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Experimental Procedures

Materials

Para-Terphenyl (TP), N-methyl-4-piperidone, iodomethane, benzene, potassium carbonate (K₂CO₃) and Dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. 1,3,5-Triphenylbenzene (TPB) was purchased from abcr GmbH (Germany). Biphenyl (BP) was purchased from Acros Organics. Trifluoromethanesulfonic acid (TFSA) was purchased from Fluorochem. Trifluoroacetic acid (TFA) was purchased from TCI. Dichloromethane (DCM) and ethyl acetate were purchased from Thermo Fisher Scientific Inc. (Suisse). All chemicals were used directly without further purification.

Synthesis of branched poly(terphenyl piperidine) (b-PTPA-x)

The typical synthetic procedure of b-PTPA-x is as follows (using b-PTP-1 as an example). In a flask, TP (3.408 g, 0.99 equiv.), TPB (0.046 g, 0.01 equiv.), and N-methyl-4-piperidone (1.70 g, 1.005 equiv.) were added into DCM (17 mL). The solution was stirred with an overhead agitator under 0 °C for 30 min. Then TFA (1.22 mL, 1.1 equiv.) and TFSA (13.3 mL, 10.05 equiv.) were added dropwise to the solution. During the reaction, the color of the solution changed from red to dark green. After 6 h, the resulting viscous solution was poured into excess amount of methanol and the precipitated white polymer fibers were cut into small pieces. These pieces were collected by filtration and washed with 1M K₂CO₃ at 50 °C overnight, followed by washing three times with deionized (DI) water and dried in oven at 80 °C under vacuum for 24 h.

Synthesis of model polymer 1: hyperbranched poly(triphenylbenzene piperidine)

In a flask, TPB (4.696 g, 1 equiv.) and N-methyl-4-piperidone (1.734 g, 1 equiv.) were added into DCM (17.45 mL). The solution was stirred with overhead agitator under 0 °C for 30 min. Then TFA (1.22 mL, 1.1 equiv.) and TFSA (13.61 mL, 10 equiv.) were added dropwise to the solution. During reaction, the color of the solution changed from light yellow to brick red. The resulted viscous solution was poured into excess amount of methanol. The white product was filtered and washed with 1M K₂CO₃ at 50 °C overnight, followed by washing three times with water and dried in oven at 80 °C under vacuum for 24 h. The obtained Model Polymer 1 is soluble in DMF, NMP, THF and CHCl₃.

Synthesis of model polymer 2: branched poly(benzene piperidine)

In a flask, benzene (1.109 g, 0.95 equiv.), TPB (0.229 g, 0.05 equiv.) and 1-methyl-4-piperidone (1.734 g, 1.025 equiv.) were added into DCM (17.45 mL). The solution was stirred with overhead agitator under 0 °C for 30 min. Then TFA (1.22 mL, 1.1 equiv.) and TFSA (13.61 mL, 10.25 equiv.) were added dropwise to the solution. The resulted viscous solution was poured into excess amount of methanol. The white product was filtered and washed with 1M K₂CO₃ at 50 °C overnight, followed by washing three times with water and dried in oven at 80 °C under vacuum for 24 h. The obtained model polymer 2 is soluble in NMP, THF and CHCl₃.

Synthesis of model polymer 3: branched poly(biphenyl piperidine)

In a flask, BP (2.190 g, 0.95 equiv.), TPB (0.229 g, 0.05 equiv.) and N-methyl-4-piperidone (1.734 g, 1.025 equiv.) were added into DCM (17.45 mL). The solution was stirred with overhead agitator under 0 °C for 30 min. Then TFA (1.22 mL, 1.1 equiv.) and TFSA (13.61 mL, 10.05 equiv.) were added dropwise to the solution. During reaction, the color of the solution changed from light yellow to brick red. The resulted viscous solution was poured into excess amount of methanol. The white product was filtered and washed with 1M K₂CO₃ at 50 °C overnight, followed by washing three times with water and dried in oven at 80 °C under vacuum for 24 h.

