A).

Volume capacitance of device were calculated based of the volume of the device according to the following equation (2):

$$C_{volume} = \frac{4 \times C}{V_{device} \times \rho} \tag{2}$$

Where C (F/g) refer to the volumetric capacitance of single electrode, ρ (g/cm^3) is the density of material.

The energy density E_{device} (mWh/cm$^{3)}$ based on the volume of device (V_{device}) were calculated according to the following equation (3):

$$E_{device} = \frac{1}{2} \times \frac{C}{V_{device}} \times \frac{(\Delta V)^2}{3600} \times 1000 \tag{3}$$

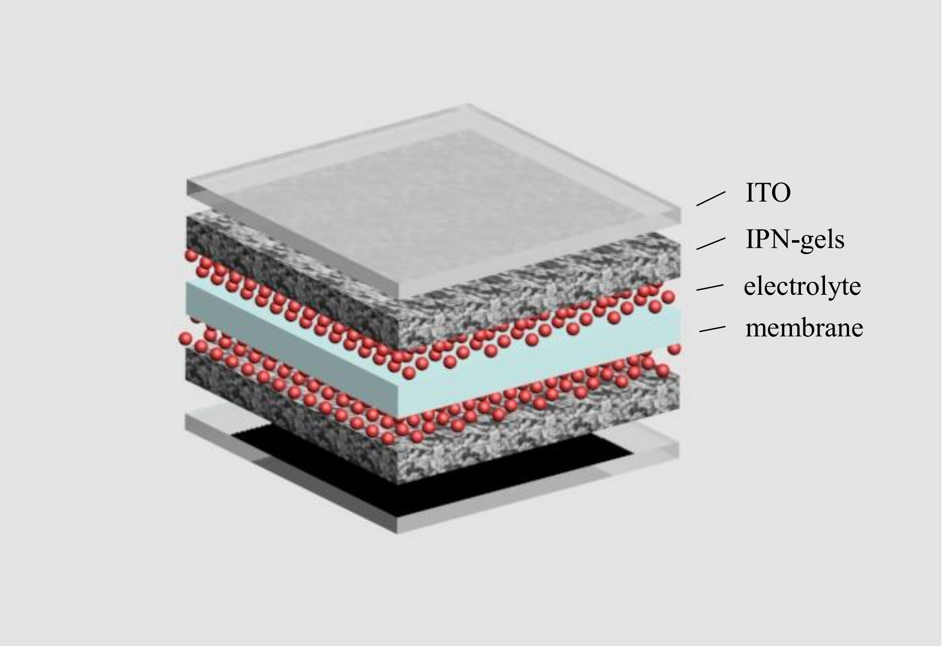

Figure S1. Structure of symmetric electronic device.

