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Ferrocene-based hyperbranched polymers: synthetic strategy for shape control and applications as electroactive materials and precursors-derived magnetic ceramics

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1. General

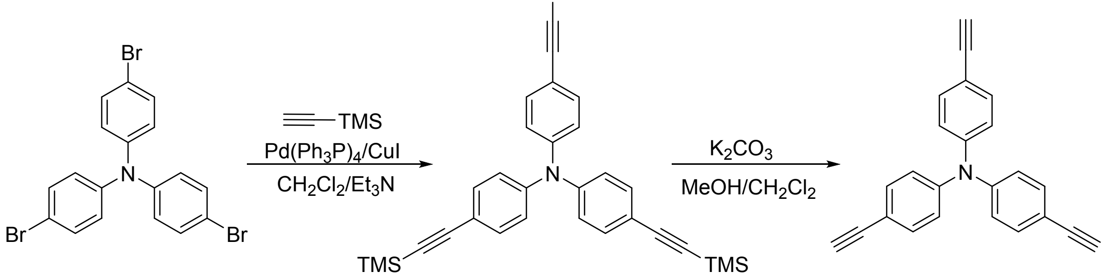
Commercially available reagents were purchased from Energy Chemical Company or local supplier, which were reagent/spectroscopic grade and used as obtained without further purification. All reactions were carried out under nitrogen unless otherwise stated. NMR spectra were measured in $CDCl_3$ on a Bruker AV 400 or VNMRS 400 NMR instrument with chemical shifts referenced against tetramethylsilane as the internal standard for ^1H, and ^{13}C NMR data. Fourier transform infrared spectroscopy

(FT-IR) were carried out on a IR Affinity-1 spectrometer (Shimadzu, Japan) with KBr pellets. Thermogravimetric analyses (TGA) were recorded on a TGA\DSC 3$^+$ (Mettler Toledo, Switzerland) thermogravimetric analyzer running from room temperature to 800 °C at a heating rate of 10 °C/min in nitrogen.

Scanning electron microcopy (SEM) images were performed using a FE-SEM (JSM-7800F & TEAM Octane Plus). Transmission electron microscopy (TEM) analysis was carried out using a JEM-2100 & X-Max80 (JEOL, Japan) unit operated at 200 kV. Energy dispersive X-ray detectors equipped with TEM were applied to study the elemental mapping. The magnetic hysteresis loops at room temperature were measured by a quantum design physical property measurement system (PPMS).

2. Synthesis of ZIF-67, monomers TEPA and FIF

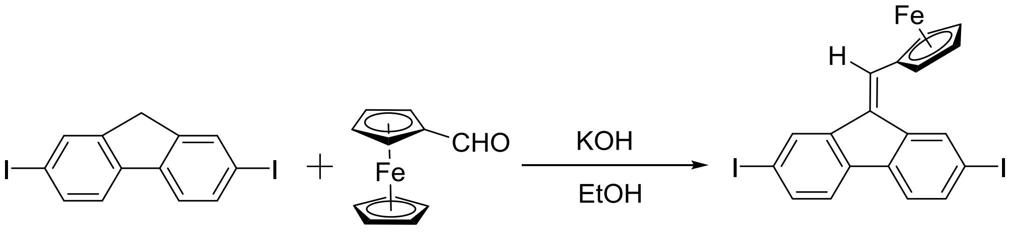
Preparation of ZIF-67: $Co(NO_3)_2 .6H_2O$ (12.5 mmol, 3.64 g) and 2-methylimidazole (224 mmol, 18.41 g) were dissolved in 20 ml of methanol to form the solutions A and B, respectively. Then the solutions A and B were mingled and stirred for 15 min to form a purple solution C. The solution C was aged in room temperature overnight to obtain purple precipitation, and the precipitation was washed and collected by centrifugal separation to give ZIF-67.



Scheme 1. Synthetic routes of tris(4-ethynylphenyl)amine.

