

Supporting information

Preparation of multifunctional organogel and its electrochemical properties

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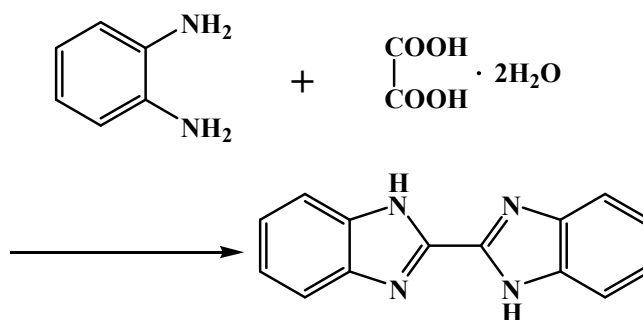
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1. Chemicals and Instrumentation

1, 2-Phenylenediamine was purchased from Tokyo Chemical Industry. Oxalic Acid, Polyphosphoric Acid, Ethyl Chloroacetate, K_2CO_3 , KI and NaOH, H_2SO_4 was purchased from Sinopharm Chemical Reagent Co., LTD (China). Dimethyl Formamide (DMF) and Polyvinyl Alcohol (PVA) was purchased from Shanghai Titan Scientific. KCl was purchased from Anhui Senrise Technology Co., LTD (China). Activated carbon was purchased from Shanghai Sino Tech Investment Management Co., LTD (China). All reactions were taken place in the air except as otherwise noted. All measurements were carried out at room temperature. All chemicals were used without further purification, unless otherwise noted.

NMR spectra were carried out on a Bruker 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references at room temperature, and the chemical shifts (δ) were showed in ppm. The FT-IR spectra of the synthesized samples and the organogel were measured on Thermo Scientific Nicolet iS5. The morphologies of the organogel were characterized with a ZEISS Gemini 300 SEM using an accelerating voltage of 1.5 kV. The UV-Vis absorption spectra were measured on UV-1750 spectrophotometer. The fluorescence spectra were measured on RF-6000 instrument. The HRMS spectra were carried out on Bruker autoflex maX MALDI-TOF (TOF). The supercapacitor was tested at different physical states by CHI660A Electrochemical Workstation.

2. Synthesis and characterization of DBA



Scheme S1 Synthesis of L

Synthesis of L: 1, 2-Phenylenediamine (10 g, 93 mmol) was mixed with Oxalic Acid (5.829 g, 46 mmol) in EG solution and was refluxed for 2 h under N₂. After the reaction mixture was added to distilled water and lots of solid powder was precipitated by filtration. Then the precipitate was filtered and washed with distilled water, then dried under vacuum to L. Yield: 3.0718 g (34.64%). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 13.51 (s, 2H, -NH-), 7.66 (dd, J=77.5, 7.6 Hz, 4H, Ar-H), 7.37-7.23 (m, 4H, Ar-H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm) 143.96 (s), 143.65 (s), 134.98 (s), 123.75 (s), 122.37 (s), 119.33 (s), 112.20 (s).

