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# Synergistic functionalization of poly(*p*-terphenyl isatin) anion exchange membrane with quaternary ammonium and piperidine cations for fuel cells†

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Research on anion exchange membrane fuel cells (AEMFCs) mainly focuses on the membrane module, and improving its performance has always been the focus of researchers. To create high-performance anion exchange membranes (AEMs), a series of side chain type AEMs were prepared by introducing different proportions of side chains containing anisotropic poly cations with relatively stable piperidinium ring cations and side quaternary ammonium cations as cation groups, using poly(*p*-terphenyl isatin) (PTI), a main chain polymer without aryl ether bonds. The dense surface of the PTI-N-*n* series membranes is shown by SEM images; TEM images show that the ion domains are clearly distributed in the membrane, so a continuous ion transport channel is constructed. PTI-N-100 has the highest hydroxide conductivity at 80 °C, reaching 96.83 mS cm<sup>-1</sup> due to multiple transport sites. The PTI-N-100 membrane has a peak power density of 180 mW cm<sup>-2</sup> based on the highest ionic conductivity. Therefore, we believe that the introduction of multi-cations contributes to the performance of anion exchange membranes.

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## 1 Introduction

At present, there are fewer and fewer non-renewable resources on earth, and the atmosphere is deteriorating. Based on the inherent requirements of sustainable development, clean energy has become a major trend in international energy development. In the past few decades, the excessive use of non-renewable energy sources such as peat, natural gas, oil, and coal has produced waste gases containing a lot of harmful substances, which has led to increasingly serious air pollution. Clean energy can eliminate the emissions of harmful substances such as carbon dioxide and sulfur dioxide, thus reducing air pollution. Moreover, using clean energy can greatly reduce the damage to the atmosphere and contribute to human health and development. The application of fuel cells is an effective way to resolve the lack of oil resources.<sup>1</sup> Many research institutes in the world automotive community are already carrying out extensive research activities targeting fuel cells in areas such as

advances in zero and ultra-low emission vehicle power. Proton exchange membrane fuel cells (PEMFCs)<sup>2</sup> have good characteristics and are considered by many research institutes and car manufacturers to be the obvious choice for fuel cells for automobiles. Unlike PEMFCs, anion exchange membrane fuel cells (AEMFCs) are superior in that: (1) the cathode has high redox capacity under alkaline conditions, so it is unnecessary to use noble metal catalyst;<sup>3</sup> (2) the alkaline medium in the AEMFCs replaces the alkaline medium in the PEMFCs, thus reducing the influence of acid corrosion.<sup>4</sup> As a strategic high-tech industry, membrane materials<sup>5</sup> are a strategic requirement for carbon neutrality targets. Not only that, but ensuring the storage of membranes in strong alkaline conditions is the most critical problem in the development of AEMFCs, so polymer formation strategies that focus primarily on high chemical stability, mechanical stability, and ionic conductivity are an effective means of promising to unlock the next phase of anion exchange membranes (AEMs). This will trigger a new wave of innovation leading to the accelerated development of highly efficient fuel cells for sustainable development.

The AEM is constructed of cationic groups and a polymer skeleton. Commonly, some polymers that have been commercially used as anion exchange membrane scaffolds are poly(ether ether ketone) (PEEK),<sup>6–8</sup> poly(phenylene oxide) (PPO),<sup>9–13</sup> and poly(ether sulfone) (PSF).<sup>14–17</sup> Their

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structures all contain aryl ether bonds that are vulnerable to attack by  $\text{OH}^-$  or  $-\text{OH}$  radicals. The presence of aryl ether bonds may lead to the breakage of the main chain and thus accelerate the degradation of the membrane. Therefore, the use of ether-free bonded polymers in anion exchange membranes has received attention from researchers, such as polyolefins,<sup>18,19</sup> polybenzimidazoles,<sup>20</sup> poly(aryl piperidinium),<sup>21–23</sup> and crown ether polymers.<sup>24,25</sup> Li *et al.*<sup>26</sup> reported a series of polyolefin copolymer-based AEMs at 80 °C for 20 days in 10 M NaOH solution, which exhibited excellent alkali stability; Zhu *et al.*<sup>27</sup> studied the anion exchange membrane based on polybenzimidazole as the skeleton through the polycondensation reaction, which showed a high alkaline stability at 80 °C in 1 M NaOH for more than 1000 hours; Wang *et al.*<sup>28</sup> fabricated AEMs containing a macrocyclic host–guest structure with dynamic self-protection. The membranes achieved a hydroxide conductivity of 114  $\text{mS cm}^{-1}$  at 80 °C. The membranes achieved 93% ion retention after immersion in 5 M KOH at 80 °C for 1000 h; Zhu *et al.*<sup>29</sup> prepared poly(aryl piperidinium) anion exchange membranes with nitrogen heterocyclic cations. The PBP-BOP-ASU (8%) membrane showed the highest ionic conductivity at 80 °C (117.43  $\text{mS cm}^{-1}$ ). When it was kept in a 2 M NaOH solution at 80 °C for 1400 hours, it showed excellent alkali stability. However, Zhu *et al.*<sup>30</sup> prepared an anion-exchange membrane with poly(terphenyl isatin piperidinium) as the main chain to further balance the “trade-off” problem. Due to the crosslinked structure and the high alkali resistance of the ether-free polymer backbone, the membranes maintained  $\geq 85\%$  hydroxide conductivity after 1600 h of treatment in a 3 M NaOH solution at 80 °C. The membrane was found to be highly resistant to alkaline attack. As a result, the alkali stability of AEMs made of ether-free polymers is outstanding.