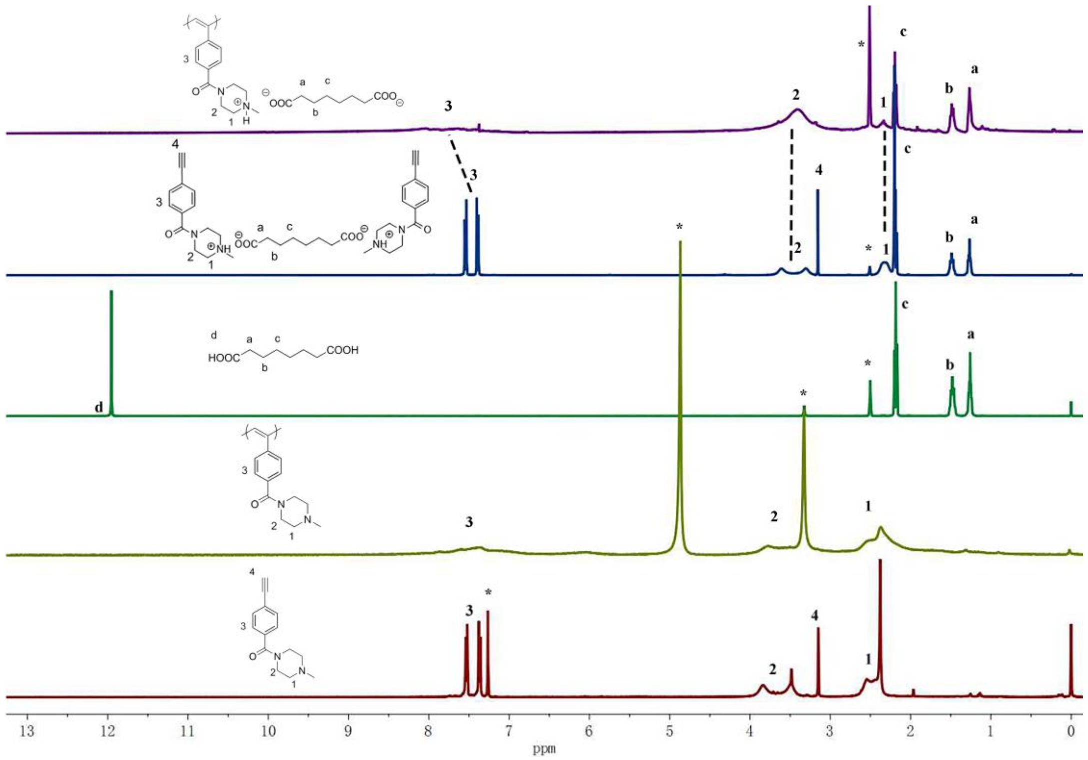

Figure S2. NMR spectra of **IPN-1As**. Compounds are **PA** (in $\mathrm{CHCl_3}$-d_3), **PPA** (MeOH-d_4), suberic acid (in DMSO-d_6), model compound (in DMSO-d_6), **IPN-1A** with functional groups ratio of 1 (in DMSO-d_6, entry 5) from bottom to top, respectively.

When IPN-gel was generated, tertiary amine captured a proton and transformed quaternary ammonium salt with emergence of the binding energy at 402.3 eV. Therefore, crosslinking degree of IPN could be calculated by the integral area of peak at 402.3 eV (C-N) and the integral area of peak at 399.9 eV (N^+).

