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Supporting Information

Proton-conductive polyimide consisting of naphthalenediimide and sulfonated units alternatively segmented by long aliphatic spacers

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EXPERIMENTAL SECTION

Materials

1,4,5,8-naphthalenetetraboxylic dianhydride, 11-aminoundecanonic acid, methanesulfonic acid and trifluoromethanesulfonic acid were all purchased from Energy-chemical, Inc., China. P_2O_5, dimethylformaldehyde (DMF), *N*-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and other solvents were supplied by Shanghai Sinopham Chemical Reagent Co. Ltd., China. All these reagents were used as received unless otherwise stated. Eaton's reagent (P_2O_5/CH_3SO_3H mixture at a weight ratio of 1/10)[1] and disodium 2,2'-di(sulfopropyloxy)biphenyl (**2**)[2] were prepared according to the literature, respectively.

Synthesis of monomer 1

As shown in Scheme S1, a three-necked flask equipped with a condensing tube and a N_2 inlet was charged with 1,4,5,8-naphthalenetetraboxylic dianhydride (2.682 g, 10 mmol), 11-aminoundecanonic acid (4.227 g, 21 mmol), and dimethylformaldehyde (DMF, 40 mL). The reaction mixture was stirred under N_2 at 145 ^oC for 5 h, then cooled to room temperature and dumped into 200 mL of water. The resulting precipitates were filtrated and washed with ethanol followed by drying in vacuo at 100 ^oC for 24 h to obtain monomer **1** (5.52 g, 87% yield) as yellow powder. FTIR (KBr pellet, cm^{-1}): 3439, 2925, 2851, 1704, 1659, 1582, 1458, 1340, 1247; ^1H NMR (400 MHz, DMSO-d_6, δ): 11.92 (COOH, s, 2H), 8.68 (Ar-H, s, 4H), 4.05 (N-CH_2, t, 4H), 2.17 (CH_2-CO, t, 4H), 1.71-1.59 (N-CH_2-$\underline{CH_2}$, m, 4H), 1.52-1.42 ($\underline{CH_2}$-CH_2-CO, m, 4H), 1.41-1.16 (NCH_2CH_2-$\underline{(CH_2)_6}$-CH_2CH_2CO, m, 24H).

Synthesis of polymer 3

A round-bottom flask equipped with a $CaCl_2$ tube was charged with monomer **1** (0.9388 g, 1.479 mmol), monomer **2** (0.7017 g, 1.479 mmol), Eaton's reagent (5.5 mL) and trifluoromethanesulfonic acid (1.0 mL). The reaction mixture was stirred at 60 ^{o}C and became an extremely viscous reddish solution within one hour which was immediately cast on a clean glass plate to form very thin film. After immersing in water, the paper-like reddish film was stripped off, washed with water followed by extraction with ethanol in a Soxhlet apparatus, and finally dried in vacuo at 60 ^{o}C to obtain SPKI in H^+ type in essentially quantitative yield.

Preparation of membrane 3

Polymer **3** was firstly dissolved in NMP to get a 6 wt% solution. The resulting solution was then cast onto a flat glass plate placed on a hot plate, heated at 60 ^{o}C to evaporate the solvent. When the surface of the membrane became tough, the glass plate together with the membrane was transferred into a vacuum and dried at 60 ^{o}C for 24 h. The membrane was stripped from the glass plate by water steam, turned into H^+ type for further measurements by soaking in 1 mol L^{-1} HCl for 48h followed by throughout washing with de-ionized water.

Measurements

^{1}H NMR spectra were recorded on an Avance 400 spectrometer (Bruker, Germany) using DMSO-d_6 (with tetramethylsilane as internal reference) as a solvent. FT-IR spectra were recorded on a Bruker Vector 22. The thermal behavior was analyzed with a Shimadzu TGA-50H analyzer at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. The inherent viscosity was determined using typical Ubbelohde method with polymer concentration of 0.5 g dL^{-1} in NMP at 25 ^{o}C. The mechanical property of wet membranes was measured using an Instron universal tester (Model 3340) at 25 ^{o}C at a crosshead speed of 10 mm/min, and tensile strength (TS) and elongation at break (E_b) values were recorded.

For transmission electron microscopy (TEM) observations, the membranes were firstly stained in 1 M lead acetate aqueous solution, rinsed with deionized water, and dried at 65 ^{o}C for 24 h. Then the stained membranes were embedded in epoxy resin, sectioned to be about 90 nm in thickness with a microtomer (Leica EM FC7 UC7, Germany). Finally, the sample slices were placed on copper grids, and their electron micrographs were taken with a JEOL-2010, Japan transmission electron microscope under an accelerating voltage of 80 kv.

Tapping mode AFM observations were performed with a Veeco diInnova SPM, using micro-fabricated cantilevers with a force constant of approximately 20 N/m. All samples in H^+ type were measured under ambient condition (25 ^{o}C, 50% RH).

