

## Supporting Information

### **Cobaltocenium-containing poly(carbazole)s towards alkaline-stable anion exchange membrane via post-polymerization modification**

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## 1. Chemicals and Materials

Carbazole, 1,6-dibromohexane, trifluoromethanesulfonic acid, and methanesulfonic acid were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. 1,1,1-Trifluoroacetone was purchased from Aladdin Reagents (Shanghai) Co., Ltd. Ethynylcobaltocenium hexafluorophosphate was synthesized according to our previous report<sup>[1]</sup>.

## 2. Synthesis

### 2.1 Synthesis of 9-(6-bromohexyl)carbazole

Carbazole (5 g, 30 mmol, 1 eq), 1,6-dibromohexane (36 g, 150 mmol, 5 eq) and tetrabutylammonium bromide (1 g, 3 mmol, 0.1 eq) were dissolved in 40 mL toluene. Potassium hydroxide aqueous solution (25 mL, 50 wt%, 11 eq) was then added dropwise. The mixed solution was heated to reflux at 120 °C for 25 h. Subsequently, the reaction was cooled to room temperature, and solvent was removed by vacuum distillation. Deionized water was poured into the resulting solid. The organic phase was extracted with dichloromethane and dried over anhydrous sodium sulfate. The dichloromethane was removed by rotary evaporation. The crude product was purified by column chromatography using petroleum ether as eluent. Finally, 7.4 g product (75% yield) was obtained as white needle-like crystal by recrystallization from absolute ethanol. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ, ppm): 8.14 (d, *J* = 7.7 Hz, 2H), 7.50 (ddd, *J* = 8.2, Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.30–7.23 (m, 2H), 4.34 (t, *J* = 7.1 Hz, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 1.98–1.80 (m, 4H), 1.56–1.38 (m, 4H). FT-IR (KBr, cm<sup>-1</sup>): 639 (ν<sub>C-Br</sub>).

### 2.2 Synthesis of poly(9-(6-bromohexyl)carbazole-co-1,1,1-trifluoroisopropane) (PC-Br)

9-(6-Bromohexyl)carbazole (0.5 g, 1.51 mmol, 1 eq) and 1,1,1-trifluoroacetone (0.19

mL, 2.16 mmol, 1.43 eq) were dissolved in 0.8 mL of anhydrous dichloromethane at 0 °C. Methanesulfonic acid (1.26 mL, 19.45 mmol, 12.85 eq) and trifluoromethanesulfonic acid (0.42 mL, 5.27 mmol, 3.48 eq) were added slowly subsequently, and stirred at 0 °C for 30 min. Then the reaction was slowly warmed to room temperature and stirred for 4 h. The light green viscous liquid obtained from the reaction was precipitated in methanol and washed with hot methanol. The resulting precipitate was dried overnight at 80 °C to afford 0.63 g of white solid (83% yield). <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>, δ, ppm): 8.43 (s, 2H), 7.55 (s, 2H), 7.33 (s, 2H), 4.35 (s, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 2.17 (s, 3H), 1.78–1.70 (m, 4H), 1.36 (s, 4H). <sup>19</sup>F NMR (376 MHz, DMF-*d*<sub>7</sub>, δ, ppm): –68.58. FT-IR (KBr, cm<sup>-1</sup>): 1136 (ν<sub>C-F</sub>), 635 (ν<sub>C-Br</sub>). Mw = 85,500.

### **2.3 Synthesis of poly(9-(6-azidohexyl)carbazole-co-1,1,1-trifluoroisopropane) (PC-N<sub>3</sub>)**

PC-Br (1.87 g, 4.41 mmol, 1 eq) and sodium azide (1.43 g, 22.04 mmol, 5 eq) were dispersed in 40 mL *N,N*-dimethylformamide in a round bottom flask, and stirred at 80 °C for 80 h. The solvent was then removed by vacuum distillation. After diluting with water, the organic phase was extracted with dichloromethane and removed by rotary evaporation. 1.63 g of the product was obtained as a beige sticky solid (96% yield). <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>, δ, ppm): 8.42 (s, 2H), 7.56 (s, 2H), 7.33 (s, 2H), 4.35 (s, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.16 (s, 3H), 1.78–1.33 (m, 8H). <sup>19</sup>F NMR (376 MHz, DMF-*d*<sub>7</sub>, δ, ppm): –68.63. FT-IR (KBr, cm<sup>-1</sup>): 2096 (ν<sub>N<sub>3</sub></sub>), 1138 (ν<sub>C-F</sub>).