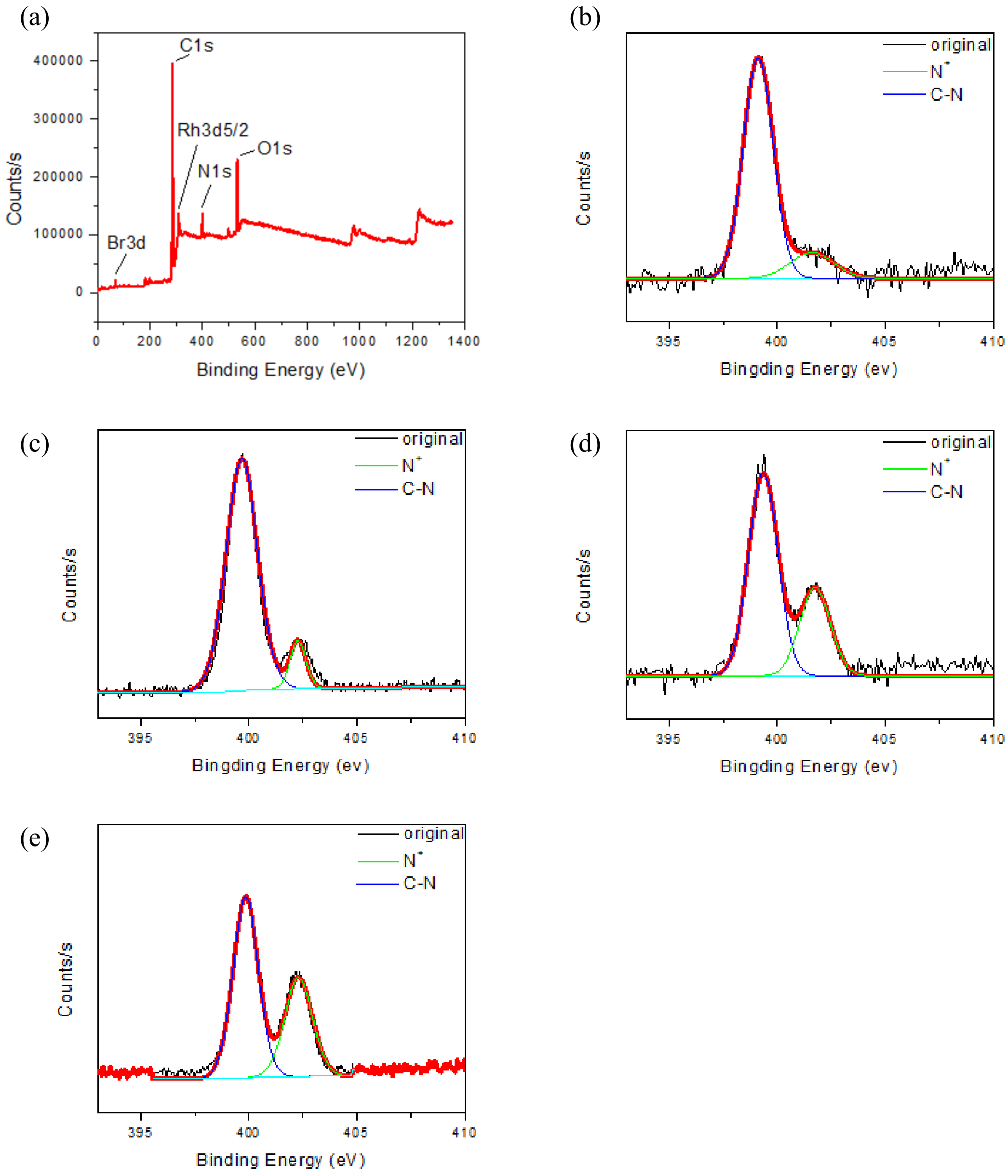

Figure S3. XPS spectra of **IPN-1Bs**. (a) full scan of sample. (b) N1s XPS spectrum of entry 6. (c) N1s XPS spectrum of entry 7. (d) N1s XPS spectrum of entry 8. (e) N1s XPS spectrum of entry 9.