Synthesis of branched poly(terphenyl piperidinium) (b-PTP-x)

In a flask, b-PTP-x (1 g) was suspended in DMSO (30 mL), and the solution was stirred at room temperature for 30 min. Subsequently, K₂CO₃ (0.39 g) and iodomethane (1 mL) were added and the reaction was kept stirred at room temperature for 24 h in the dark. Ethyl acetate was added to the resulting viscous solution. The light-yellow precipitate was filtered, washed three times with water, and dried in oven at 80 °C under vacuum for 24 h.

Membrane preparation
b-PTP-x (1 g) was dissolved in 30 mL DMSO and the polymer solution was filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter and casted onto a clean glass plate. Subsequently, the solution was evaporated at 80 °C for 12 h, 120 °C for 12 h, and dried at 120 °C under vacuum for 24 h to completely remove the residual solvent. The membrane in I form was peeled off from glass plate. Membrane in Br form was obtained by ion exchanging in 1 M KBr solution at 80 °C for 12 h, followed by washing with deionized water for 3 times to remove residual salts. Membrane in OH form was obtained by ion exchanging in 1 M KOH solution at 80 °C for 12 h, followed by washing with degassed deionized water for 3 times under N2 atmosphere. Membrane in OH form was stored under N2 to avoid contamination by CO2 and the formation of carbonate.

Intrinsic viscosity

The intrinsic viscosity ([η]) was determined by using an Ubbelohde viscometer. b-PTP-x was dissolved in DMSO into four different concentrations. The efflux time of each concentration was recorded four times at 22 °C. The reduced viscosity (η_red) and inherent viscosity (η_inh) were calculated by:

\[ \eta_{\text{red}} = \frac{t_s - t_b}{c} \]  
\[ \eta_{\text{inh}} = \frac{\ln(t_s)}{t_b - \frac{t_s}{c}} \]  

where \( t_b \) (s) is the efflux time of DMSO, \( t_s \) (s) is the efflux time of the polymer solution at concentration \( c \) (g dL\(^{-1}\)). The intrinsic viscosity ([η]) was obtained by extrapolating η_red and η_inh to c=0 and the average value was adopted.

\(^1\)H nuclear magnetic resonance spectroscopy

The \(^1\)H spectra of protonated b-PTPA-x and model polymers, as well as the b-PTP-x, were measured by a Bruker Avance 400 spectrometer using DMSO-d\(_6\) with 5% vol% TFA. By adding TFA, the peak of water was shifted so that the peaks of piperidine/piperidinium ring could be observed.

Scanning electron microscopy

Surface morphology of dry b-PTP-x membranes in I form was observed with a Zeiss Merlin microscope at 1 kV and equipped with an Inlens secondary electron detector. Membrane samples were coated with gold before analysis.

Thermal and mechanical properties

The thermal properties of b-PTPA-1 powder, protonated b-PTPA-1 powder, b-PTP-1 (I form) powder, as well as b-PTP-x membranes (I form) were measured by a Perkin Elmer TGA 4000 under N\(_2\) atmosphere. Samples were held at 120 °C for 10 min to remove adsorbed water, and then heated from 50 °C to 800 °C with a heating rate of 10 °C min\(^{-1}\).

The mechanical properties of b-PTP-x membranes were measured by Universal Testing Machine (UTM; AGS-500NJ, Shimadzu, Tokyo, Japan) at room temperature. Membrane samples were cut into a dumbbell-like shape with effective area of 2 mm \( \times \) 10 mm and stretched at 1 mm min\(^{-1}\).

Dynamic mechanical analysis

The storage modulus and tan δ of PTP and b-PTP-2.5 membranes in I form were measured by a dynamic thermomechanical analysis (DMA, Q800. TA instrument, DE, USA) system. Membrane samples were cut into 9 mm \( \times \) 20 mm rectangle shape and then measured with a preload force of 0.01 N and a force track of 125% under N\(_2\) atmosphere. The sample was ramped at 4 °C min\(^{-1}\) until 450 °C. The peak of tan δ stands for the glass transition temperature (\( T_g \)) of membrane sample.