### **2.4 Synthesis of cobaltocenium-containing polycarbazole (PC-CoCp)**

PC-N<sub>3</sub> (1.7 g, 1.4 mmol, 1 eq), ethylnylcobaltocenium hexafluorophosphate (2.05 g, 5.72 mmol, 1.3 eq) and 2,2'-bipyridine (3.44 g, 22 mmol, 5 eq) were dissolved in 100 mL *N,N*-dimethylformamide, and degassed with N<sub>2</sub> for 30 min. Then cuprous bromide

was added rapidly, the reaction was stirred at 50 °C for 48 h. The reaction solution was centrifuged to remove insoluble blue-green viscous impurities. Then the resulting solution was precipitated in an ethylene diamine tetraacetic acid disodium salt solution (0.3 g in 400 mL ethanol and 400 mL water) to afford a green flocculent precipitate. The precipitate was collected by centrifugation and freeze-dried to give 1.97 g dark green powder (60% yield). <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>, δ, ppm): 8.81 (s, 1H), 8.50 (s, 2H), 7.62 (s, 2H), 7.31 (s, 2H), 6.44 (s, 2H), 6.01 (s, 2H), 5.74 (s, 5H), 4.47 (br, 4H), 2.19 (s, 3H), 1.90–1.82 (m, 4H), 1.38 (br, 4H). <sup>19</sup>F NMR (376 MHz, DMF-*d*<sub>7</sub>, δ, ppm): –67.64, –69.13, –71.02. FT-IR (KBr, cm<sup>-1</sup>): 1140 (ν<sub>C-F</sub>), 3119 (ν<sub>C-H</sub>), 1449 (ν<sub>N=N</sub>), 1054 (ν<sub>C-N</sub>), 478 (ν<sub>C-O</sub>), 833(ν<sub>P-F</sub>).

## 2.5 Synthesis of quaternary ammonium-containing polycarbazole (PC-QA)

PC-Br (2.5 g, 5.89 mmol, 1 eq) was dissolved in 40 mL *N,N*-dimethylformamide, and an aqueous solution of trimethylamine (3.88 mL, 30 wt %, 3 eq) was added slowly. The reaction was stirred at room temperature for 48 h. The solvent and unreacted trimethylamine were then distilled off under reduced pressure. After precipitating in ether for 3 times, the white powder was dried at 80 °C overnight to afford 2.82 g product (99% yield). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 8.43 (s, 2H), 7.58 (s, 2H), 7.21 (s, 2H), 4.39–4.35 (m, 2H), 3.27 (s, 2H), 3.05–2.99 (m, 9H), 2.27–2.15 (m, 3H), 1.90–1.54 (m, 4H), 1.47–1.21 (m, 4H). <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): –67.61. FT-IR (KBr, cm<sup>-1</sup>): 1141 (ν<sub>C-F</sub>).

## 2.6 Preparation of AEM

The AEM was prepared by solution casting method. Generally, the polymer was dissolved in DMSO to give a 5 wt% solution. Then, the well-mixed solution was cast onto a glass Petri dish and dried at 80 °C for 24 h to give the targeted AEM with an average thickness of 50 μm. To improve the mechanical properties of the

PC-CoCp-based AEM, semi-interpenetrating polymer network was introduced by adding 16 wt% polyvinyl alcohol.

### **3. Characterization**

Gel permeation chromatography using a Waters Breeze model from Waters, USA, equipped with a Waters 2414 refractive index detector. The synthetic polymers' molecular weight and polydispersity index ( $\bar{M}_w/\bar{M}_n$ ) were measured. The mobile phase was a 0.05 M lithium bromide THF solution. The system was operated at 25 °C and the flow rate was 1 mL min<sup>-1</sup>. Polystyrene was used as the standard.