In addition, common cations are linked to the main chain in the form of benzyl groups. However, under strong base conditions, benzyl groups are unstable and vulnerable to attack by hydroxide ions, which can be degraded by the  $\text{S}_{\text{N}}2$  reaction.<sup>31</sup> To solve this problem, on the one hand, imidazoles,<sup>32,33</sup> quaternary phosphonium<sup>34,35</sup> and metal cations<sup>36–38</sup> have been found; on the other hand, many teams have focused on the design aspects of molecular structures, such as the introduction of cross-linking reagents.<sup>39</sup> Such proposed cross-linking strategies are a successful way to enhance the mechanical characteristics of membranes and reduce gas permeation. However, after the introduction of cross-linking agents without conductive sites, the alkali resistance is improved, but the ionic conductivity is sacrificed accordingly. In order to solve this problem, the researchers put forward cationic groups far away from the main chain to promote micro-phase separation.<sup>40–42</sup> Build ion transport channels by using hydrophilic cationic groups to separate from the hydrophobic polymer backbone to construct a more pronounced micro-phase separation structure. This enhances the base resistance stability of the anion exchange membrane while improving conduction. However, in order to improve

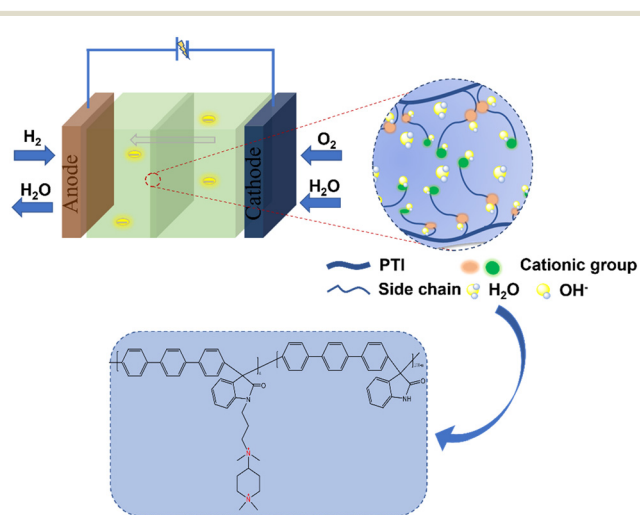
conduction more effectively, methods of establishing multiple transmission points have been proposed.<sup>43</sup>

In the current work, ether-free bonded poly(*p*-terphenyl isatin) (PTI) was prepared as the backbone of an anion exchange membrane by introducing different polycationic side chains in different proportions through a simple and nontoxic super acid catalytic reaction, and an anion exchange membrane with good ionic conductivity was developed. A series of tests will be carried out to investigate the effect of quaternary ammonium cations and piperidine cations acting together as side chains on membrane properties such as hydrophilicity, ionic conductivity, and base stability. In this study, the molecular structure of AEMs is schematically shown in Scheme 1.

## 2 Results and discussion

### 2.1 Synthesis and molecular structure characterization

The  $^1\text{H}$  NMR spectrum of PTI-*N-n* is an important basis for testing whether the product was successfully prepared. The synthesis path of PTI-*N-n* is shown in Scheme 2. Fig. 1a shows the  $^1\text{H}$  NMR characteristics of each of 4-ClPq and 3-*N*-4-ClPq. Fig. 1b shows the  $^1\text{H}$  NMR spectrum of PTI, which was successfully synthesized from hydroquinone and indirubin by a metal-free “click reaction” under the catalysis of superacid. The single peak at 10.87 ppm is the N–H proton signal on the indigo, and the signal at 7.02–7.78 ppm comes from the phenyl proton on the main chain of *p*-terphenyl and the isatin benzene ring, which proves that the main chain is successfully synthesized. Fig. 2 takes PTI-*N*-80 as an example, and compares the spectra of PTI and PTI-*N*-80. From the Fig. 2, the peak of the indigo N–H proton signal at 10.87 ppm in PTI-*N*-80 is significantly weakened, indicating that some of isatin N–H reaction. The signal peak at 3.01 ppm belongs to the cationic group, and the signal peaks at 3.83 ppm is attributed to methylene protons on the connected isatin and quaternary ammonium groups, respectively. The