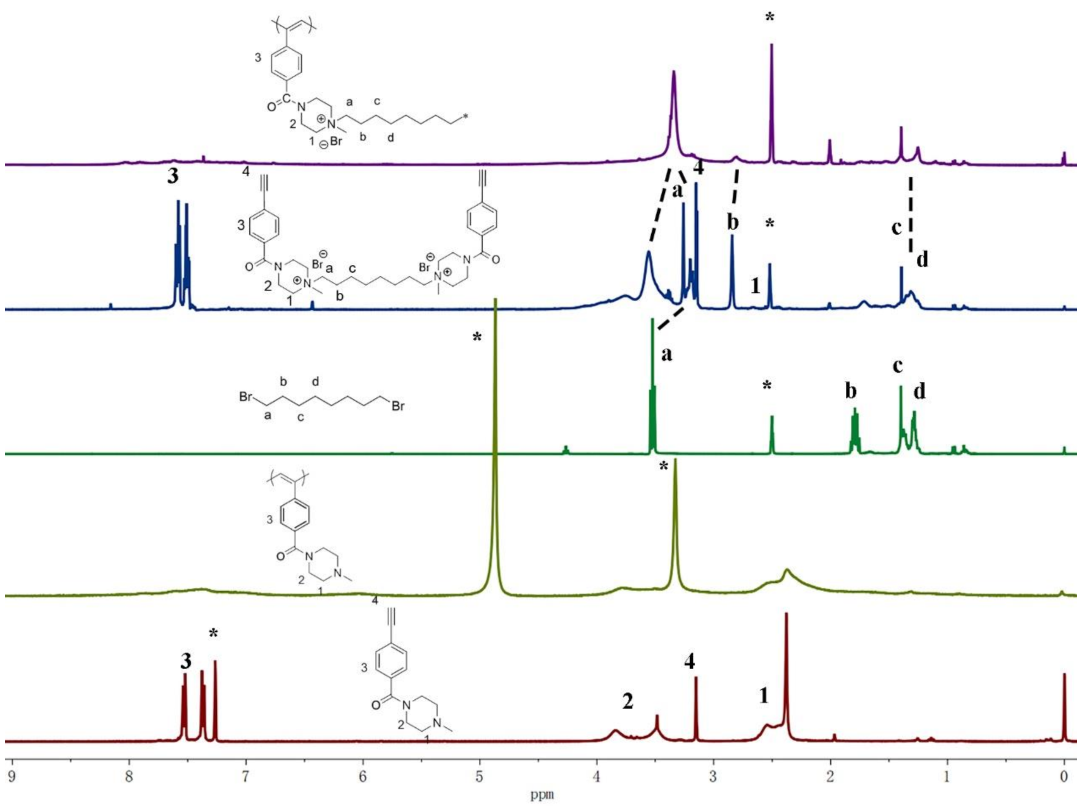

Figure S4. NMR spectra of **IPN-1Bs**. Compounds are **PA** (in CHCl$_3$-d_3), **PPA** (MeOH-d_4), 1,8-dibromooctance (in DMSO-d_6), MC (in DMSO-d_6), **IPN-1B** with functional groups ratio of 1 (in DMSO-d_6, entries 9) from bottom to top respectively.

