

A hyperbranched conjugated Schiff base polymer network: a potential negative electrode for flexible thin film batteries

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1. Materials

Phosphorus oxychloride (AR) was purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. and used as received. N,N-Dimethylformamide (AR), dichloromethane (AR), petroleum ether (60~90 °C), dimethyl sulfoxide (AR), acetone (AR) were purchased from Shanghai Danfan Network Science & Technology Co., Ltd. and used as received. Triphenylamine (AR) and *p*-phenylenediamine (AR) were purchased from Aladdin Co., Ltd. and used as received. *d*₆-DMSO was purchased from Sigma Aldrich Co., Ltd. Silica gel (100~200 mesh) was heated in an oven at 120 °C for 24 hours before use.

2 Synthesis

2.1 Synthesis of 4,4',4''-nitrilotribenzaldehyde

The synthesis of 4,4',4''-nitrotribenzaldehyde was done following the procedure described in Ref ¹ with modification. 10.0 g of triphenylamine was added to 41.0 mL of DMF under argon protection at 0 °C. 37.5 mL of phosphorus oxychloride was added dropwise. After stirring for 1 h, the mixture was heated to 105 °C for another 4 hours. Upon cooling to room temperature, ice water was poured into the mixture slowly while stirring. The mixture was left to stand for 3 hours to precipitate completely. The precipitate was collected via filtration. Subsequently, the material was washed with 50 mL of a saturated sodium hydrocarbonate solution three times followed by washing with a saturated sodium chloride solution once. The crude product was purified by column chromatography (DCM/petroleum ether=1/2, v/v) to yield dialdehyde substituted triphenylamine (8.636 g, 70.3%) as a yellow solid. ¹H NMR (400 MHz, d₆-DMSO) δ 9.87 (s, 2H), 7.84 (d, *J* = 8.6 Hz, 4H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 4H). 8.636 g of dialdehyde substituted triphenylamine was added to 35.3 mL of DMF under argon protection at 0 °C. 32.3 mL of phosphorus oxychloride was added dropwise. After stirring for 1 hour, the mixture was heated to 105 °C for 1 hour. Upon cooling to room temperature, ice water was added slowly while stirring. The mixture was left to stand for 3 hours to precipitate completely. The precipitate was collected via filtration. The product was then washed with 50 mL of a saturated sodium hydrocarbonate solution three times followed by washing with a saturated sodium chloride solution once. The crude product was purified by column chromatography (DME/petroleum ether=1/1, v/v) to yield 4,4',4''-nitrotribenzaldehyde (3.210 g, 34.0%) as a bright yellow solid. ¹H NMR (400 MHz, d₆-DMSO) δ 9.93 (s, 3H), 7.91 (d, *J* = 8.2 Hz, 6H), 7.28 (d, *J* = 8.2 Hz, 6H) (Fig. S1).