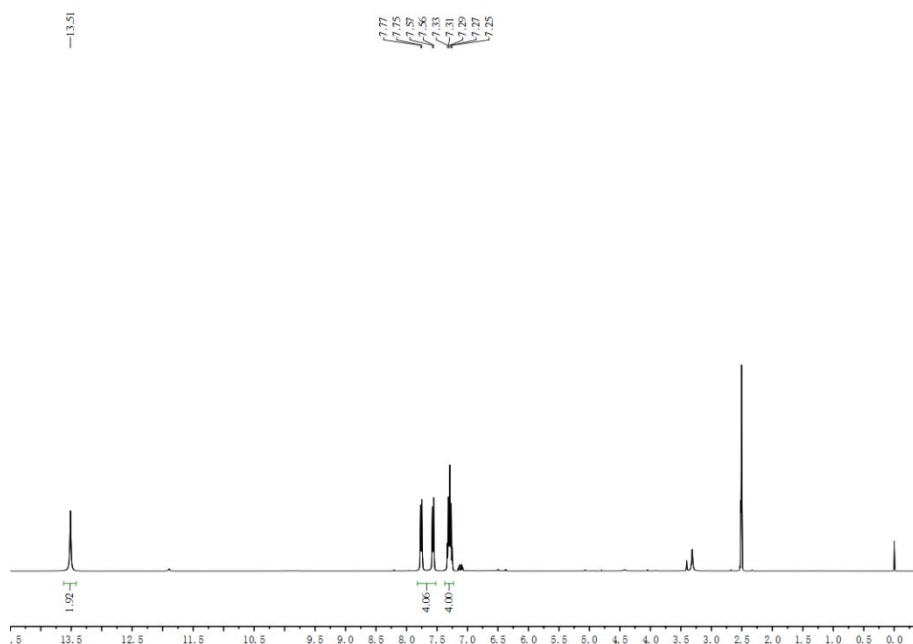


Fig. S1 ¹H NMR spectrum of L

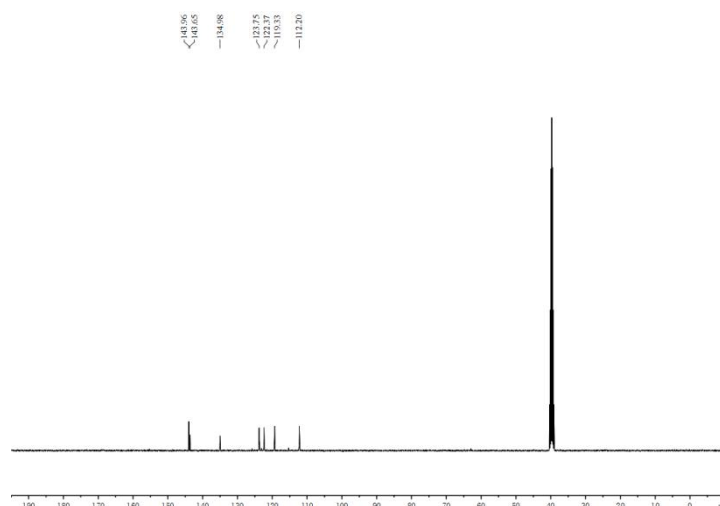
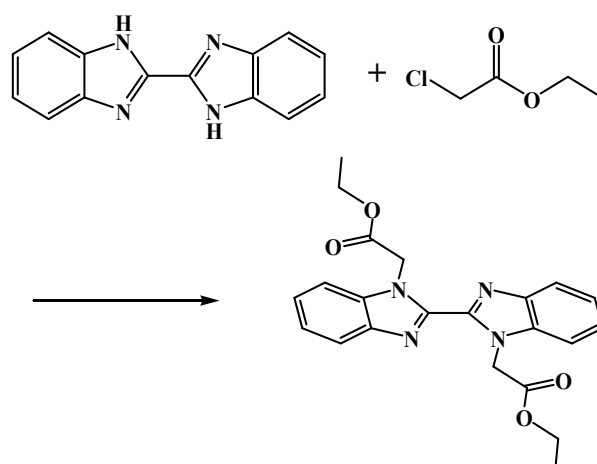


Fig. S2 ^{13}C NMR spectrum of L



Scheme S2 Synthesis of M

Synthesis of M: L (3.0088 g, 12.84mmol) was mixed with Ethyl Chloroacetate (3 mL, 28.34 mmol) in DMF solution and was refluxed for 8 h. After the reaction mixture was cooled to room temperature, the mixture was added to distilled water and lots of solid powder was precipitated by filtration. Then the precipitate was filtered and washed with distilled water, then dried under vacuum to M. Yield: 3.9142 g (77.86 %). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ (ppm) 7.77 (dd, $J=11.8, 7.6$ Hz, 4H, Ar-H), 7.38 (dtd, $J=15.0, 7.2, 1.2$ Hz, 4H, Ar-H), 5.77 (s, 4H, CH_2 -), 4.19 (q, $J=7.1$ Hz, 4H, $-\text{CH}_2$ -), 1.23 (dd, $J=9.4, 4.7$ Hz, 6H, $-\text{CH}_3$). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ (ppm) 168.32 (s), 142.38 (s), 141.53 (s), 135.74 (s), 124.24 (s), 123.06 (s), 119.77 (s), 110.92 (s), 60.89 (s), 47.13 (s), 14.10 (s).