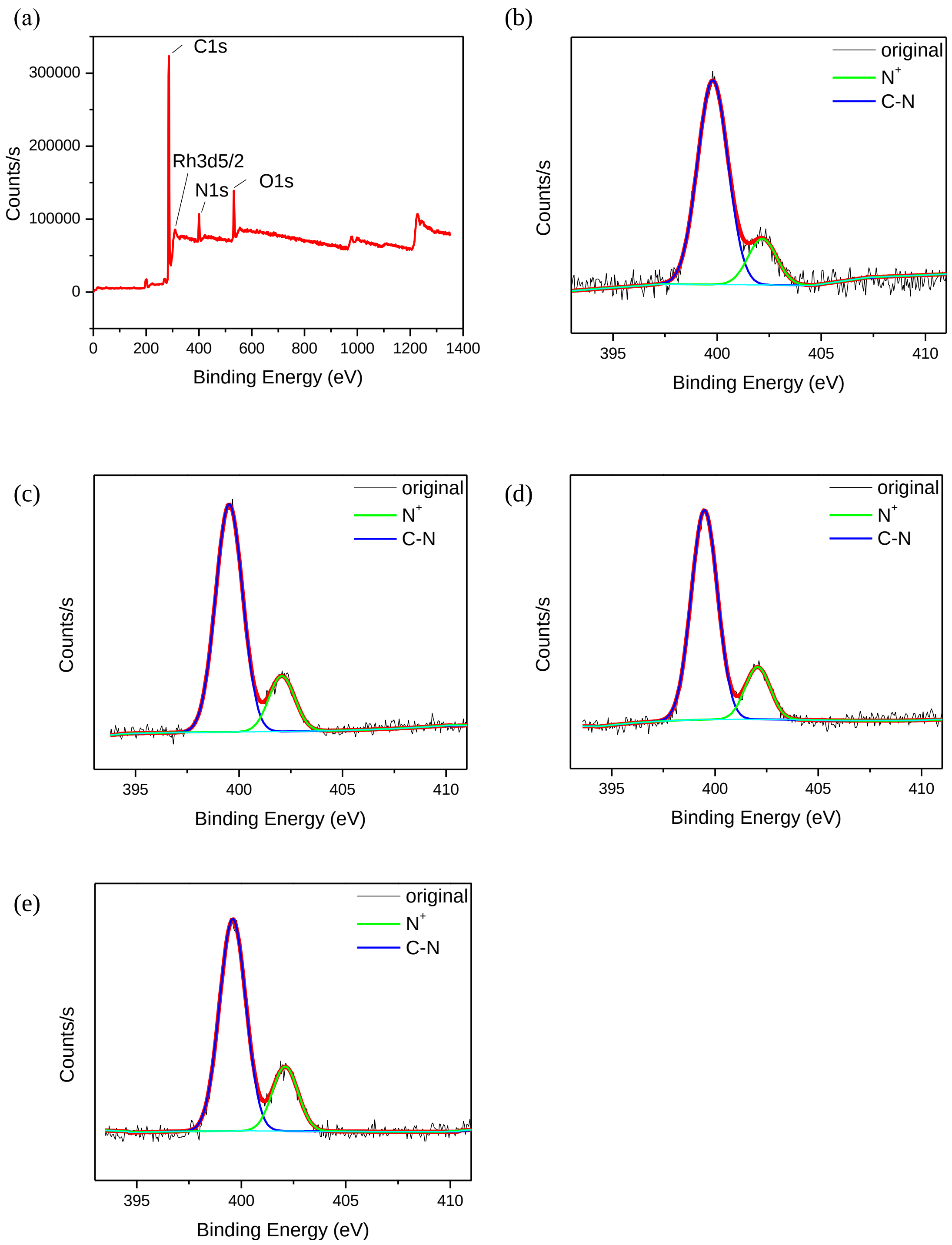

Figure S5. XPS spectra of **IPN-2As**. (a) Full scan of sample. (b) N1s XPS spectrum of entry 11. (c) N1s XPS spectrum of entry 12. (d) N1s XPS spectrum of entry 13. (e) N1s XPS spectrum of entry 14.

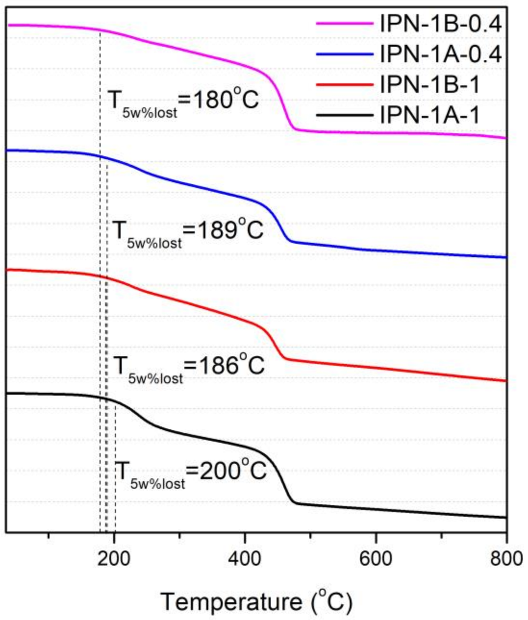

Figure S6. TGA curves of **IPN-1As** (entry 4 and entry 5) and **IPN-1Bs** (entry 8 and entry 9). Temperature of thermal 5% weight lost were noted as insertion.

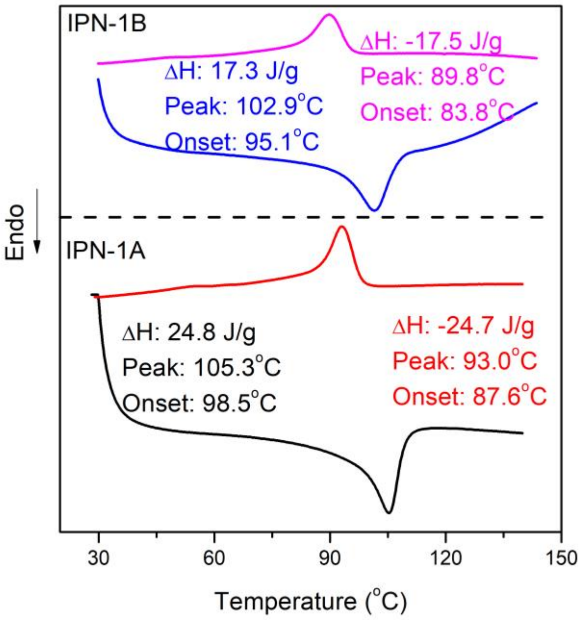

Figure S7. DSC curves of **IPN-1A** (entry 5) and **IPN-1B** (entry 9).