The thermogravimetric analysis was carried out under nitrogen atmosphere on a NETZSCH TG 209F3 thermogravimetric analyzer. A German ZEISS Gemini SEM 300 field emission scanning electron microscope was used to observe the morphology of AEM. Before the test, the polymer membrane was placed on tin foil, followed by freezing with liquid nitrogen and breaking with tweezers. Atomic force microscopy was carried out using a Dimension Icon-type instrument from Bruker, Germany. The polymer was dissolved in DMF to configure a 0.5 wt% solution and the dissolution was then dropped onto mica flakes, oven-dried overnight at 80 °C and the samples were tested in the air in the smart phase diagram mode. SAXS analysis (PLS-II 3C beamline) was carried out at 20% relative humidity (R. H.) using Odili Anton Paar SAXS point 2.0 to characterize the microstructure of the membrane.

The mechanical properties of the membranes were tested on a Shimadzu AGS-X (Japan) type universal testing machine. Wet 10 mm × 30 mm membrane samples were taken and the thickness of the membrane was recorded using micron calipers. The surface was wiped with paper towel before the experiment and the stretching rate was 5 mm min<sup>-1</sup>.

### **Ion exchange capacity (IEC)**

The theoretical ion exchange capacity (IEC<sup>a</sup>) of the membrane was obtained by dividing the molarity of the cobalt dichloride cation by the weight of the membrane, and then the titrimetric ion exchange capacity (IEC<sup>b</sup>) of the membrane was determined by back titration. The AEM samples were dried overnight in a vacuum oven as hydroxide-form and then immersed in a solution of 0.01 M hydrochloric acid for 48 h. Then, the membrane was removed and the residual hydrochloric acid was determined by titration with 0.01 M NaOH using phenolphthalein as an indicator. IEC was calculated from the following equation (1).

$$IEC = \frac{0.01 \times (V_{HCL} - V_{NaOH})}{m^{dry}} \quad (1)$$

$V_{HCL}$ ,  $V_{NaOH}$  represents the volume of hydrochloric acid solution and the volume of sodium hydroxide solution consumed by the titration, and  $m^{dry}$  denotes the weight of dry AEM in the form of OH<sup>-</sup>.

### **Water uptake and swelling ratio**

The membranes with size of 3 cm × 3 cm are prepared via exchanging the counteracting ions to OH<sup>-</sup> by immersion in a 1 M KOH solution at room temperature for 24 hours. The membranes were dried in a vacuum oven to obtain the weight ( $W_w$ ), thickness ( $t_d$ ), and length ( $l_d$ ) of the dried membranes in OH<sup>-</sup> form. Subsequently, the dried membranes were immersed in deionized water at 25 °C for 24 hours to fully hydrate. Subsequently, excess water was wiped off the membrane surface with a paper towel and the weight ( $W_w$ ), thickness ( $t_w$ ), and length ( $l_w$ ) of the fully hydrated membranes were then measured. Water absorption (WU) and dimensional changes are calculated using the following equations (2-1)-(2-4):

$$WU(\%) = \frac{(W_w - W_d)}{W_d} \times 100\% \quad (2-1)$$

$$\Delta t = (t_w - t_d)/t_d \quad (2-2)$$

$$\Delta l = (l_w - l_d)/l_d \quad (2-3)$$

$$\Delta v = (v_w - v_d)/v_d \quad (2-4)$$

### **Ionic conductivity**

OH<sup>-</sup>-form polymeric membranes (50 μm) were mounted in a membrane test system to study the in-plane conductivity of hydroxides. The samples were exposed to a continuous gas stream containing nitrogen at a constant 100% relative humidity from 25-80 °C. The ionic resistance of the membrane was measured every 30 minutes using a standard 4-probe technique until stable. Open circuit EIS was performed using an impedance analyzer over a frequency range of 0.1-20 kHz. The conductivity of the sample was calculated using equation (3):