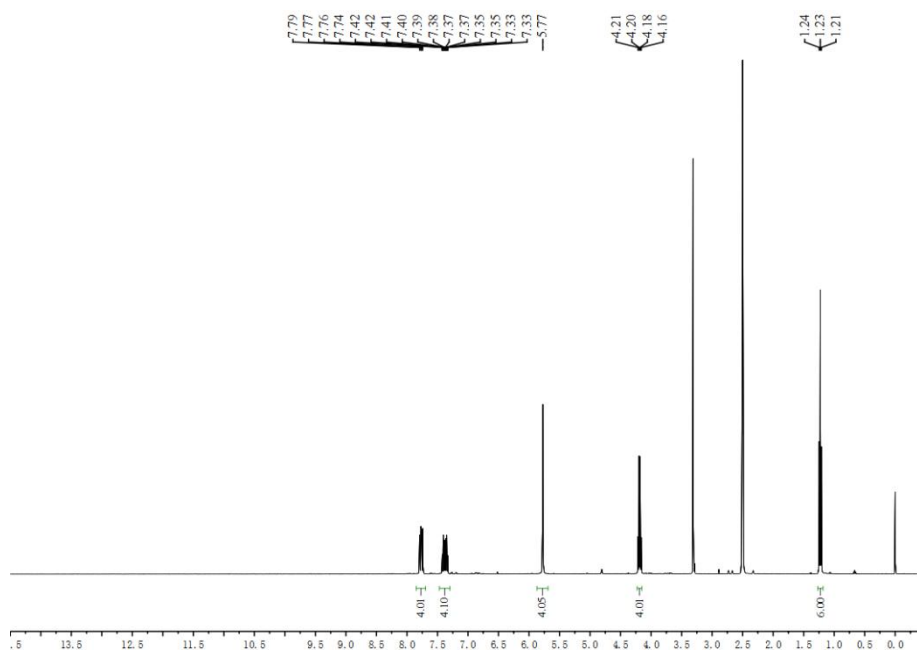


Fig. S3 ^1H NMR spectrum of M

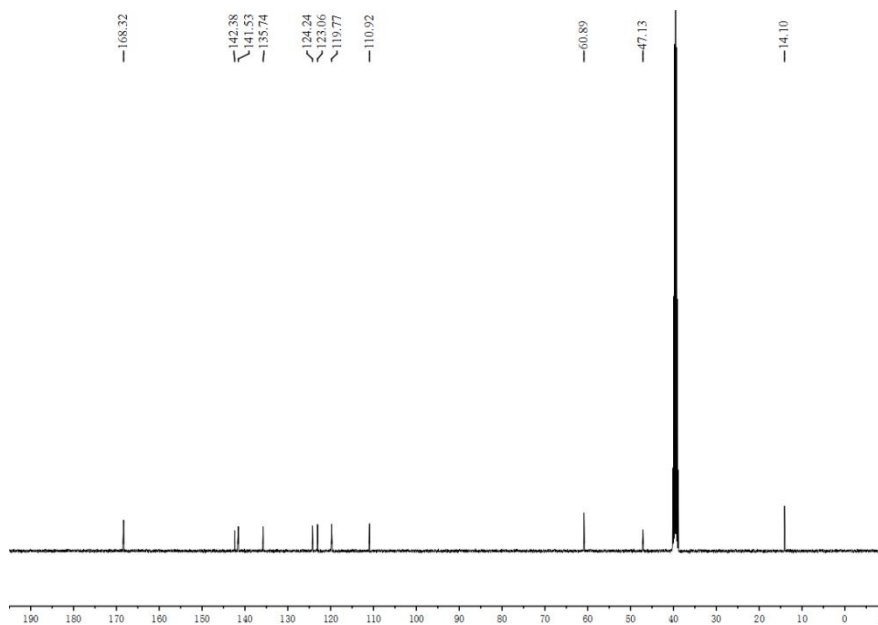
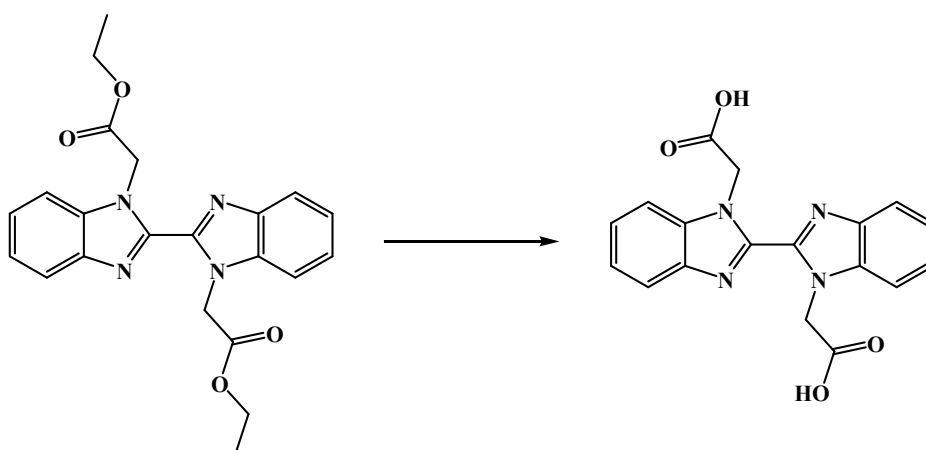


Fig. S4 ^{13}C NMR spectrum of M



Scheme S3 Synthesis of DBA

Synthesis of DBA: M (2.0165 g, 5mmol) was mixed with a sodium hydroxide solution of 10 percent. and was refluxed for 8 h. After the reaction mixture was cooled to room temperature, the mixture was acidified with aqueous HCl till pH=2 and lots of solid powder was precipitated by filtration. Then the precipitate was filtered and washed with distilled water, then dried under vacuum to G. Yield: 1.5604 g (89.78%).
1H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 13.08 (s, 2H, -COOH), 7.76 (dd, J=15.9, 4H, Ar-H), 7.37 (dtd, 7.2, 4H, Ar-H), 5.77 (s, 4H, -CH₂-). 13C NMR (101 MHz, DMSO-*d*₆) δ (ppm) 169.62 (s), 142.52 (s), 141.58 (s), 135.82 (s), 124.16 (s), 122.96 (s), 119.81 (s), 111.01 (s), 46.95 (s).