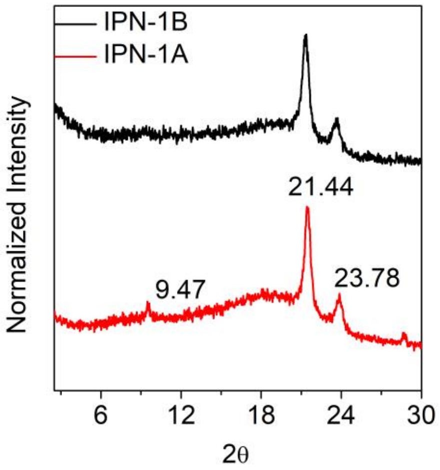

Figure S8. XRD spectra of **IPN-1A** (entry 5) and **IPN-1B** (entry 9).

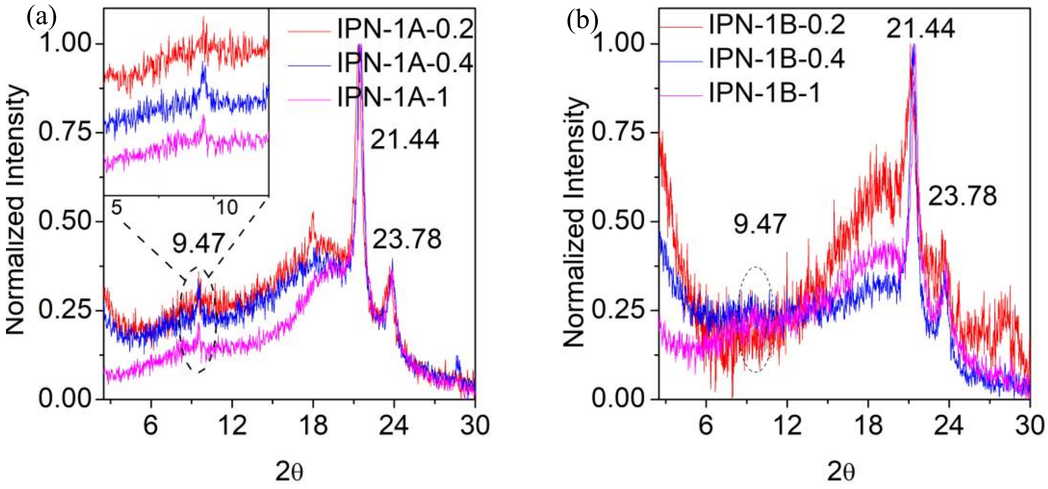

Figure S9. XRD spectra of **IPN-1As** and **1Bs.** (a) XRD spectra of **IPN-1A** at different functional groups ratio of COOH (entries 3-5). (b) XRD spectra of **IPN-1B** at different functional groups ratio of Br (entries 7-9).

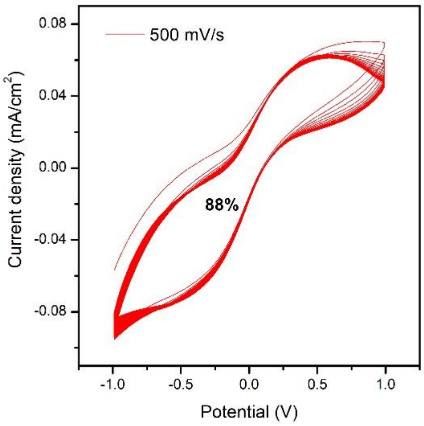

Figure S10. Cyclic voltammetry cures of **IPN-1A** device between -1 V to 1 V at 500 mV/s with 7000 cycles. 88% retention of original capacitance after 7000 cycles.