$$\text{Ionic conductivity}(mS\ cm^{-1}) = l/R \times S \quad (3)$$

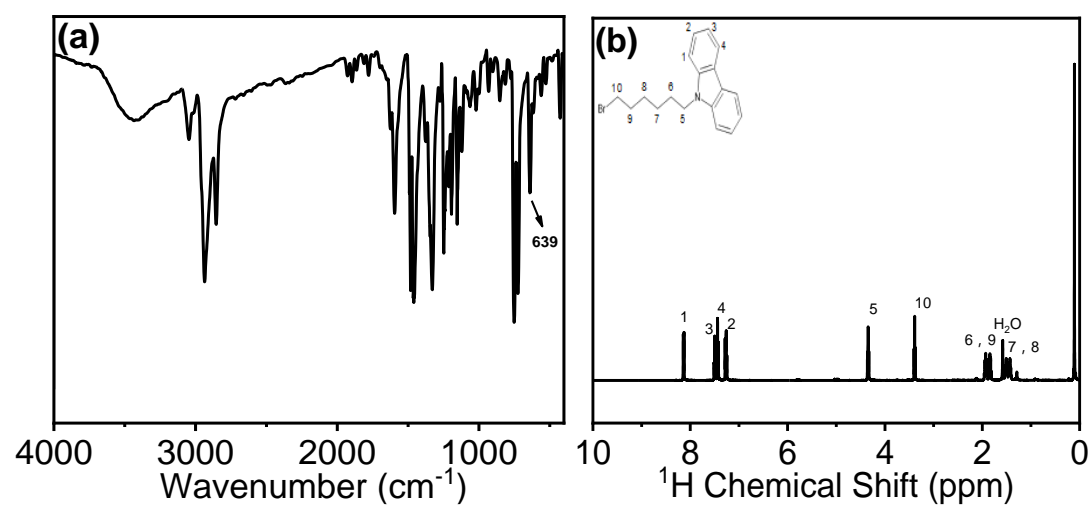
$l$  denotes the distance between the electrodes,  $R$  denotes the impedance of the membrane and  $S$  denotes the cross-sectional surface area of the membrane.

### **Membrane electrode assembly fabrication and fuel cell testing**

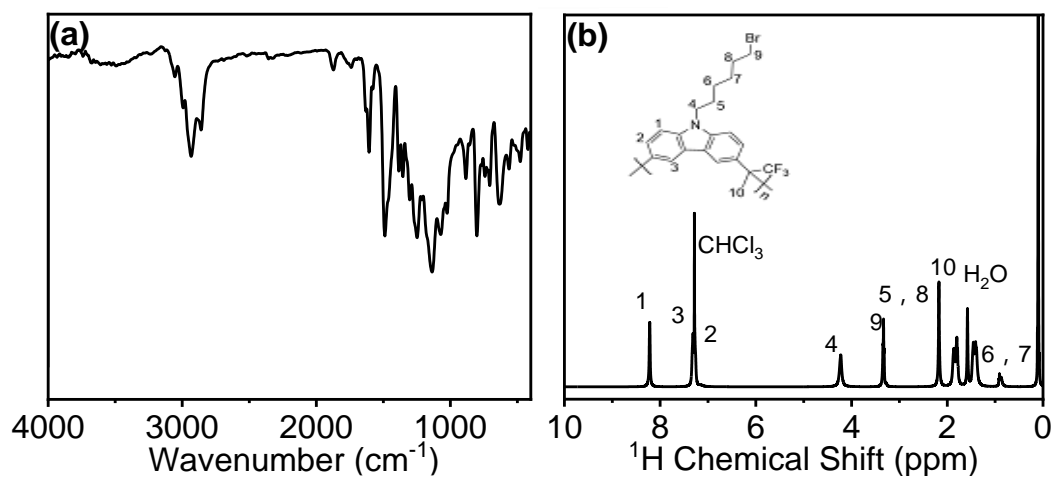
The membrane electrode assembly (MEA) was fabricated by the gas diffusion electrode (GDE) strategy. 60 wt% Pt/C catalyst (60 wt%, Johnson Matthey Co.) and ionomer (Fumion, FuMA Tech, Germany) were dispersed by magnetic stirring and ultrasonication to prepare the catalyst ink. The resulted catalyst ink was sprayed on SGL 25 BC (SGL group, Germany) carbon paper until the loading of Pt and ionomer were 0.50 mg/cm<sup>2</sup> and 25 wt%, respectively. The MEA was obtained by sandwiching the AEM between the Pt loaded carbon paper and the active area of AEM was 5 cm<sup>2</sup>. The single cell performance was observed on a commercial fuel cell system (Scribner