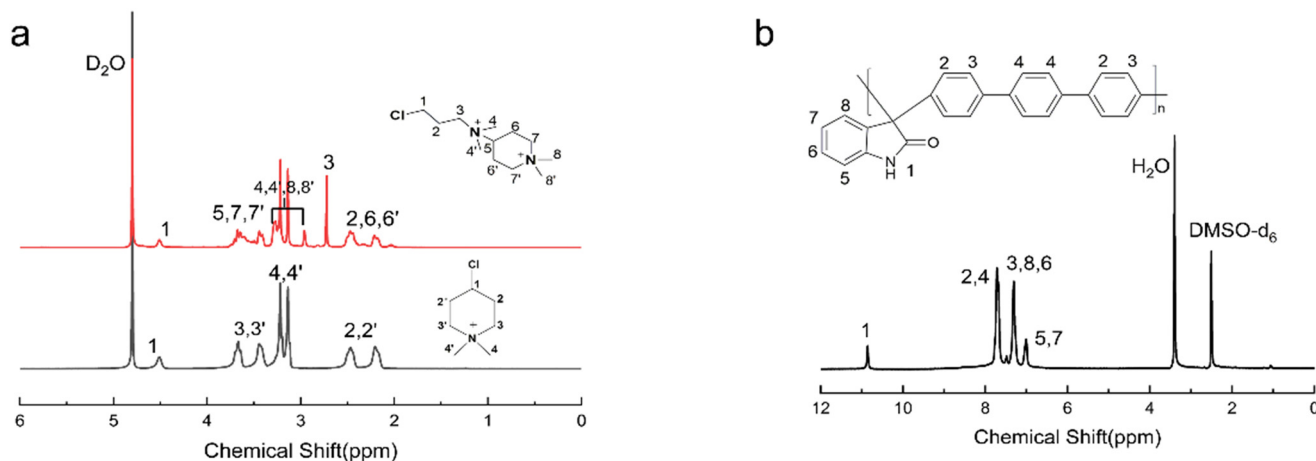


**Scheme 1** Schematic diagram of the molecular structure of AEMs with multi-cation side alkyl chains.





Scheme 2 Synthesis route of PTI-N-n.

Fig. 1  $^1\text{H}$  NMR spectra of (a) 4-ClPq and 3-N-4-ClPq; (b) poly(*p*-terphenyl isatin).

signal peaks of methylene and alkyl chain protons in the piperidine ring on 4-ClPq were found at 1–2 ppm, which proved that PTI-N-80 was successfully synthesized by comparison.

Besides, the FT-IR spectra is an important way to prove the successful synthesis of the products. PTI-N-100 was taken as an example, as shown in Fig. 3, we tested the infrared spectra of PTI and PTI-N-100. The bending vibration peak of  $-\text{NH}$  at  $3381\text{ cm}^{-1}$  and the stretching vibration peak of  $-\text{NH}$  at  $1662\text{ cm}^{-1}$  appeared in the infrared image of PTI, but disappear in the infrared image of PTI-N-100, indicating that the reaction of  $-\text{NH}$  group on the main chain has been completed. In the IR image of PTI-N-100, a characteristic absorption peak of  $-\text{CH}_2-$  on the alkyl side chain appears at  $1354\text{ cm}^{-1}$ , which is not found on PTI. In short, it can be proved that PTI-N-100 was successfully synthesized.

## 2.2 Micromorphology

In Fig. 4, the images of the surface and cross section of PTI-N-100 membrane were recorded by SEM. The membrane surface is smooth and compact without holes, preventing fuel leakage. The thickness of the PTI-N-100 is  $22\text{ }\mu\text{m}$ , which is appropriate for fuel cells. As shown in Fig. 4a and b, after repeated immersion and washing in deionized water, the PTI-N-100 membrane showed no obvious defects or cracks in both pictures of the membrane, which indicated that the grafted functionalized monomer successfully existed in the membrane without being dissolved in deionized water, on the other hand, it also showed the dense structure of the membranes.

The micro-phase separation structure of AEMs is closely related to the performance of the membrane, and TEM is





Fig. 2  $^1\text{H}$  NMR spectra of PTI-N-80.



Fig. 3 FT-IR spectra of PTI and PTI-N-100.

one means of observing the structure within the membrane. The TEM images of PTI-N-20, PTI-N-60, and PTI-N-100 in  $\text{OH}^-$  form are shown in Fig. 4c–e, in which the phase separation structure with obviously curved bands can be clearly observed. The light and dark phases each represent the hydrophobic and hydrophilic phases of the AEM. Therefore, as shown in Fig. 4, with the increase of the proportion of the hydrophilic side chain, the range of the dark areas increases accordingly. The comparison shows that the PTI-N-100 has the most remarkable microphase separation, so it has the highest ionic conductivity, which follows the same pattern as the ion conductivity test results.

We further demonstrated the microscopic phase separation morphology of PTI-N-*n* series membranes by AFM. The dark area represents the hydrophilic domain in the

membrane, while the light area indicates the hydrophobic domain of the main chain in the membrane. As can be seen from Fig. 5a and b, PTI-N-100 presents a more obvious microphase separation structure than PTI-N-20. This is the same as the TEM test results, so the increase in the proportion of side chains can bring about obvious micro-morphological changes.