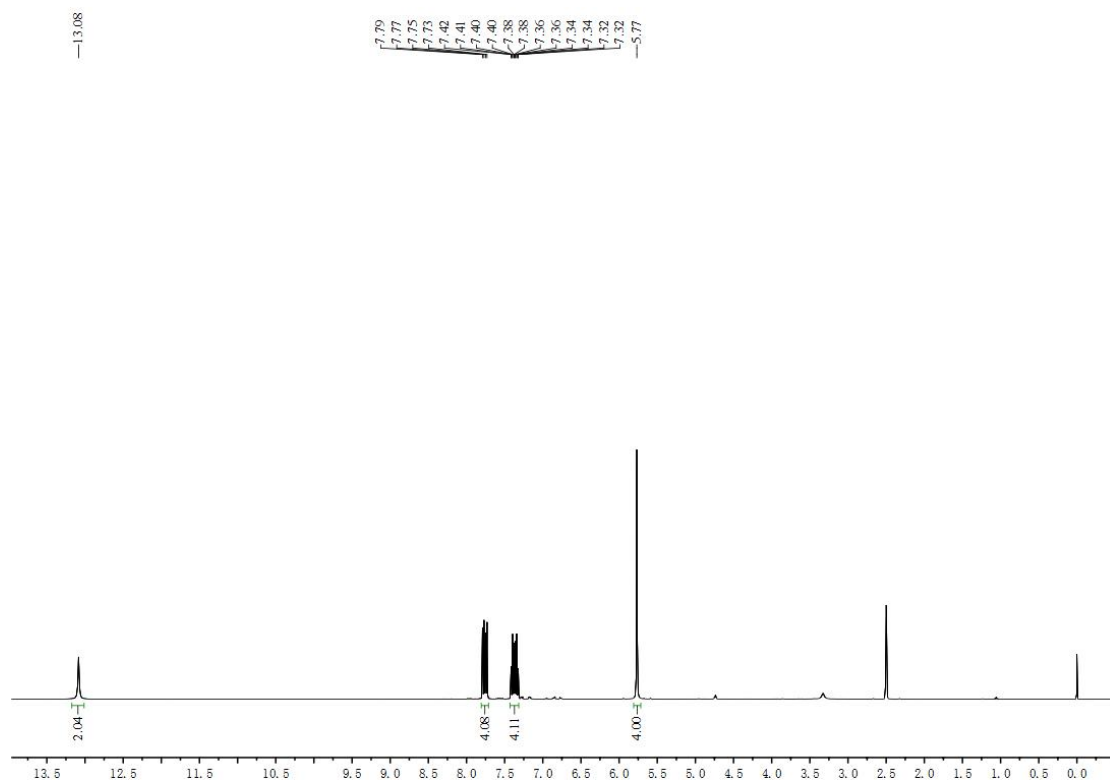


Fig. S5 ^1H NMR spectrum of DBA

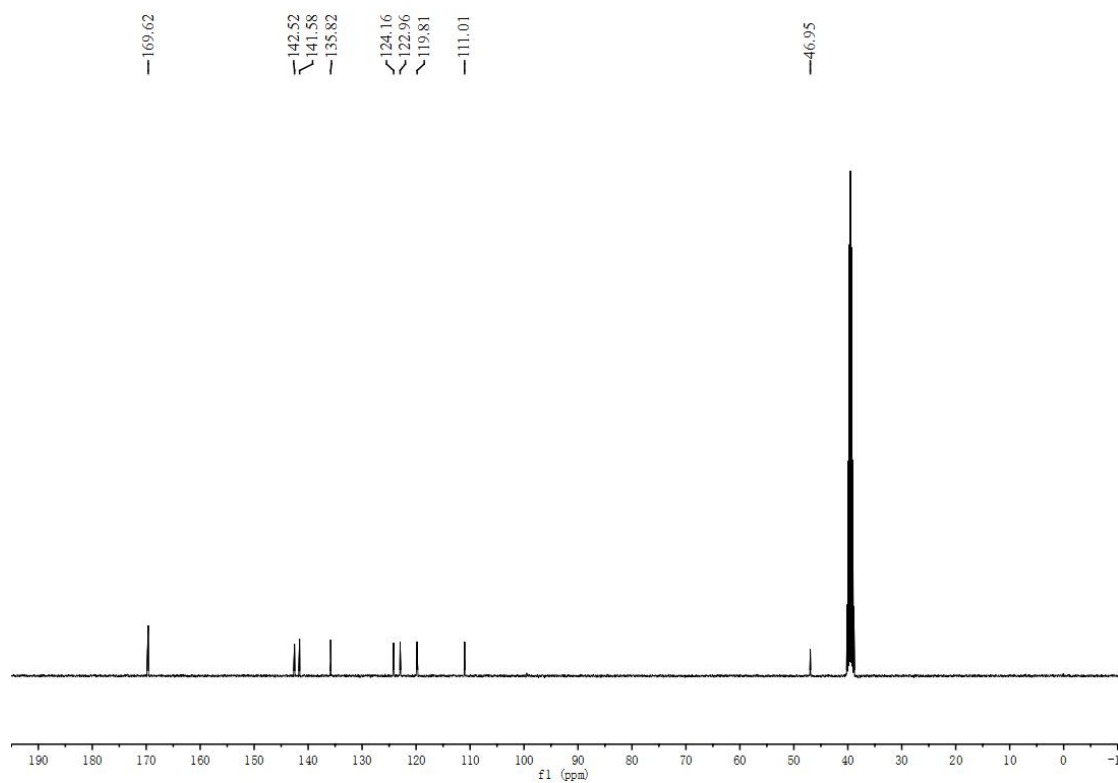


Fig. S6 ^{13}C NMR spectrum of DBA

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T: FTMS + p ESI Full ms [50.0000-750.0000]