IEC measurement

The ion exchange capacity (IEC) of b-PTP-x membranes was measured by Mohr titration. Weights (\( W_{\text{dry}} \)) of membrane samples in Br form were recorded after drying in an oven under vacuum at 80 °C overnight. Then, the samples were ion exchanged with 0.1 M
**Supporting Information**

\( \text{NaNO}_3 \) at 50 °C for 12 h and repeated three times. The solutions were combined and titrated by 0.01 M AgNO\(_3\) using K\(_2\)CrO\(_4\) as indicator. The IEC (mmol g\(^{-1}\)) of b-PTP-x membranes in Br and OH form can be calculated by:

\[
\text{IEC(Br}^{-}) = \frac{0.01 \times V_{\text{AgNO}_3}}{W_{\text{dry}}} \\
\text{IEC(OH}^{-}) = \frac{0.01 \times V_{\text{AgNO}_3}}{W_{\text{dry}} - 0.629 \times V_{\text{AgNO}_3}}
\]

where \( V_{\text{AgNO}_3} \) is the volume (mL) of consumed AgNO\(_3\) solution.

**Water uptake and swelling ratio**

Dry weight (\( W_{\text{dry}} \)) and length (\( L_{\text{dry}} \)) of b-PTP-x membranes samples were recorded after drying in an oven at 80 °C under vacuum. Then the samples were immersed in degassed deionized water for 12 h at different temperatures under N\(_2\). The wet weight (\( W_{\text{wet}} \)) and length (\( L_{\text{wet}} \)) of the samples were recorded after wiping excessive water from the surface. The water uptake (\( WU \)) and swelling ratio (\( SR \)) can be calculated by:

\[
WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%
\]

\[
SR(\%) = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%
\]

The hydration number (\( \lambda \)) is the number of adsorbed water molecules per piperidinium group. It can be calculated by:

\[
\lambda = \frac{1000 \times WU}{\text{IEC(OH}^{-}) \times M(H_2O)}
\]

where \( M(H_2O) \) is the relative molecular weight of water (18 g mol\(^{-1}\)).

**Conductivity measurement**

The in-plane ion conductivity (mS cm\(^{-1}\)) of b-PTP-x membranes was measured by an Autolab PGSTAT302N equipped with a Scribner 740 MTS. Membrane samples in 10 mm × 30 mm were assembled into a four-electrode cell and tested using the alternative current (AC) impedance in the frequency range of 1 Hz to 0.1 MHz. The assembly and measurement were operated under N\(_2\) to avoid CO\(_2\) contamination. The measurements were carried out at different temperature at 100% RH. The ion conductivity \( \sigma \) (mS cm\(^{-1}\)) of membrane samples can be calculated by:

\[
\sigma = \frac{L}{AR}
\]

where \( L \) (cm) is the distance between working and counter electrode, \( A \) (cm\(^2\)) is the cross-sectional area calculated by the thickness (cm) and width (cm) of the membrane samples, \( R \) (kΩ) is the Ohm impedance obtained from electrochemical impedance spectra.

**Gas permeability**

The H\(_2\) permeabilities of PTP, b-PTP-2.5, commercial FAA-3-50 and Nafion 212 membranes were measured by a gas permeability testing system equipped with gas chromatography (GC, 490 Micro GC, Agilent Technologies, USA) and two mass flowmeters (MFC, M3030V, Line Tech, Korea).\(^{1,2}\) The measurements were conducted under different RHs with 2.2 bar unilateral backpressure at 80 °C. Gas permeability \( P \) (Barrer, 1 Barrer = 10\(^{-10}\) cm\(^3\) (STP) cm cm\(^{-2}\) s\(^{-1}\) cmHg\(^{-1}\)) can be calculated by:

\[
P = \frac{V M_{\text{gas}} d_p}{P_{\text{feed}} RT A_p d_t}
\]

where \( V \) (cm\(^3\)), \( M_{\text{gas}} \) (g mol\(^{-1}\)), \( d \) (um) and \( P_{\text{feed}} \) (760 mmHg) are the volume of measurement cell, molecular weight of permeating gas, membrane thickness and the pressure of feed gas, and \( R \) (L mmHg K\(^{-1}\) mol\(^{-1}\)), \( T \) (K), \( A \) (cm\(^2\)) and \( d_t \) (g cm\(^{-3}\)) are the gas constant, testing temperature, effective area of samples and the density of permeating gas, respectively. \( \frac{d_p}{d_t} \) denotes the change rate of permeated gas pressure over time.
**SUPPORTING INFORMATION**