Associates, Inc., 850e). The fuel cell performance was measured at 60 °C with a flow rate of 200 mL/min for fully humidified H<sub>2</sub> and O<sub>2</sub> without backpressure. After the full activation of MEA under potentiostatic mode, the polarization curve was measured by holding the fuel cell at serial constant currents for 30 s. Parallel tests were repeated to minimize errors.

## Figures

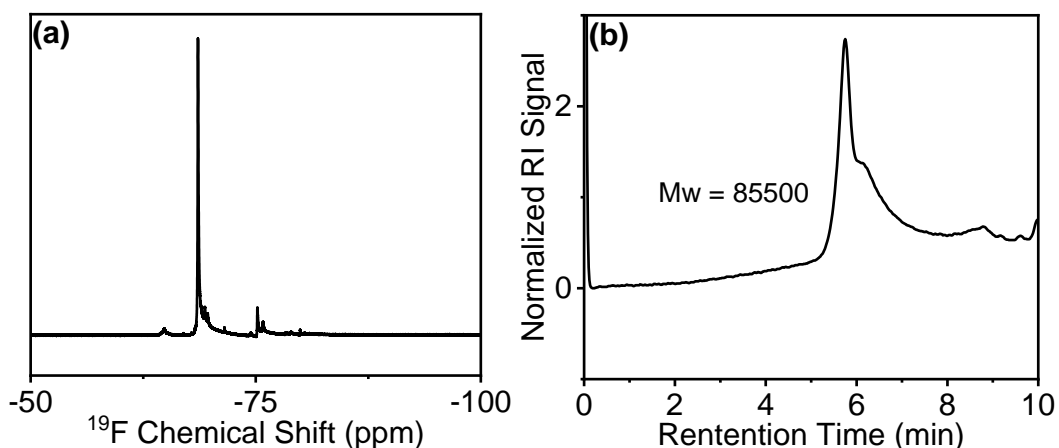


**Figure S1.** (a) FT-IR and (b) <sup>1</sup>H NMR spectrum of 9-(6-bromohexyl)carbazole in CDCl<sub>3</sub>.

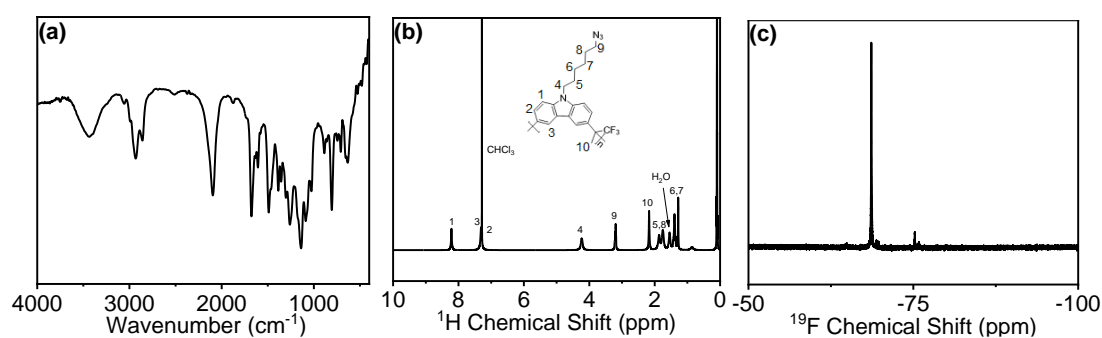