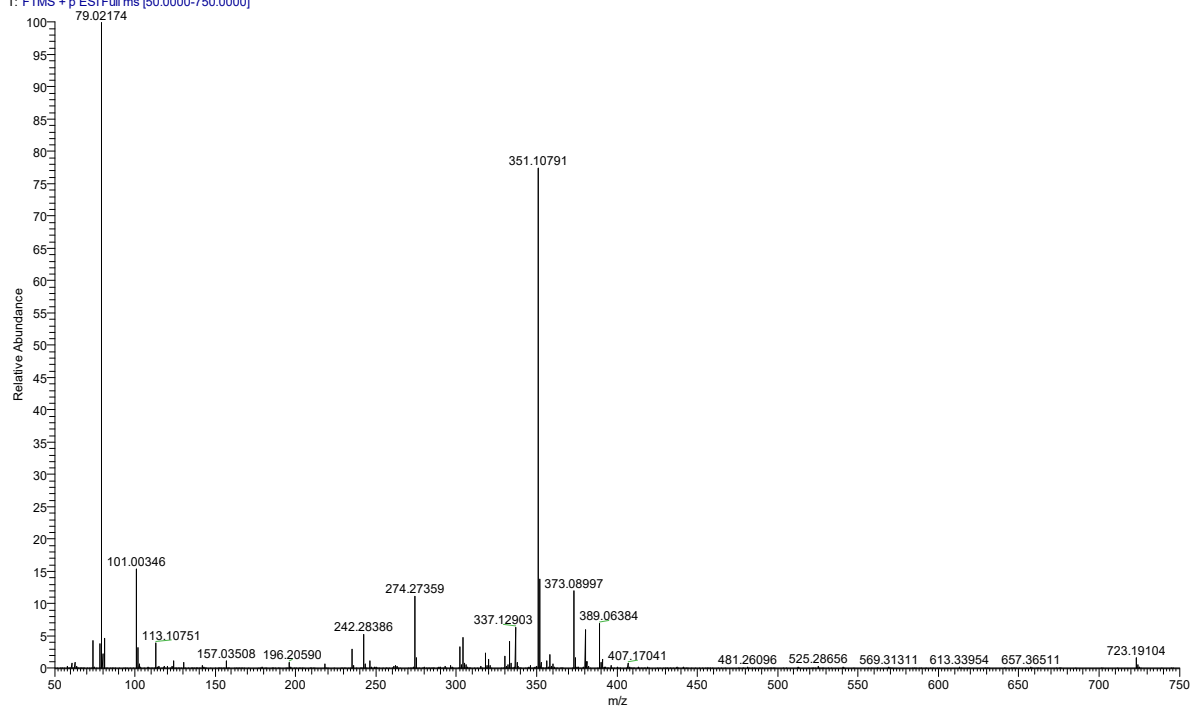


Fig. S7 HRMS spectra of DBA+H

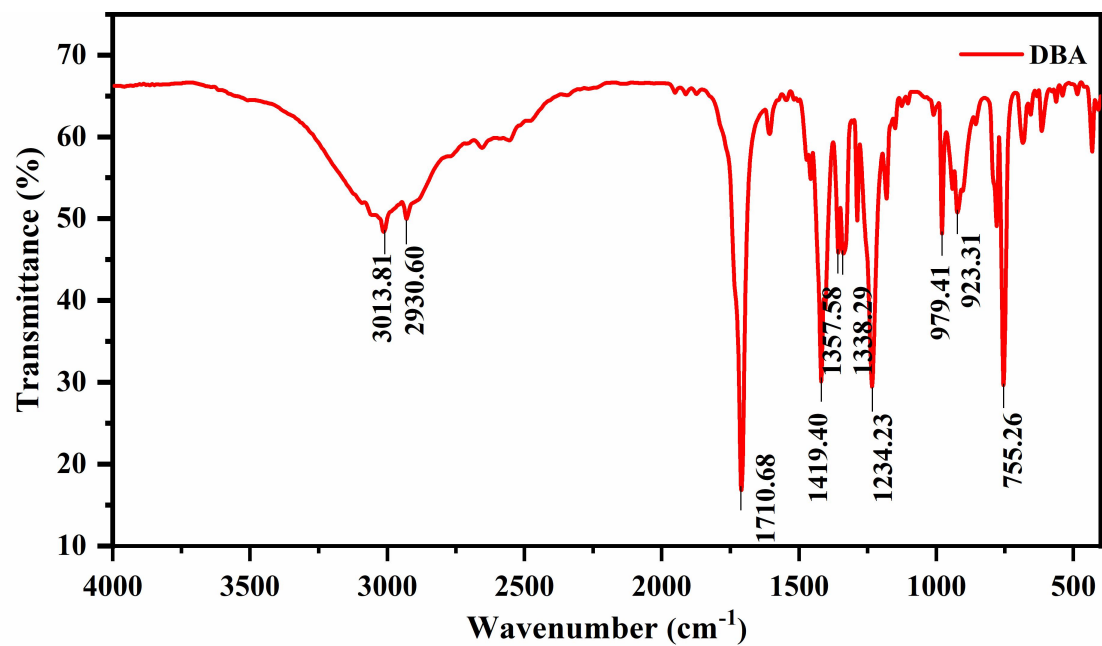


Fig. S8 FT-IR spectra of DBA

Scheme S5 Preparation Method of PVA -gel and PVAD-gel.

PVA-gel: PVA (2g) was dissolved in DMSO (12 mL) with agitation at 120°C for 3 h to form a homogeneous and low-viscous solution. After the mixture was poured to plastic petri dishes and cooled for 12 h at -10°C, the PVA -gel was obtained.