**Alkaline stability**

The alkaline stability of b-PTP-2.5 membrane was measured by immersing into 1 M and 3 M KOH at 80 °C over 1500 h. The KOH solution was refreshed weekly. Before testing the conductivity, the sample was washed three times with degassed deionized water under N₂. To measure ¹H NMR spectra, surface morphology and mechanical property, the sample was ion exchanged with 1M KI at 80 °C for 12 h, followed by washing three times with deionized water and drying.

**Fuel cell performance**

The single fuel cell performance was measured by a fuel cell station (CNL, Seoul, Republic of Korea). The anode slurry was prepared by adding 12.5 mg Pt-Ru/C (40 wt% Pt, 20 wt% Ru, Hispec, Alfa Aesar, USA) and 5 mg poly(fluorenyl-co-biphenyl piperidinium) (PFBP, 5 wt% in DMSO) ionomers to isopropanol/water (1.2 mL/0.12 mL) solution. The composition of ionomer: carbon: Pt-Ru is 1: 75: 1.5. The cathode slurry was prepared by adding 12.5 mg Pt/C (40 wt% Pt, Hispec, Alfa Aesar, USA) and 3.75 mg PFBP ionomer to isopropanol/water (1 mL/0.1 mL) solution. The composition of ionomer: carbon: Pt is 1: 2: 1.33. The slurries were sonicated for 45 min at 0 °C before spraying. Then, the anode and cathode slurries were sprayed onto both sides of b-PTP-2.5 membranes (I-form) along with metal catalyst loadings of 0.6 and 0.4 mg cm⁻², respectively. The prepared catalyst-coated membrane (CCM) was immersed in 1 M NaOH at room temperature for 12 h, followed by washing three times in deionized water. After that, the CCM was assembled with gas diffusion layers (GDLs), PTFE gaskets and graphite bipolar plates into single cell at a torque of 60 in-lb. The effective area of the cell is 5 cm².

The assembled cell was connected with gas lines and heating system. After the temperature of humidifier and gas lines reached the set values, cell temperature was increased to 70 °C. The cell was activated at a constant voltage of 0.5 V at flowrate of H₂ and O₂ at 1000 mL min⁻¹ until no fluctuation of current density. After that, the temperature of cell was increased to 80 °C and the polarization curve was recorded.

The in-situ durability of fuel cell was measured under a constant current density of 0.2 A cm⁻² at 60 °C with 400/400 mL min⁻¹ H₂/O₂ flowrate with Anode (A)/Cathode (C) dew points of 53 °C and 60 °C. The cell was refreshed two times during durability test. After durability test, the membrane was disassembled from the MEA and used for ¹H NMR, surface morphology and mechanical property measurements.
Figure S1. DLS intensity-based size distribution for PTP and b-PTP-x.
The linear PTP reference exhibited one DLS peak at around 14 nm. This peak was shifted to higher size and its intensity was decreased with increasing branching degree. Meanwhile, another peak at around 100 nm appeared for the branched polymers. The size and intensity of the latter peak increased with increasing branching degree. Although the interpretation of the DLS spectra of b-PTP-x is difficult, the data are consistent with a higher molecular weight upon branching.
Figure S2 $^1$H NMR spectra of model polymer 2 and its linear reference in DMSO-d$_6$ with 5% TFA. TFA can improve the solubility by protonating the amine groups. Meanwhile, TFA shifts the water peak from 3.3 ppm to 12-14 ppm.
Figure S3 $^1$H NMR spectra of model polymer 3 and its linear reference in DMSO-d$_6$ with 5% TFA. TFA can improve the solubility by protonating the amine groups. Meanwhile, TFA shifts the water peak from 3.3 ppm to 12-14 ppm.
Figure S4 ¹H NMR spectra of PTPA, b-PTPA-2.5 and b-PTPA-5 in DMSO-d₆ with 5% TFA. TFA can improve the solubility by protonating the amine groups. Meanwhile, TFA shifts the water peak from 3.3 ppm to 12-14 ppm.
Figure S5 $^1$H NMR spectrum of b-PTP-2.5 in DMSO-d$_6$ with 5% TFA. TFA can improve the solubility by protonating the amine groups. Meanwhile, TFA shifts the water peak from 3.3 ppm to 12-14 ppm.
**Figure S6** TGA curves of b-PTP-x AEMs in OH⁻ form under N₂ atmosphere.
Figure S7 Mechanical toughness test of b-PTP-2.5 in I form (20 μm). a) fresh membrane, b) and c) kneaded membrane, d) recovered membrane.
Figure S8: H₂ permeability of b-PTP-2.5 membrane (I form) at different RH and 80 °C. The values of commercial FAA-3-50 and Nafion 212 membranes are presented for comparison.
Figure S9 Surface morphology of PTP reference membrane, b-PTP-2.5 membrane, b-PTP-2.5 membrane after a 500 h in-situ durability test, b-PTP-2.5 membrane after a 1500 h treatment in 1 M and 3 M KOH at 80 °C.
Figure S10 $^1$H NMR spectra of b-PTP-2.5 membrane after immersing in 1 M KOH at 80 °C for different durations.
Figure S11 Alkaline stability of the b-PTP-2.5 membrane in 3M KOH at 80 °C. a) remaining hydroxide conductivity at different immersing time, b) 1H NMR spectra and c) mechanical properties before and after 1500 h alkaline treatment.
Figure S12 $^1$H NMR spectra of b-PTP-2.5 membrane after being immersed in 3 M KOH at 80 °C for different durations.