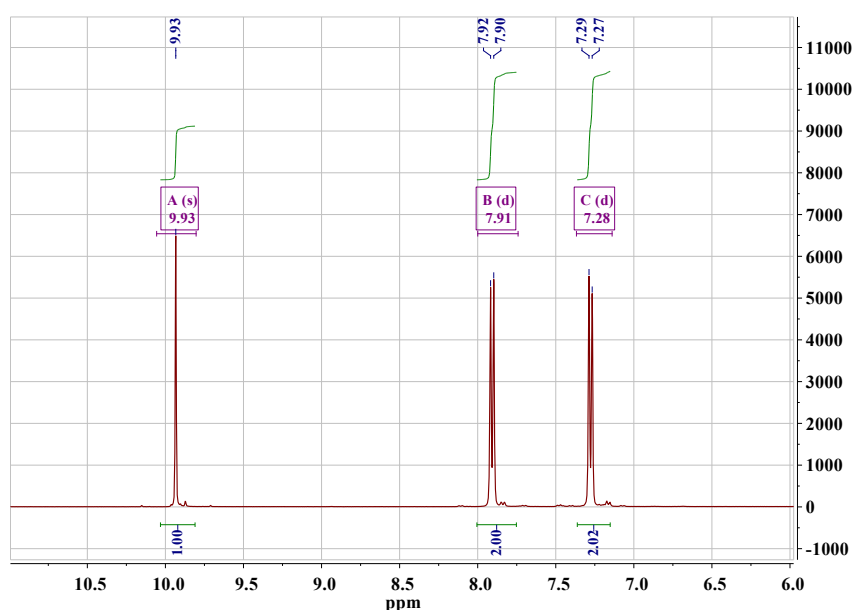


Figure S1. ¹H NMR spectrum of 4,4',4''-nitrotribenzaldehyde

2.2 Synthesis of poly (4,4',4''-nitrotribenzaldehyde-co-*p*-phenylenediamine)

0.454 g of *p*-phenylenediamine and 0.896 g of 4,4',4''-nitrotribenzaldehyde were measured in a flask separately. 10.0 mL of a DMSO solvent was added under argon protection to obtain a clear solution. The reactants were heated to 180 °C for several hours for polycondensation. The

precipitate was collected by filtration followed by washing with acetone, tetrahydrofuran, dichloromethane, separately. The final product is an orange red solid (0.675 g, 56.1%) (Fig. S2).



Figure S2. Image of the hyperbranched conjugated Schiff base polymer

3. Characterization

3.1 Characterization of the morphology, organo functional group and thermal stability

^1H NMR spectra were taken on a 400 MHz NMR instrument (AVANCE III HD 400 MHz, Swiss BRUKER) in deuterated dimethyl sulfoxide. FTIR spectra were recorded with a spectrophotometer (VERTEX 70 FTIR, Germany BRUKER). Thermogravimetric analysis was conducted with an instrument (NETZSCH STA 409 PG/PC) from 80 °C to 800 °C at the heating rate of 10 °C \cdot min $^{-1}$ under nitrogen gas atmosphere. Morphology was probed by scanning electron microscopy (FE-SEM, SU8010, HITACHI). Prior to the test, the sample was coated with gold by magnetron sputtering under vacuum.

3.2 Mechanical test of the Schiff base electrode film

A mixture of 50 wt% of the Schiff base polymer, 40 wt% of acetylene carbon and 10 wt% of PTFE was grinded in a mortar to obtain a uniform powder mixture. The product was made into a slice by a roller and cut into a rectangular shaped film with 10 mm wide, 50 mm long and 130 μm thick followed by vacuum dry. The mechanical property was measured with an electronic tensile tester (XLW(PC), Labthink, China) under a constant displacement rate of 25 mm \cdot min $^{-1}$ (the lower limit of the apparatus).

3.3 Electrochemical measurement

3.3.1 Cyclic voltammetry & half-cell test

The hyperbranched conjugated Schiff base polymer was first measured in a half cell. A mixture of 50 wt% of the Schiff base polymer, 40 wt% of acetylene carbon and 10 wt% of PTFE was grinded in a mortar to obtain a uniform powder mixture. The product was made into a slice by a roller and cut into small rounds with a diameter of 10 mm. The active material loading is around 2 mg \cdot cm $^{-2}$. Before battery assembly these electrode discs were dried at 120 °C under vacuum for 24 hours. Battery assembly was conducted in a glove box with a lithium foil as the negative electrode. The

lithium foil and the polymer electrode were separated by a Celgard 2400 film. A solution of 1 M of LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) ($v/v=1/1$) was used as the electrolyte. Cyclic voltammetry for the half cells was performed by an Arbin battery workstation at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ at $25 \text{ }^\circ\text{C}$, recording fifteen cycles. The CV curves of first five cycles are presented in Fig. 2(a) in the main text, and another ten cycle curves are presented in Fig. S3 in ESI. Charge and discharge measurements were conducted using a LAND battery tester at $25 \text{ }^\circ\text{C}$.