**Figure S2.** (a) FT-IR and (b) <sup>1</sup>H NMR spectrum of PC-Br in CDCl<sub>3</sub>.

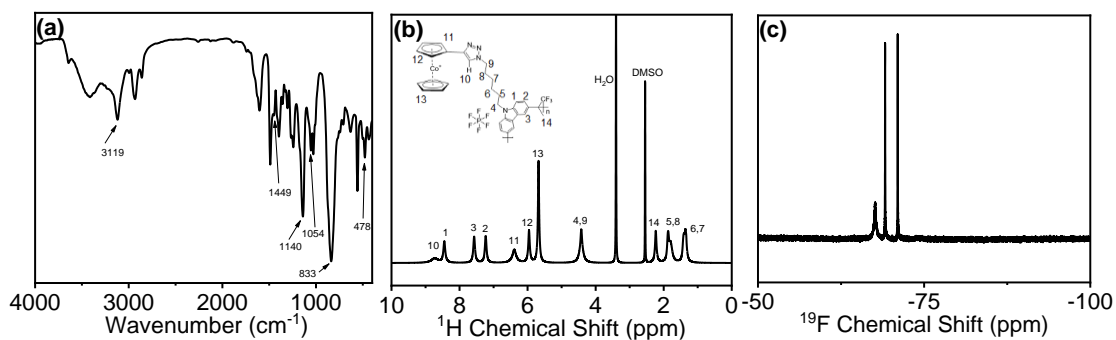




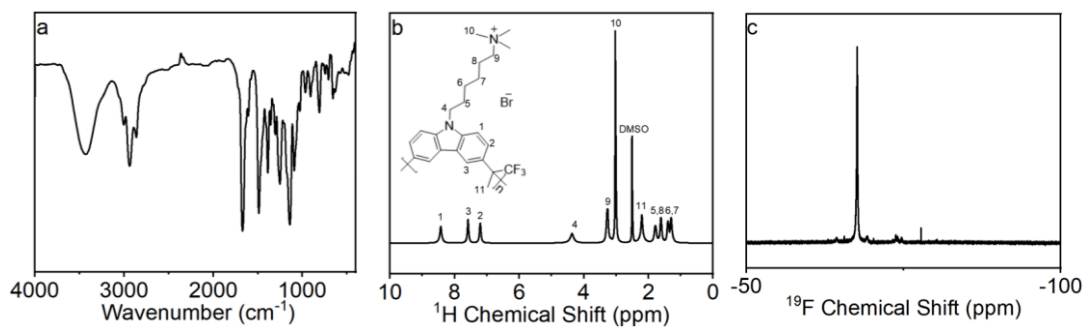
**Figure S3.** (a)  $^{19}\text{F}$  NMR spectrum in  $\text{CDCl}_3$  and (b) GPC trace of PC-Br.



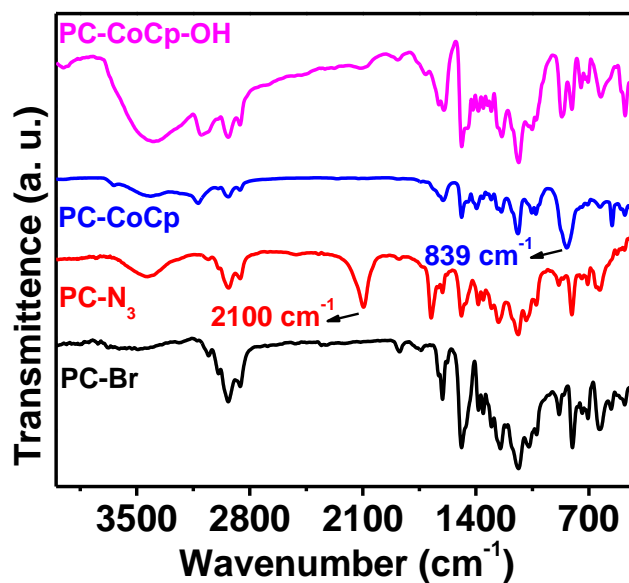
**Figure S4.** (a) FT-IR spectrum, (b)  $^1\text{H}$  NMR spectrum, and (c)  $^{19}\text{F}$  NMR spectrum of PC- $\text{N}_3$  in  $\text{CDCl}_3$ .