In addition, we conducted a SAXS test (Fig. S1 $^\dagger$ ). However, as can be seen in the figure, no scattering peaks were found in the interval. The reason for this result may be due to the high rigidity of the poly(*p*-terphenyl isatin) main chain, which is consistent with the previous literature reports on poly(arylene) AEMs.<sup>30,44,45</sup>

### 2.3 Ion exchange capacity (IEC), water uptake (WU), swelling rate (SR)

The ion exchange capacity (IEC) represents the content of cationic groups through which anions are transported in the AEM. Generally speaking, with the increase of cationic groups, IEC tends to rise. In addition, the rise of temperature will lead to the instability of water uptake as well as swelling ratio, so it is necessary to ensure an appropriate increase in water uptake as well as swelling ratio and ionic conductivity.<sup>46</sup> This shows that the measured IEC is close to the theoretical IEC and PTI-N-100 has the highest IEC value, which is attributable to the fact that the more side chains effectively increase the number of anion transport sites.<sup>47</sup> Accordingly, a higher IEC leads to a higher concentration of hydrophilic cationic groups, and an increase of hydrophilic areas leads to a corresponding increase in water uptake.<sup>48</sup> Similar to other isatin-based membranes, the WU of PTI shows low dependence on temperature.<sup>49–51</sup> However, PTI-N-*n* series membranes all have a suitable swelling ratio, all of which are lower than 45%, showing good dimensional stability. Meanwhile, as the temperature increases, the WU and SR are positively related to the temperature. In order to further characterize the water uptake of the PTI-N-*n*, as shown in Fig. 6c, the water contact angle of PTI-N-100 is 62.9°, while the water contact angle of PTI-N-20 is 75.7°, which is consistent with the increasing trend of WU, showing good hydrophilicity of the prepared membrane.<sup>52–54</sup> This is consistent with the consequence of the microphase separation morphology shown in transmission tests (Table 1).

### 2.4 Hydroxide ion conductivity ( $\sigma$ )

The ionic conductivity is an important index for determining the performance of AEMs, which represents the strength of the anion exchange membrane's ability to transport ions. As shown in Fig. 6d, we have tested the ionic conductivity of AEM with different proportions of heterologous polycationic side chains. According to Fig. 6d, PTI-N-*n* series membranes are positively correlated with temperature. The reason is that the increase of temperature accelerates the molecular movement inside the membranes, increases the  $\text{OH}^-$  mobility and improves the conductivity of PTI-N-*n*. The hydroxide conductivity of PTI-N-80 is 41.76  $\text{mS cm}^{-1}$  at 30 °C as well as





Fig. 4 (a) Surface and (b) cross-sectional SEM images of the PTI-N-100 membrane; TEM images of (c) PTI-N-20, (d) PTI-N-60 and (e) PTI-N-100 membranes, respectively.

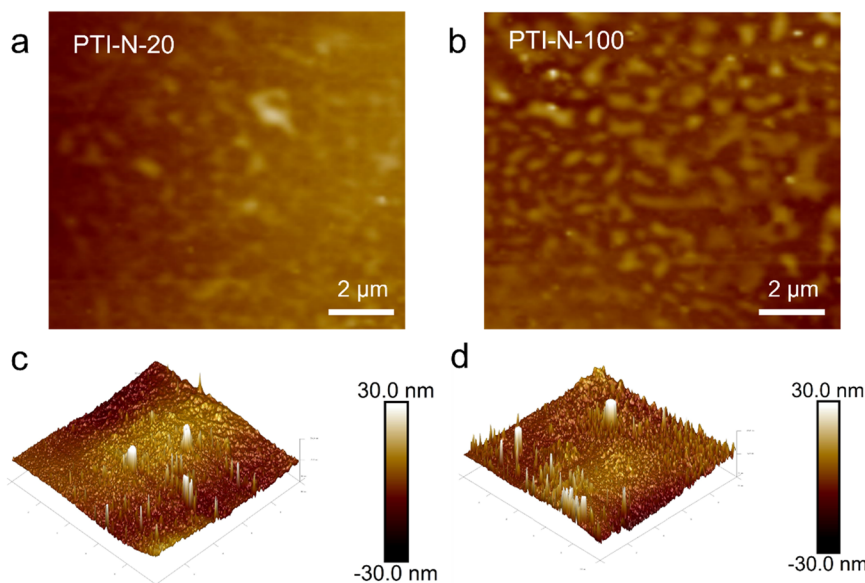


Fig. 5 AFM phase images and 3D height topography of PTI-N-20 and PTI-N-100.

80.92 mS cm<sup>-1</sup> at 80 °C. With the increase of temperature, the ionic conductivity shows an upward trend. In addition, the side chain content increased gradually, and the ionic conductivity also presented a trend of increasing. Due to the influence of multiple transmission sites, the PTI-N-100 membrane presented the highest ionic conductivity at 80 °C, which was 96.83 mS cm<sup>-1</sup>. The formation of microphase separation structure in PTI-N-100 membrane is effectively improved by high cation concentration, which makes it easier to form the aggregation of hydrophilic regions and thus improves ionic conductivity. This is because many cations are introduced, more OH<sup>-</sup> transport sites are provided and multiple ion transport channels are established. The whole series of AEMs has good ionic conductivity. As shown in

Fig. 6e, the Arrhenius plot of the fitted membrane was used to calculate its activation energy from the slope of the straight line. We found that the PIT-N-100 membrane has the lowest activation energy, which proves that it requires less ion migration energy and is more prone to ion migration. This is consistent with the pattern of OH<sup>-</sup> ion conductivity.