Degradation degree = \[
\frac{\text{Area of Protone } b \times 12}{68.16} \times 100\% \approx 17\%
\]

Figure S12 $^1$H NMR spectra of b-PTP-2.5 membrane after being immersed in 3 M KOH at 80 °C for different durations.

Degradation degree = \[
\frac{\text{Area of Protone } b \times 12}{\text{Area of Aromatic protons}} \times 100\%
\]
Table S1 Polymerization conditions of b-PTPA-x.

| Entry | TFSA: Piperidone | Monomer Conc. mol L⁻¹ | TP: TPB: Piperidone | Reaction Time, h | Yield | Viscosity dL g⁻¹ |
|-------|------------------|-----------------------|---------------------|------------------|-------|-----------------|
| 1     | 6.1              | 0.45                  | 100:0:100           | 6                | -     | -               |
| 2     | 10               | 0.45                  | 100:0:100           | 6                | 91.4% | 2.84            |
| 3     | 10               | 0.1                   | 97.5:2.5:101.25     | 6                | 48.5% | 1.73            |
| 4     | 10               | 0.3                   | 97.5:2.5:101.25     | 6                | 92.8% | 2.67            |
| 5     | 10               | 0.45                  | 97.5:2.5:101.25     | 6                | 89.2% | 6.18            |
| 6     | 10               | 0.6                   | 97.5:2.5:101.25     | 6                | 92.5% | 4.46            |
| 7     | 10               | 0.45                  | 97.5:2.5:101.25     | 24               | 90.8% | Not Measurable  |
| 8     | 10               | 0.45                  | 99:1:100.5          | 6                | 91.5% | 5.52            |
| 9     | 10               | 0.45                  | 95:5:102.5          | 6                | 86.2% | Not Measurable  |

*X is the molar ratio (in percent) of 1, 3, 5-triphenyl benzene to the aryl monomers.*
### Table S2 Comparison of viscosity among reported poly(aryl piperidinium)s.