PVAD-gel: PVA (2g) was dissolved in DMSO (12 mL) to form a homogeneous and low-viscous solution. DBA (0.1g) was added to the above solution with constant stirring at 120°C for 24 h. Finally, the resultant mixture was poured to plastic petri dishes and cooled for 12 h at -10°C, the PVAD -gel was obtained.

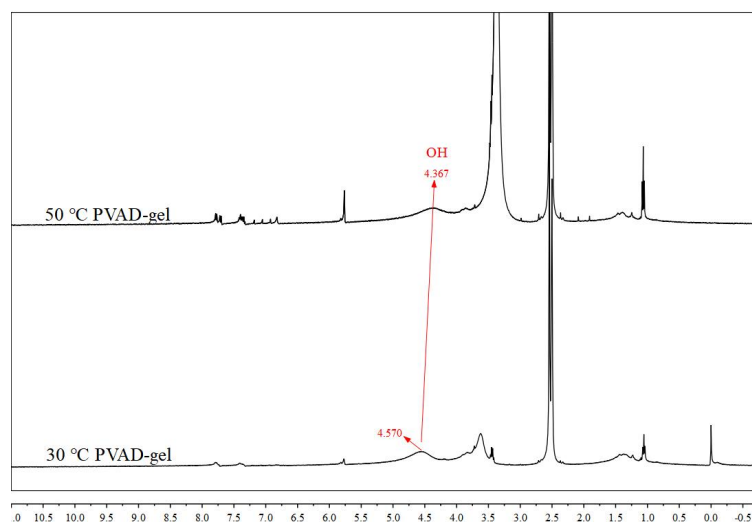


Fig. S9 Varied temperature ^1H NMR spectroscopy of PVAD

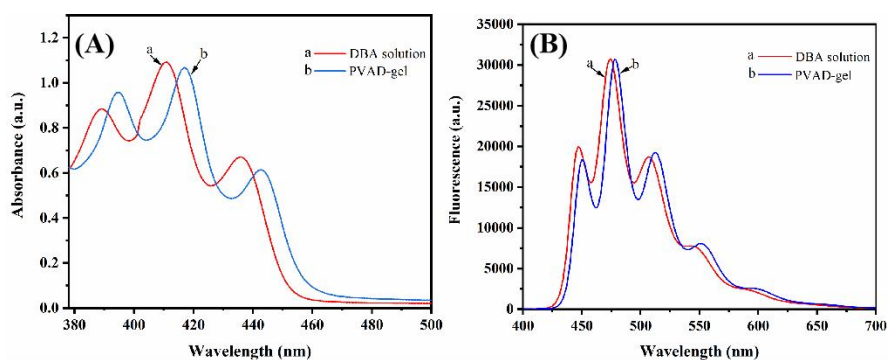


Fig. S10 (A) UV-vis of DBA solution and PVAD-gel ;
 (B) Fluorescence spectra of DBA solution and PVAD-gel