## 2.5 Thermal stability

The anion exchange membranes prepared must not only have good dimensional stability, but also maintain good stability under certain temperature environments. For AEMs, good thermal stability can be effective in avoiding performance losses of alkaline fuel cells during operation. As shown in



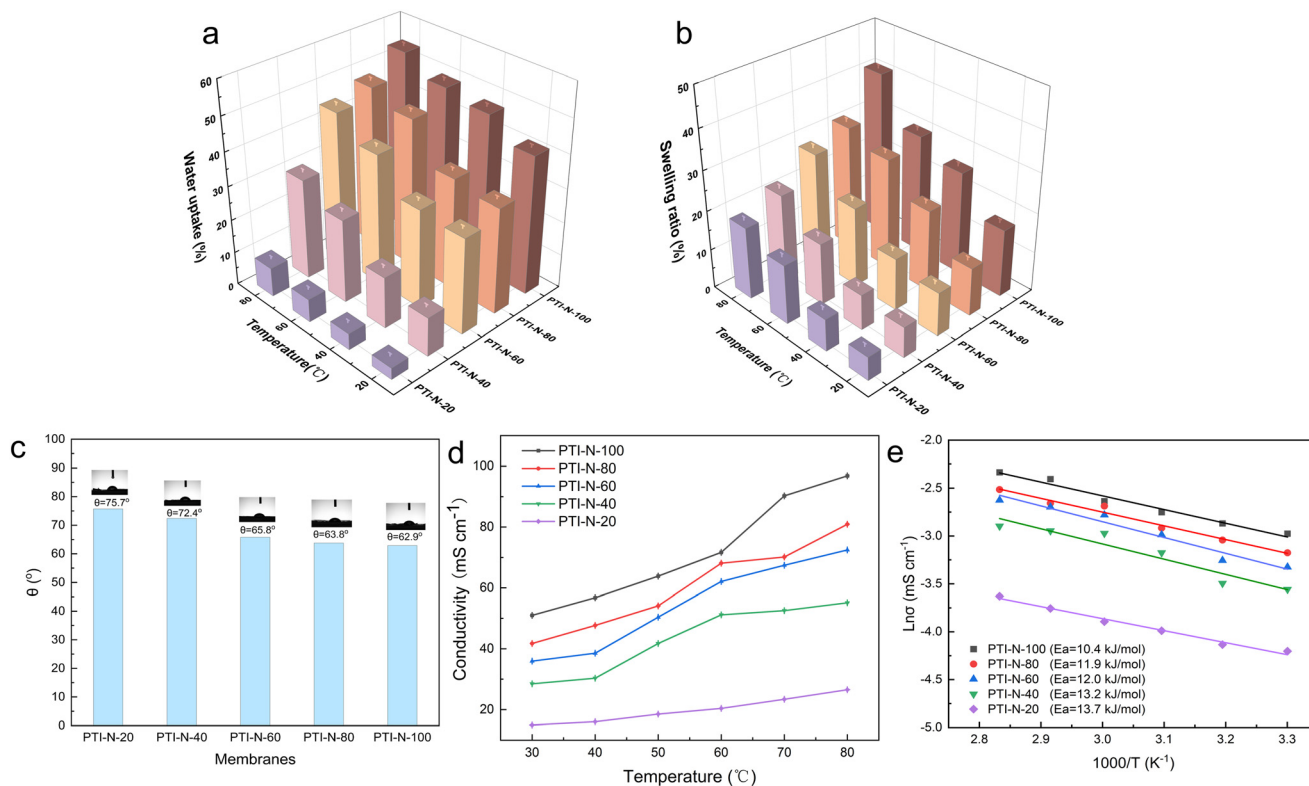


Fig. 6 (a) Water uptake and (b) swelling ratio of the PTI-N-*n* membranes; (c) the water contact angle; (d) hydroxide conductivity and (e) Arrhenius plots of PTI-N-*n* membranes.

Table 1 IEC, WU, SR, and  $\sigma$  of PTI-N-*n*

Samples	IEC (mmol g <sup>-1</sup> )		WU (%)		SR (%)		$\sigma$ (mS cm <sup>-1</sup> )	
	Theoretical value	Measured value	20 °C	80 °C	20 °C	80 °C	30 °C	80 °C
PTI-N-100	3.38	3.16	41.27	54.10	17.13	41.05	51	96.83
PTI-N-80	2.93	2.74	31.58	48.00	12.16	31.18	41.76	80.92
PTI-N-60	2.41	2.07	28.57	45.00	11.02	28.30	35.95	72.44
PTI-N-40	1.77	1.62	11.54	30.00	7.71	22.05	28.47	55.14
PTI-N-20	0.99	0.97	3.42	8.70	5.93	18.32	14.96	26.52

Fig. 7a, the weight loss before 150 °C is due to the evaporation of traces water and solvent remaining in the AEM. Evaporation of combined water and some solvents in the membrane will lead to a slight decrease in the thermogravimetric curve. The second stage of degradation at 220 °C to 350 °C, which is mainly due to the degradation of the cations. The loss of the cationic groups at this temperature is enough for the application of AEMFCs. In the third stage, degradation of the primary chain of the polymer occurred above 550 °C, which indicates that the poly(*p*-terphenyl isatin) had good high temperature resistance. According to TGA curve, a series of AEMs prepared by experiment have good thermal stability, as well as after high temperature TGA analysis, the quality of PTI-N-*n* series membranes is retained at least 40%, the results show that this series of AEM are enough to meet the requirements of AEMFCs. It also demonstrates the good thermal stability of poly(*p*-terphenyl isatin) as an AEM backbone, which has a

long-term application prospect in alkaline temperature fuel cell applications.