Synthesis of tris(4-((trimethylsilyl)ethynyl)phenyl)amine: Tris(4-bromophenyl)amine (3 mmol, 1.45 g) was dissolved in freshly distilled triphenylamine (30 mL) and dichloromethane (20 mL) solution, and then Pd(PPh_3)$_4$ (200 mg) and CuI (50 mg) was added. After the solution was stirred for 30 min at room temperature, trimethylsilylacetylene (3 mL) was added and the suspension was stirred for 30 min at room temperature before being heated. The mixture was heated to 75 °C for 24 h and then allowed to cool to room temperature. The crude product was purified using column chromatography on silica gel using n-hexane/dichloromethane as the eluent to provide tris(4-((trimethylsilyl)ethynyl)phenyl)amine as a light brown solid (1.31 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (d, $J = 8.4$ Hz, 6H), 6.95 (d, $J = 8.8$ Hz, 6H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 146.9, 133.3, 124.0, 117.9, 105.0, 94.1.

Synthesis of tris(4-ethynylphenyl)amine (TEPA): Tris(4-((trimethylsilyl)ethynyl)phenyl)amine (2.81 mmol, 1.5 g) and excess K_2CO_3 (7.24 mmol, 1 g) were dissolved in MeOH/CH_2Cl_2 (30 mL, v/v = 1/1), and the mixture was stirred overnight at room temperature. The solvents were removed and the crude product was purified using column chromatography to provide **TEPA** in a quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (d, $J = 7.6$ Hz, 6H), 7.01 (d, $J = 7.6$ Hz, 6H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.0, 133.3, 123.9, 116.8, 83.4.



Scheme 1. Synthetic routes of 9-ferrocenylidene-2,7-Diiodo-9H-fluorene.

Synthesis of 9-ferrocenylidene-2,7-diiodo-9*H*-fluorene (FIF): 2,7-diiodo-9*H*-fluorene (1 mmol, 0.418 g) and ferrocenylcarboxyaldehyde (1.1 mmol, 0.235 g) were dissolved in 80 mL of ethanol, and then KOH (2 mmol, 0.112 g) was added to the solution. After the mixture was refluxed overnight, the product was purified by column chromatography and obtained as a red solid (1.31 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.60 (s, 1H), 8.08 (s, 1H), 7.66 (t, J = 1.2 Hz, 1H), 7.66 (dd, J_1 = 14.8 Hz, J_2 = 1.6 Hz, 1H), 7.46 (t, J = 6.4 Hz, 3H), 4.71 (s, 2H), 4.56 (s, 2H), 4.25 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.4, 138.9, 138.4, 136.6, 136.3, 136.0, 133.0, 130.9, 129.6, 128.8, 121.3, 121.2, 92.4, 92.1, 80.4, 71.1, 70.8, 69.9.

3. Charaterizations

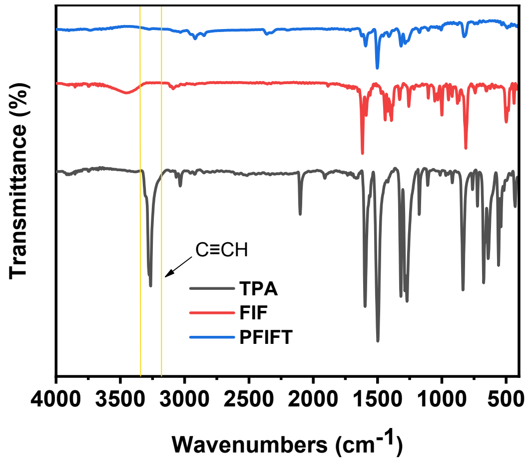


Fig. S1 FT-IR spectra of monomers **TPEA**, **FIF** and the as-synthesized polymer **SP**.

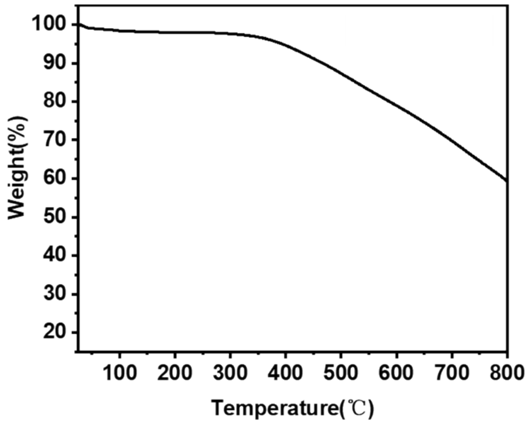


Fig. S2 Thermogram of polymer **SP** at the heating rate of 20 °C/min under N_2.