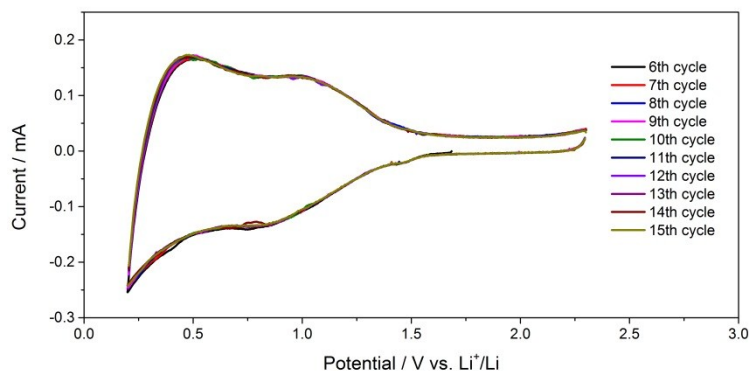


Figure S3. CV curves of the subsequent ten cycles at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$

3.3.2 Bending test of a pouch cell

The Schiff base was made into a slice with 80 mm long, 10 mm wide and $\sim 100 \text{ }\mu\text{m}$ thick by the above procedures. After vacuum dry, it was transferred into the glove box protected by argon ($<1 \text{ ppm H}_2\text{O}$ and O_2). Both the Schiff base electrode film and lithium foil were fixed on copper foils separately by press rolling in the glove box. And then, the composite Schiff base electrode was inserted into a pocket made of Celgard film to avoid direct contact with lithium. At last, these electrodes were sealed in a piece of polymer coated aluminum foil via the same way as the conventional pouch cell. The as-prepared pouch cell is 100 mm long and 30 mm wide (Fig. S4).



Figure S4. Image of a pouch cell

After standing for 24 hours, the pouch cell was firstly scanned to 0.2 V (vs. Li^+/Li) and then reverse-scanned to a cut-off voltage of 0.5 V (vs. Li^+/Li) at $25 \text{ }^\circ\text{C}$. EIS measurement was performed on VMP3 electrochemistry workstation from 0.1 MHz to 0.1 Hz at potential amplitude of 10 mV at the open circuit potential under different bending radii (9 mm and 14 mm) and bending degrees (90° and 180°) with the Schiff base electrode facing outwards. The measuring order was as follows: unbent state $\rightarrow 90^\circ$ bending under radius of 14 mm $\rightarrow 180^\circ$ bending under radius of 14 mm $\rightarrow 90^\circ$ bending under radius of 9 mm $\rightarrow 180^\circ$ bending under radius of 9 mm (Fig. S5).

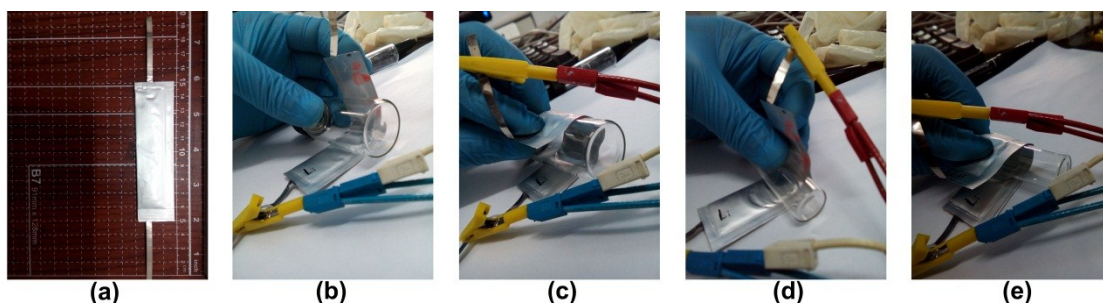


Figure S5. Image of bending test under different bending radii and bending degree with the polymer electrode facing outwards. (a) unbent state, (b) 90° bending under radius of 14 mm, (c) 180° bending under radius of 14 mm, (d) 90° bending under radius of 9 mm, (e) 180° bending under radius of 9 mm.

References:

1. Y. X. Wang, M. K. Leung, 4,4',4''-tris(acetoxymethylene)triphenylamine: an efficient photoacid promoted chemical cross-linker for polyvinylcarbazole and its applications for photolithographic hole-transport materials, *Macromolecules*, 2011, **44**, 8771-8779