## 2.6 Mechanical properties

During the process of fuel cell assembly and testing, there are some harsh conditions which require that the anion exchange membranes have enough mechanical properties to withstand the test. At 100% relative humidity, the mechanical properties of PTI-N-*n* membranes were tested as shown in Fig. 7b. The tensile strengths of the membranes ranged from 20.13–59.53 MPa, as well as the elongations at break were all in the range of 5–17.64%. The pure PTI membrane shows excellent dimensional stability, and the tensile strength is 59.53 MPa. However, the tensile strength of the membranes will decrease with the increase of the content of side chain branching. As the content of branched chains increases, the unit volume of the molecular chain increases, increasing the





Fig. 7 The graphs of (a) TGA curves of PTI-N-*n* membranes; (b) stress-strain curves of PTI-N-*n* membranes.

water uptake of the AEMs, which weakens the interaction of the polymer backbone and leads to a decrease in tensile strength.<sup>55–57</sup> All PTI-N-*n* membranes showed suitable tensile strength, which proves the good prospect of poly(*p*-terphenyl isatin) as the skeleton of anion exchange membrane (Table 2).

## 2.7 Alkaline stability

The alkali-resistant stability of AEM is an important factor to check whether the fuel cell can operate stably, and it is also the main reason to restrict the development of fuel cell. The attack of nucleophilic OH<sup>-</sup> on cations and main chains is the main cause of degradation of AEM. The retention rate of ionic conductivity for PTI-N-100 and PTI-N-20 are shown in Fig. 8a, in which AEM was continuously immersed in a 2 M KOH at 80 °C for nearly 800 hours. During this period, the ionic conductivity of the membrane was tested at several time intervals, and the data was used to continuously monitor the overall downward trend of ionic conductivity. The monitoring data (a) showed that PTI-N-100 had good alkali stability, and after 792 hours, PTI-N-100 still maintained its initial ionic conductivity of 65.46%. This is due to the special geometric conformation of the piperidine ring cation in the side chain. Through the elimination of transition state and the geometric constraint of substitution, OH<sup>-</sup> corrosion can be effectively reduced, thus improving the alkali resistance.<sup>58</sup> In

addition, the selection of the main chain without ether bond reduces the probability of OH<sup>-</sup> attacking the ether bond of the main chain, and the alkali resistance is further improved.<sup>44</sup>

Fig. 8b shows the <sup>1</sup>H NMR comparison diagram of PTI-N-100 before and after the alkali stability test. From the comparison diagram, it is easy to see that the proton characteristic peaks on the benzene ring of poly(*p*-terphenyl isatin) have not obviously moved or changed, which proves the excellent alkali stability of the poly(*p*-terphenyl isatin). The possible causes of membrane degradation derived from the NMR are (1) nucleophilic substitution of the QA functional group by OH<sup>-</sup> attack, leading to the formation of alkyl alcohols,<sup>59</sup> a degradation pathway that is identified by the appearance of the signal at 4.5 ppm and 0.86 ppm. (2) Hofmann elimination reaction of β-H of the piperidinium due to attack by OH<sup>-</sup>, identified by the signal peaks at 5.01 ppm and 5.68 ppm in the nuclear magnetogram.<sup>60</sup> As can be seen from the figure, the main degradation is carried out by the above two ways. It is worth mentioning that the alkali resistance of quaternary ammonium cations was poor in previous studies,<sup>61</sup> and we expected that the introduction of piperidone with special geometrical conformations and ether-free bonded backbones would improve the alkali resistance of the membranes. From the comparison of the results, this synergistic structural design did improve the alkali resistance.

Table 2 Mechanical properties of PTI-N-*n* membranes

Samples	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)
PTI	25	59.53	17.64
PTI-N-40	23	30.93	5.06
PTI-N-60	26	29.36	7.73
PTI-N-100	22	20.18	8.94

## 2.8 Single H<sub>2</sub>/O<sub>2</sub> fuel cell performance

Fuel cell performance is a necessary indicator to test the commercialization and viability of AEMs. To some extent, it reflects their practical application. For the tests, we used PTI-N-100 to assemble the membrane electrodes. The polarization curve of PTI-N-100 is shown in Fig. 9. Fuel cells assembled from PTI-N-100 membrane have 0.86 V open-





Fig. 8 (a) Curves of ionic conductivity retention versus immersion time of the membranes in 2 M KOH at 80 °C; (b) <sup>1</sup>H NMR of PTI-N-100 membranes after alkali stability testing and (c) schematic diagram of degradation mechanism.