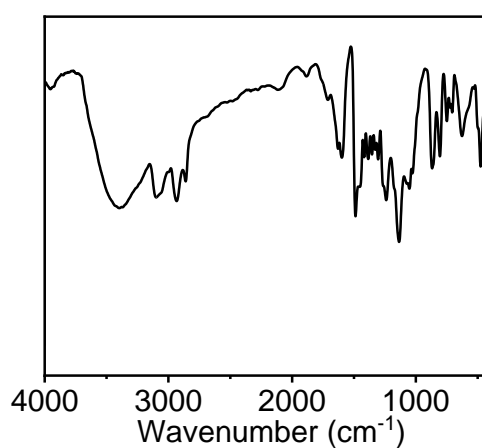
**Figure S5.** (a) FT-IR spectrum, (b)  $^1\text{H}$  NMR spectrum, and  $^{19}\text{F}$  NMR spectrum of PC-CoCp in  $\text{DMSO-}d_6$ .



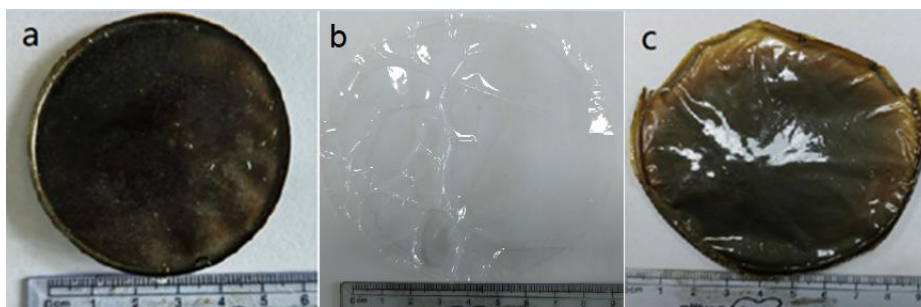
**Figure S6.** (a) FT-IR spectrum, (b)  $^1\text{H}$  NMR spectrum, and  $^{19}\text{F}$  NMR spectrum of PC-QA in  $\text{DMSO-}d_6$ .



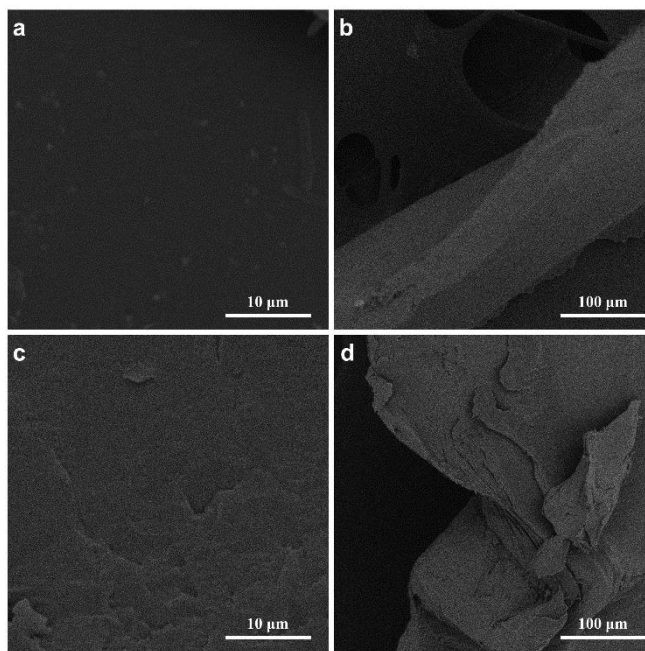
**Figure S7.** FT-IR spectra of PC-Br, PC- $\text{N}_3$ , PC-CoCp and PC-CoCp-OH.