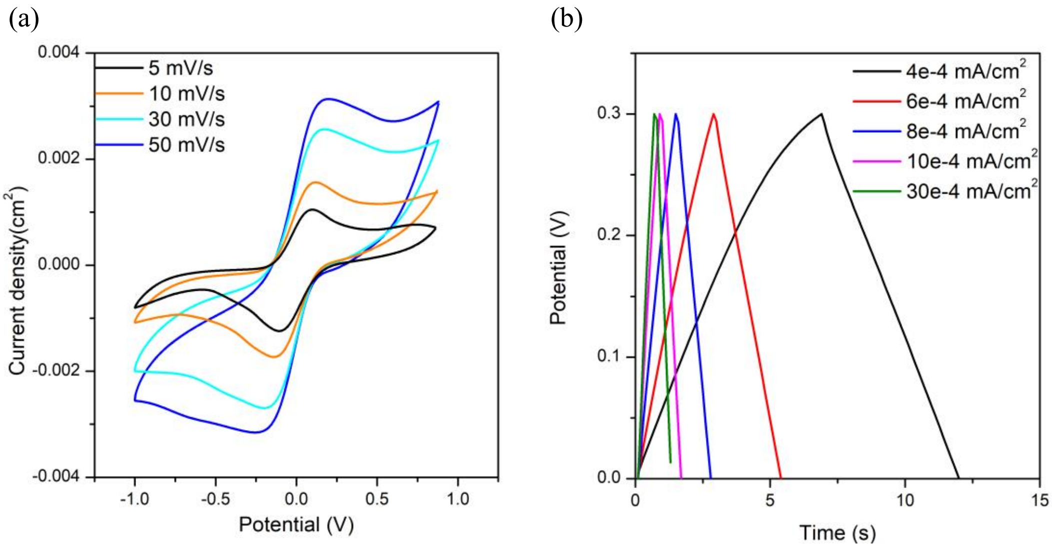

Figure S11. (a) Cyclic voltammetry cures at different scanning rates ranging from 5 to 50 mV/s and (b) Galvanostatic charge and discharge curves at different current densities of PPA.

The strain sweep spectra of the **IPN-1A** gel showed a liner viscoelastic regime below ca. 3% strain. The storage modulus (G') is larger than that of loss modulus (G") at this regime, indicating that the **IPN-1A** gel was elastic gel (Figure S12a and b). The damage to internal crosslinks in **IPN-1A** gel may be avoided at ca. 10% strains, due to the presence of additional adhesive strength imparted by the cross-linker. The viscosity of the gel reduced as frequency rate increased, confirming the shear thinning nature of gels (Figure S12c).