Fig. 9 (a) PTI-N-100 membrane electrode physical photo; (b) single-cell performance of AEMFCs with PTI-N-100 membranes at a cell temperature of 80 °C.





circuit voltage and  $180 \text{ mW cm}^{-2}$  peak power density, and there is no back pressure (Fig. 10).<sup>62–66</sup>

### 3 Conclusion

In summary, PTI polymers functionalized with different ratios of heterogeneous multi-cation side chains were designed. The preparation for developing excellent AEMs with good conductivity and long-term stability is made by molecular structure design. PTI-N-100 has an appropriate swelling rate of 41.05% at 80 °C, but it has high IEC, water absorption, good hydrophilicity and obvious microphase separation structure. The reason is that the dense cation groups in the membrane are beneficial to the transmission of anions. The introduction of multi-cations provides more  $\text{OH}^-$  transport sites and constructs multiple ion transport channels, thus making the ionic conductivity of AEM better. This series of PTI-N-*n* membranes reached a maximum of  $96.83 \text{ mS cm}^{-1}$  at 80 °C. Its wet mechanical strength is good, which is greater than 20 MPa. The thermal performance test shows that the main chain has higher thermal decomposition temperatures, which can reach 550 °C respectively. The hydroxide conductivity of PTI-N-100 remained 65.46% after nearly 800 h of alkali stability testing in 2 M KOH by AEMs, showing good long-term alkali stability. It shows that the highly rigid polymer skeleton has made outstanding contributions to improving the performance of AEM. The construction of an ether-free backbone reduces the chance that  $\text{OH}^-$  attacks the backbone. At the same time, the combination of two different half-life cations ensures the alkali stability of the AEM. The test results show that the good comprehensive properties of PTI anion exchange membrane functionalized by quaternary ammonium and piperidine cations can be compared with most AEMs reported so far. PTI-N-100 membrane have 0.86 V open-circuit voltage and  $180 \text{ mW cm}^{-2}$  peak power density.



Fig. 10 Plot of power density and conductivity of PTI-N-100 with those of AEMs in other reports.

This means that different molecular structure design schemes have an important impact on improving the performance of anion exchange membranes.

### 4 Experimental section

#### 4.1 Materials

4-Chloro-1-methylpiperidine (98%), *p*-terphenyl (99%), isatin (98%), 3-chloro-1-(*N,N*-dimethyl) propylamine (98%),  $\text{K}_2\text{CO}_3$  (99%), trifluoroacetic acid (TFA, 99%), iodomethane (99%), trifluoromethanesulfonic acid (TFSA, 98%) were purchased from Aladdin. The dichloromethane (99.5%) and dimethyl sulfoxide (DMSO) were purchased from Tianjin Fine Chemical Co., Ltd.

#### 4.2 Synthesis of polymers

Poly(*p*-terphenyl isatin) (PTI) was synthesized by super acid-catalyzed stepwise polymerization. In a three-necked flask, *p*-terphenyl (1.0 g, 4.3 mmol) and isatin (0.69 g, 4 mmol) were dissolved in dichloromethane at 0 °C. TFSA (3.3 mL) and TFA (3.3 mL) were slowly dropped into the flask and mixed for 45 minutes. When the color of the mixed solution turns red-brown, it slowly precipitates in methanol to form a slightly yellowed solid. The polymer was cut into small pieces, boiled with an ethanol and deionized water solution, and dried at 40 °C for 24 hours.

**4.2.1 Synthesis of 4-ClPq.** 4-Chloro-1-methylpiperidine (1.2934 g, 9.68 mmol) was dissolved in ethyl acetate (50 mL) and stirred at 25 °C for 5 minutes. Methyl iodide (4.8458 g, 34.14 mmol) was added under magnetic stirring, and the mixture was stirred for 24 hours at 25 °C.

**4.2.2 Synthesis of 3-N-4-ClPq.** 3-Chloro-1-(*N,N*-dimethyl) propylamine (1 g, 0.009 mol) was dissolved in 20 mL of DMSO and stirred for 5 minutes. Then, 4-ClPq (2 g, 0.0099 mol) was added dropwise to the solution and reacted at 80 °C for 48 hours.

**4.2.3 Synthesis of PTI-N-*n*.** The specific synthesis steps for PTI-N-100 are: purge the three-necked flask several times with  $\text{N}_2$ . PTI (1 g, 0.0035 mol) was completely dissolved in 20 mL DMSO, then 3-N-4-ClPq (2.7 g, 0.007 mol) and  $\text{K}_2\text{CO}_3$  (0.96 g, 0.007 mol) were added at 65 °C and reacted for 48 h. The unreacted  $\text{K}_2\text{CO}_3$  was filtered out, and the solution was poured into ethyl acetate and dried at 40 °C to obtain a yellowish solid. Due to the adjustment of the molar ratio of PTI main chain and 3-N-4-ClPq, PTI-N-*n* (*n* = 80, 60, 40, 20) is obtained.

**4.2.4 Membrane preparation.** PTI-N-*n* was dissolved in DMSO (2 wt%) to prepare AEM, the solution was evenly spread on the glass board, and the glass board was dried in an oven at 80 °C for 24 h.