Water uptake (WU) and linear swelling ratio (LSR) were calculated by measuring the change of weight and length of membranes before and after being immersed in water at a certain temperature for 24 h according to Equation (S1) and (S2), respectively.

$$WU = {(W_{wet} - W_{dry})}\Big/{W_{dry}} \times 100\% \qquad \text{(S1)}$$

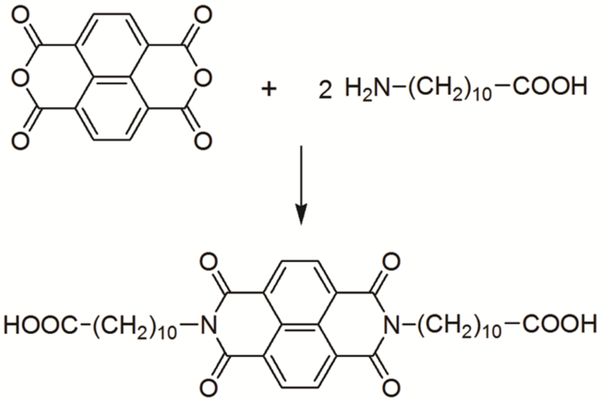
$$LSR = {(L_{wet} - L_{dry})}\Big/{L_{dry}} \times 100\% \qquad \text{(S2)}$$

where W_{dry} and L_{dry} were the weight and length of dry membrane while W_{wet} and L_{wet} were those of wet membrane.

Ionic conductivity of membranes was measured using a standard four-electrode AC impedance technique on a PGSTAT302N autolab (Metrohm China Ltd.) as described in previous report [2].

Hydrolytic stability was tested by soaking a strip of membrane **3** (H^+ type, 3.5 cm × 3.5 cm × 79 μm) in hot water at 80 °C, while oxidative stability was tested by immersing membrane **3** in freshly-made Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C.

RESULTS AND DISCUSSION



1

Scheme S1. Synthesis of monomer **1**.

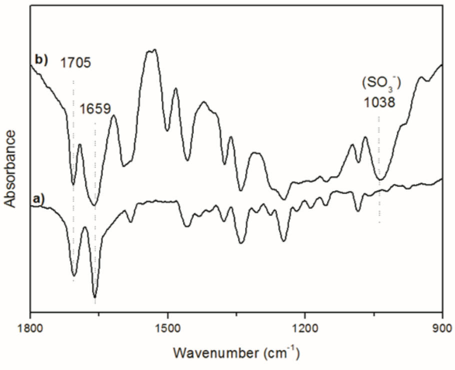


Figure S1. FT-IR spectra of a) monomer **1** and b) polymer **3**.

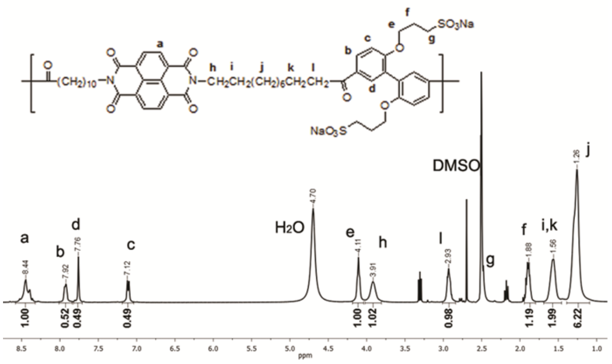


Figure S2. ^{1}H NMR spectrum of polymer **3** in DMSO-d_6.

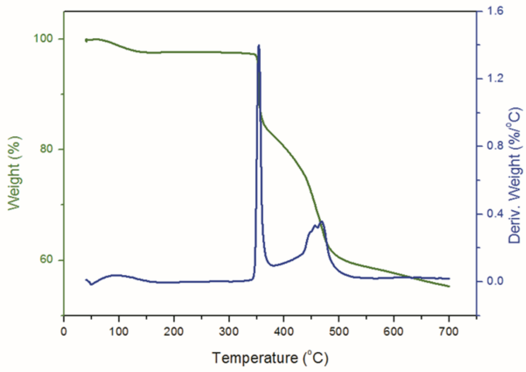


Figure S3. TGA of polymer **3** (Na^+ type).

Table S1. Some properties of polymer 3

Polymer	η_{inh}[a] (dL g^{-1})	IEC (mmol g^{-1})		TS[d] (MPa)	E_b[e] (%)
		Theo.[b]	Exp.[c]		
3	1.87	1.94	1.90	25	23%

[a]Inherent viscosity (dL g^{-1}) determined by the typical Ubbelohde method. [b]Theoretical values based on adding ratio of monomers. [c]Determined by acid-base titration. [d]Tensile strength. [e]Elongation at break.

References

1. Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.

2. Zhang, Z. H.; Wu, L.; Xu, T. W. *J. Mater. Chem.* **2012**, *22*, 13996.