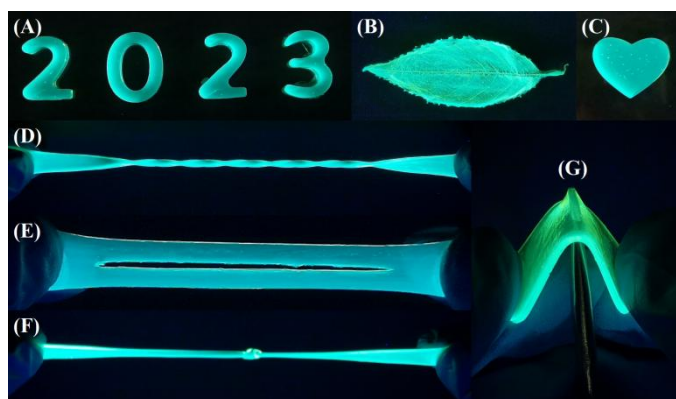


Fig. S11 Fluorescence photo of PVAD-gel: Free-shapeable properties (A, B, C); Ordinary stretching with twists, punching and a knot (D, E, F); Puncture resistance (G)

Scheme S6 Preparation method of supercapacitors

PVA-gel Supercapacitors: Let a pair of the AC electrodes and the PVA-gel soak for 10 min in potassium chloride solution. A two-electrode test supercapacitor was fabricated with a pair of the AC electrodes and the PVA-gel. The PVA-gel served as electrolyte and separator, and the two nickel net with the electrode material used as current collectors.

PVAD-gel Supercapacitors: Let a pair of the AC electrodes and the PVAD-gel soak for 10 min in sulfuric acid solution. A two-electrode test supercapacitor was fabricated with a pair of the AC electrodes and the PVAD-gel. The PVAD-gel served as electrolyte and separator, and the two nickel net with the electrode material used as current collectors.

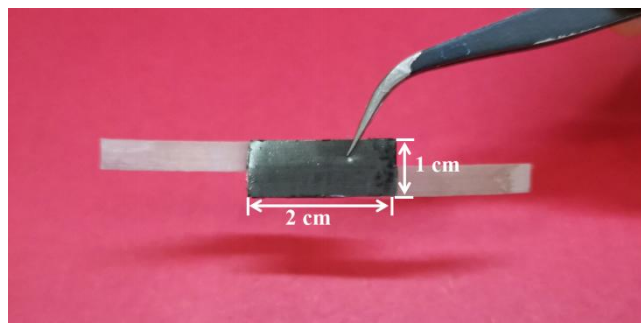


Fig. S12 Fabricated supercapacitor

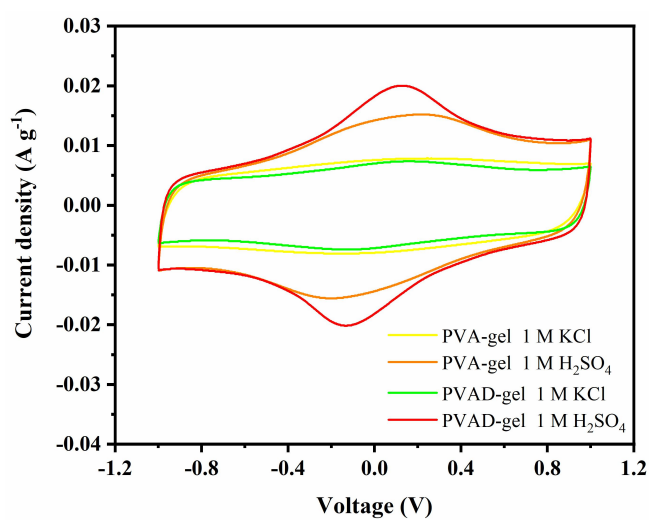


Fig. S13 CV curves of PVA-gel (or PVAD-gel) supercapacitor with a pair of the AC electrodes and the PVA-gel (or PVAD-gel) soak in 1 M KCl or 1 M H₂SO₄ solution.