#### 4.3 Characterization and measurements

**4.3.1 Structure characterization.** Molecular structures of PTI and PTI-N-*n* (*n* = 100, 80, 60, 40, 20) were confirmed by nuclear magnetic resonance hydrogen spectroscopy ( $^1\text{H}$



NMR). The  $^1\text{H}$  NMR spectra were obtained at 500 MHz by a Bruker NMR spectrometer. FTIR was measured by the Nicolet Avatar-360 spectrometer, and the scanning range was from 700 to 4000  $\text{cm}^{-1}$ .

**4.3.2 Performance characterization.** Scanning electron microscopy (SEM) was used to observe the external morphology of the membrane. SEM tests were carried out on a JEOL-7610F. AEM was washed in deionized water, then dried under vacuum, and the images were observed at a 15 kV accelerated voltage. TEM was analyzed with an 80 kV accelerating voltage on the JEOL-2000 EX. Before measurement, samples were prepared by soaking the product in a 0.5 M KI solution for 2 days, then drying it overnight in vacuum, dissolving it in dimethyl sulfoxide, and fishing out the membrane with a copper mesh.

**4.3.3 Ion exchange capacity (IEC), water uptake (WU), swelling ratio (SR).** The IEC value is calculated by molar titration of the number of effective functional groups in the membrane. The IEC of AEM is determined by the reverse titration method. First, immerse the AEM samples in the form of  $\text{OH}^-$  in the standard solution of  $V_1$  mL, 0.01  $\text{mol L}^{-1}$  ( $C_1$ ) HCl for ion exchange. After that, the membranes were removed and washed with deionized water to remove the residual salt on the surface, and the membrane samples were dried to a constant weight, and the dry weight  $m_{\text{dry}}$  was recorded. Finally, adding phenolphthalein as indicator, titrating with 0.01  $\text{mol L}^{-1}$  ( $C_2$ ) NaOH standard solution and recording the volume of alkali consumed ( $V_2$ ). The IEC formula is as follows:

$$\text{IEC} = \frac{C_1 V_1 - C_2 V_2}{m_{\text{dry}}}$$

The water uptake test of AEM is to dry the membrane sample in an oven at 80  $^\circ\text{C}$  and dry it to the constant weight of  $m_{\text{dry}}$ . The film samples were immersed in deionized water at 20  $^\circ\text{C}$ , 40  $^\circ\text{C}$ , 60  $^\circ\text{C}$  and 80  $^\circ\text{C}$  respectively for 24 h. After 24 h, the membrane samples were removed, and the surface moisture of the membrane samples was quickly dried with filter paper and weighed to obtain  $m_{\text{wet}}$ . WU was calculated as follows:

$$\text{WU} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%$$

The swelling rate test of AEM is roughly the same as the water absorption test: after drying the membrane sample, the membrane thickness was measured to  $d_{\text{dry}}$ . At different temperatures, the membrane thickness was measured by soaking for 24 h and drying the surface water to obtain  $d_{\text{wet}}$ . SR was calculated as follows:

$$\text{SR} = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \times 100\%$$

**4.3.4 Ion conductivity.** Ion conductivity is measured from 0.1 Hz to 105 Hz by using the four-probe impedance method (AC). AEM is installed in a PTFE mold, and the distance between the reference electrodes is 1 cm. Fully hydrated samples with a size of 1  $\times$  5 cm were immersed in a water bath for testing.  $A$  ( $\text{cm}^2$ ) is the cross-sectional area of the membrane and  $L$  (cm) is the distance between the mold electrodes. Hydroxide conductivity ( $\sigma$ ,  $\text{mS cm}^{-1}$ ) was calculated as follows:

$$\sigma = \frac{L}{R \times A}$$

**4.3.5 Thermal stability.** The thermal stability test of AEM was completed on PerkinElmer Pyris thermogravimetric analyzer. The test process is in  $\text{N}_2$ . Heat from 30  $^\circ\text{C}$  to 800  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C min}^{-1}$ . The thermal stability of the test sample was tested in the form of  $\text{OH}^-$ .

**4.3.6 Mechanical properties.** The mechanical strength of AEM was tested by Shimadzu AGS-X electronic universal testing machine (100 N, Japan). The membrane was cut into 5 mm wide and 30 mm long membrane samples and tested at a stretching rate of 1  $\text{mm min}^{-1}$ .

**4.3.7 Alkaline stability.** The AEM samples were immersed in 2  $\text{mol L}^{-1}$  KOH solution at 80  $^\circ\text{C}$  for a period of time. After washing the alkaline solution on the surface of the membrane with ultra-pure water, the ionic conductivity data were tested and the alkali resistance curve was obtained.

**4.3.8 Fuel cell performance.** First, the Pt/C catalyst was coated on the surface of the carbon papers, and the loading content of the catalyst for both two electrodes was 0.5  $\text{mg cm}^{-2}$ . Then the membrane was immersed in 1 M NaOH aqueous solution at ambient temperature for 24 h and sandwiched in the middle of carbon papers to fabricate membrane electrode assemblies (MEAs). Finally, the performance of the single  $\text{H}_2/\text{O}_2$  fuel cell was tested at 75  $^\circ\text{C}$  at the anode and 77  $^\circ\text{C}$  at the cathode with both  $\text{H}_2$  and  $\text{O}_2$  fluxes of 150  $\text{mL min}^{-1}$  and no back pressure.

## Conflicts of interest

The authors declare no conflict of interest.

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