| Polymers       | Viscosity (dL g⁻¹) | Ref.   |
|---------------|-------------------|-------|
| b-PAP-2.5     | 6.18              | This work |
| PFTP-13       | 4.08              | [1]   |
| PDTP-75       | 5                 | [2]   |
| PAP-TP-x      | 4.71              | [3]   |
| PTPipQ1       | 0.39 (30 °C)      | [4]   |
| PBPA          | 2.18 (30 °C)      | [5]   |
### Table S3: Summary of AEMs, ionomers, anode and cathode catalysts, PPDs, and durability of AEMFCs

| AEMs    | Ionomers | Anode catalyst      | Cathode catalyst    | PPD (W cm\(^{-2}\)) | Durability | Ref. |
|---------|----------|---------------------|---------------------|----------------------|------------|------|
| b-PTP-2.5 | PFBP-14  | Pt/Ru/C (0.60 mg cm\(^{-2}\)) | Pt/C (0.40 mg cm\(^{-2}\)) | 2.3 | >500 h | this work |
| FAA-3-50\(^b\) | Fumion  | Pt/C (0.33 mg cm\(^{-2}\)) | Pt/C (0.33 mg cm\(^{-2}\)) | 0.3-0.4 | <48 h | [1] |
| PFTP-13\(^b\) | PFBP-14  | Pt/Ru/C (0.42 mg cm\(^{-2}\)) | Pt/C (0.33 mg cm\(^{-2}\)) | 2.34 | 200 h | [1] |
| PDTP-25\(^b\) | PFBP-14  | Pt/Ru/C (0.39 mg cm\(^{-2}\)) | Pt/C (0.26 mg cm\(^{-2}\)) | 2.58 | 100 h | [2] |
| QAPPT\(^b\) | QAPPT   | Pt/C (0.4 mg cm\(^{-2}\)) | Pt/C (0.4 mg cm\(^{-2}\)) | 1.45 | 120 h | [6] |
| PAP-TB-85\(^b\) | PAP-BP-100 | Pt/C (<0.15 mg cm\(^{-2}\)) | Ag/C (1 mg cm\(^{-2}\)) | 0.92 | 300 h | [3] |
| TPN\(^b\) | FLN-55   | Pt/Ru/C (0.50 mg cm\(^{-2}\)) | Pt/C (0.60 mg cm\(^{-2}\)) | 1.46 | 350 h | [7] |
| BTMA-HDPE\(^c\) | BTMA-ETFE | Pt/Ru/C (0.70 mg cm\(^{-2}\)) | Pt/C (0.60 mg cm\(^{-2}\)) | 2.35 | 1000 h | [8, 9] |
| HTMA-DAPP\(^c\) | FLNs    | Pt/Ru/C (0.75 mg cm\(^{-2}\)) | Pt/C (0.60 mg cm\(^{-2}\)) | 0.54 | 933 h | [10] |
| GT64-15\(^c\) | GTXX    | Pt/Ru/C (0.70 mg cm\(^{-2}\)) | Pt/C (0.60 mg cm\(^{-2}\)) | 3.2 | 2000 h | [11] |
| PX75-TSO\(^d\) | -       | Pt/Ru/C (0.50 mg cm\(^{-2}\)) | Pt/C (0.50 mg cm\(^{-2}\)) | 0.73 | 400 h | [12] |
| TminPPO\(^d\) | CBQPPO  | Pt/Ru/C (0.50 mg cm\(^{-2}\)) | Pt/C (0.50 mg cm\(^{-2}\)) | 1.37 | <48 h | [13] |
| Other PPO series\(^d\) | Other PPO series | Pt/C (0.4-0.5 mg cm\(^{-2}\)) | Pt/C (0.4-0.5 mg cm\(^{-2}\)) | <0.4 | - | [14, 15] |
| HMT-PMBI\(^d\) | HMT-PMBI | Pt/C (0.4 mg cm\(^{-2}\)) | Pt/C (0.4 mg cm\(^{-2}\)) | 0.37 | 110 h | [16] |

\(^a\)commercial AEMs membranes and ionomers;  
\(^b\)PAP-family AEMs and ionomers;  
\(^c\)state-of-the-art AEMFCs with durability > 1000 h;  
\(^d\)poly(phenylene oxide) (PPO) and polybenzimidazole (PBI) membranes and ionomers;
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Author Contributions

X. Wu and X. Hu conceived the idea. X. Wu synthesized and characterized the polymer and membrane. N. Chen tested the dynamic mechanical analysis, Gas permeability, mechanical properties, fuel cell performance and in-situ durability. X. Wu and X. Hu wrote the paper, with the support from other co-authors. All authors analyzed and discussed the data. X. Hu and Y.M. Lee supervised the work.