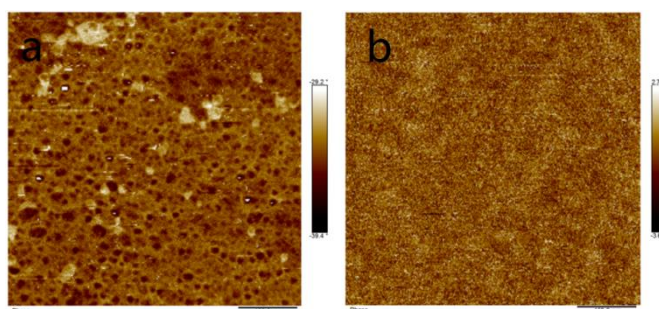
**Figure S8.** FT-IR spectrum of PC-CoCp membrane after ion exchange with  $\text{OH}^-$ .



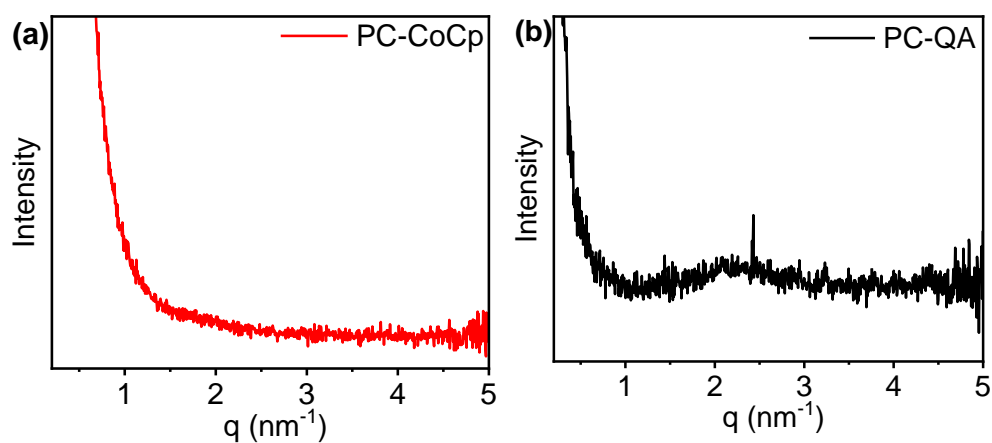
**Figure S9.** Images of (a) PC-CoCp, (b) PC-QA, and (c) PVA-PC-CoCp.



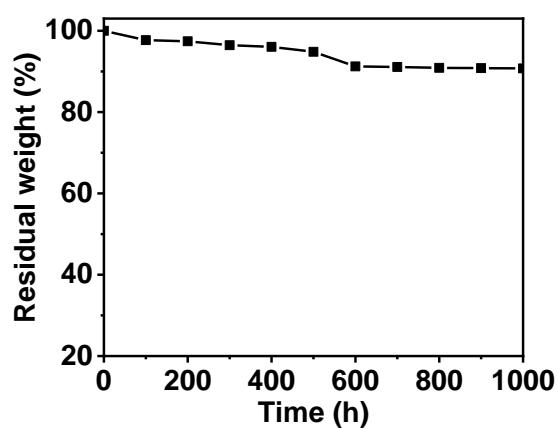
**Figure S10.** (a) SEM image of the surface of PC-CoCp membrane; (b) cross-sectional SEM image of PC-CoCp membrane; (c) SEM image of the surface of PC-QA membrane; (d) cross-sectional SEM image of PC-QA membrane.



**Figure S11.** (a) AFM phase image of PC-CoCp membrane; (b) AFM phase image of PC-QA membrane.



**Figure S12.** SAXS diagram of (a) PC-CoCp membrane and (b) PC-QA membrane.



**Figure S13.** Residual weight of PC-CoCp membrane after immersion in Fenton's reagent (containing 3% H<sub>2</sub>O<sub>2</sub> and 4 ppm Fe<sup>2+</sup>) at 40 °C for 1000 h.

Reference:

- [1] Yi Yan, Jiuyang Zhang, Yali Qiao, Chuanbing Tang, *Macromol. Rapid Commun.*, **2014**, *35*, 254-259.