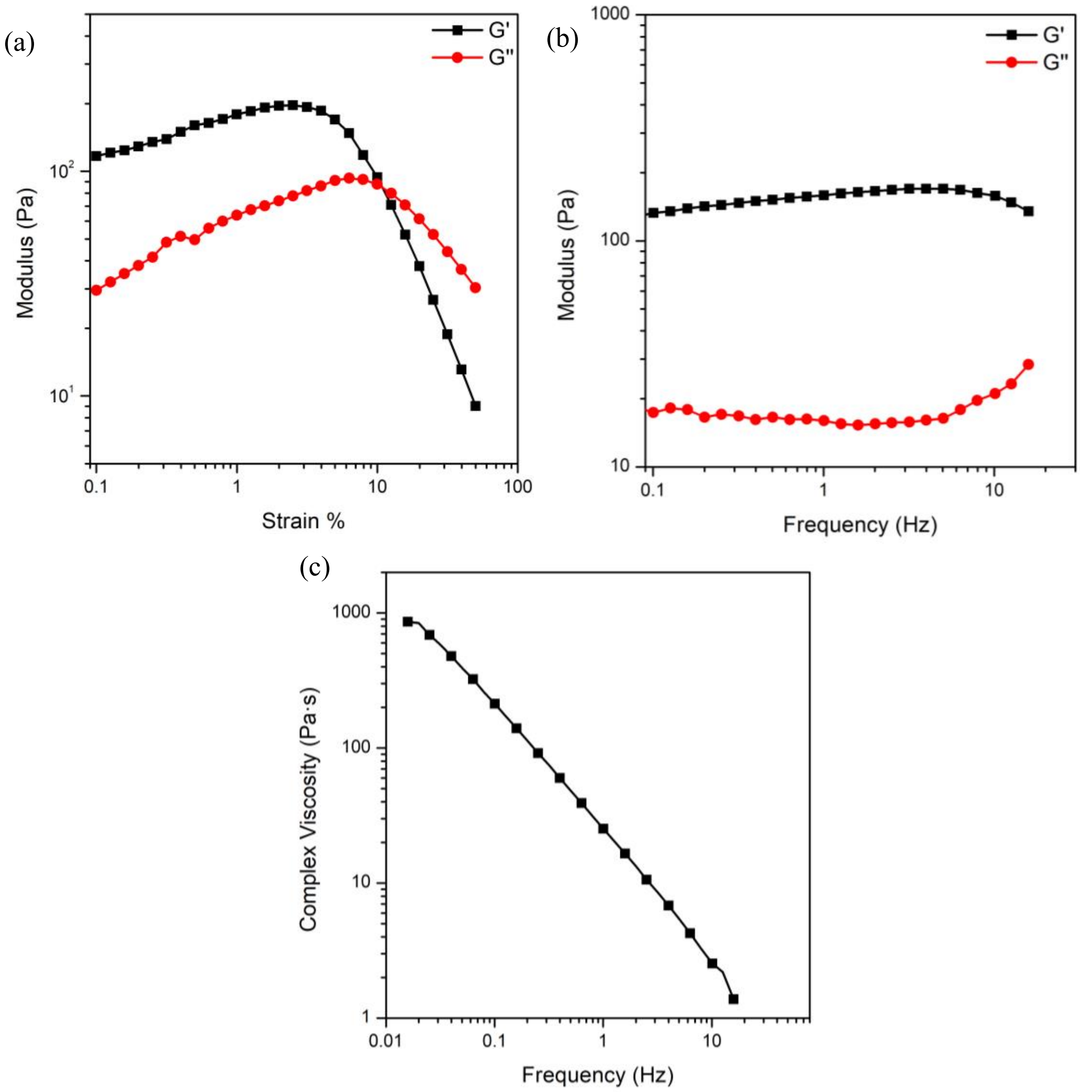

Figure S12. (a) Frequency sweep graphs for **IPN-1A** at 0.1% strain at room temperature. (b) The plot of relationship between frequency and complex viscosity. (c) Strain sweep of **IPN-1A** gel at 0.1 rad/s from 0.1% to 50% strain at room temperature.

Table S1. Electrical properties of devices

	Configuration of PPA	Species of cross-linker	Species of electrolyte	E_{device} (mWh/cm^3)^a	σ(S/m)^a	R_b (cm^2)^a	W (10^3 cm^2)^a
IPN-1A^b	trans-cisoild , cis% = 34%	suberic acid	-	$4.5*10^{-4}$	$(5.7 \pm 0.3)*10^{-4}$	-	-
IPN-1B^b	trans-cisoild , cis% = 34%	1,8-dibromooctance	-	$2.9*10^{-4}$	$(1.9 \pm 0.1)*10^{-4}$	-	-
IPN-1A	trans-cisoild , cis% = 34%	suberic acid	PVA/H_2SO_4	0.37	$(5.4 \pm 0.7)*10^{-3}$	107 ± 12	4.2 ± 1.2
IPN-1B	trans-cisoild , cis% = 34%	1,8-dibromooctance	PVA/H_2SO_4	0.051	$(3.6 \pm 0.7)*10^{-3}$	71 ± 22	15.7 ± 2.2

a: Average data, error represents s.d., n = 3.

b: The device without electrolyte.