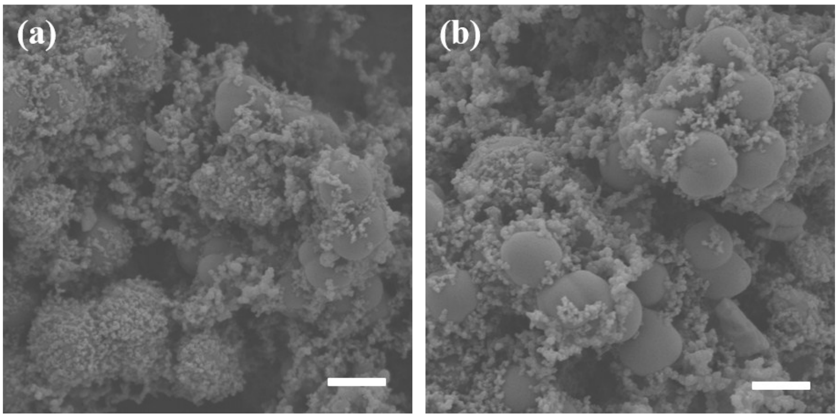


Fig. S3 SEM images of the electroactive anode on the Cu foil (a)at the initial state and (b) after 200 charge-discharge cycles.

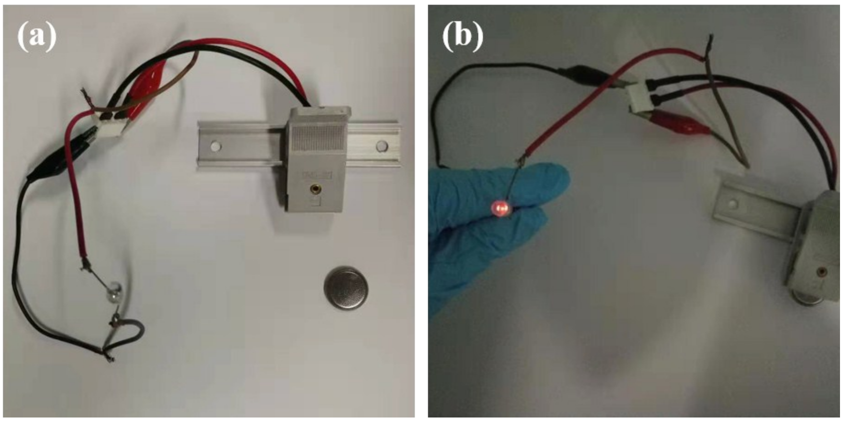


Fig. S4 Photos for the process of lighting up the bulb.

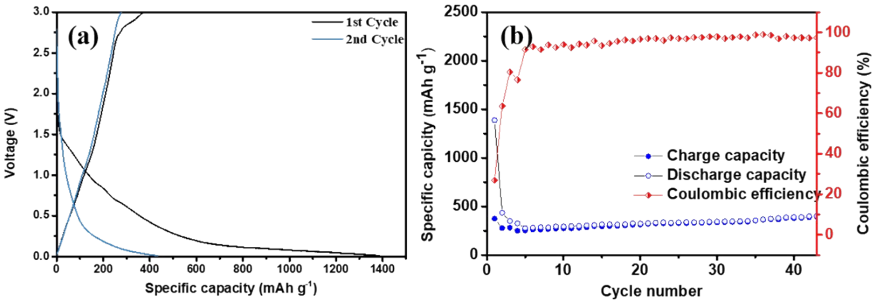


Fig. S5 The electrochemical performances of the H**P** anodes: (a) Charge-discharge curves for the initial three cycles at current density of 20 mA g^{-1}, (b) cycling stability and coulombic efficiency at 100 mA g^{-1}.