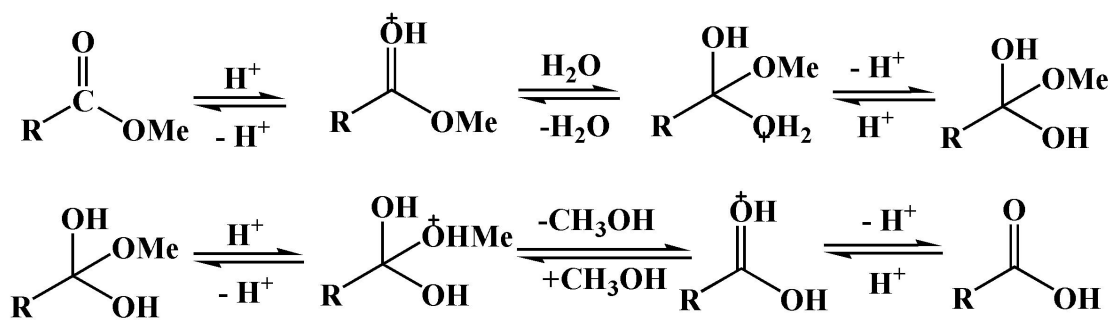


Fig. S14 Schematic diagram of redox for gel polymer electrolyte

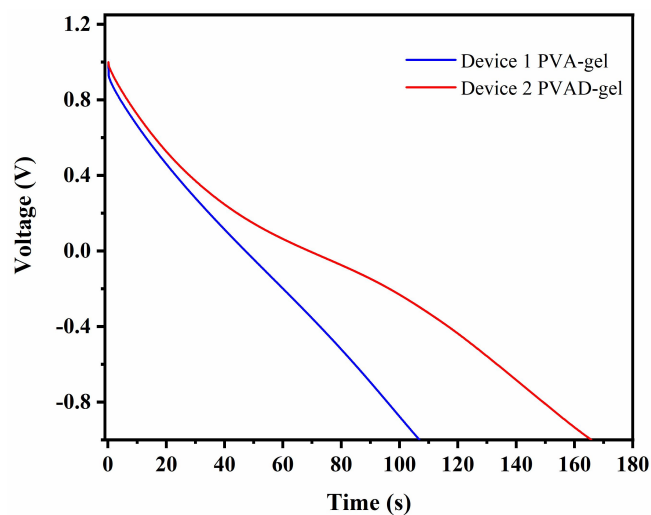


Fig. S15 Discharge of PVA-gel supercapacitors (Device 1) and PVAD-gel supercapacitors (Device 2) at current density of 0.5 A g^{-1} .

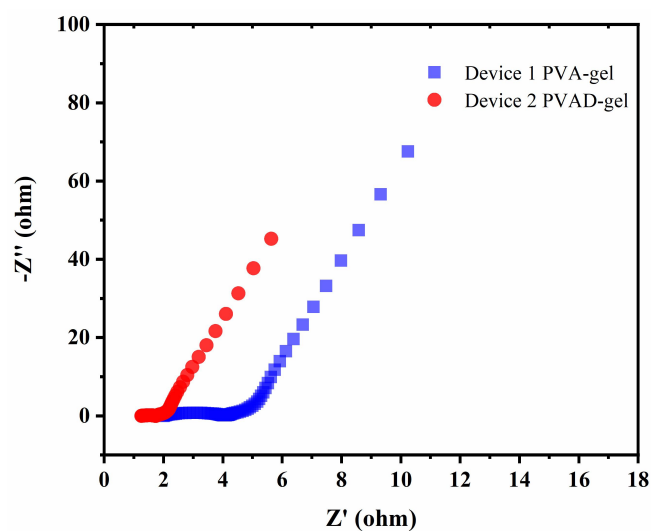


Fig. S16 Nyquist plot of PVA-gel supercapacitor (Device 1) and PVAD-gel supercapacitor (Device 2) at frequencies from 10^5 Hz to 10^{-2} Hz.

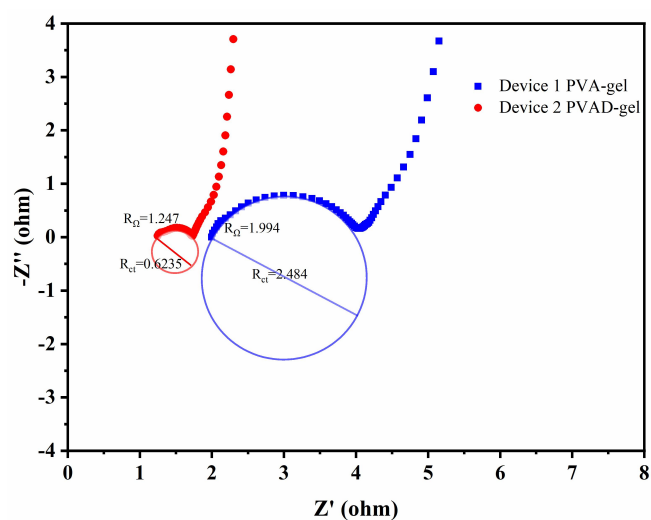


Fig. S17 The Nyquist plots of PVA-gel (Device 1) and PVAD-gel (Device 2) supercapacitors showed a equivalent series resistance of and charge transfer resistance