

RAPID COMMUNICATION

Novel aromatic proton exchange membranes based on thiazolothiazole units

Polymer Journal (2017) 49, 745–749; doi:10.1038/pj.2017.47; published online 30 August 2017

INTRODUCTION

Owing to their high energy and low-environmental load, polymer electrolyte fuel cells (PEFCs) have received considerable attention as an alternative energy source. Moreover, because these cells possess a thin electrolyte layer, they can be miniaturized for automotive, domestic and mobile devices and are expected to become the main energy source of these devices.¹ In PEFCs, proton transport from anode to cathode occurs through proton exchange membranes (PEMs). Sulfonated aromatic copolymers, such as polyphenylenes,^{2,3} polyimide,⁴ [poly(arylene-ether-ether-ketone)s]^{5,6} and [poly(arylene-ether-sulfone)] (SPES),^{7,8} are novel PEMs that offer lower cost and better thermal stability than conventional PEMs (for example, Nafion).⁹ The hydrophobic components in a polymer affect the properties and morphology of its corresponding SPES membrane.¹⁰ In addition, the effects of different chemical compositions of aromatic copolymers on the performance of PEMs have been investigated.^{11,12} For example, coplanar units (such as naphthalene) of aromatic copolymers modulate the swelling behavior and membrane morphology.¹¹ These investigations indicate that the physical properties of a membrane are influenced by the introduction of a specific hydrophobic moiety in aromatic copolymers. Furthermore, we have recently reported a novel design concept for PEMs based on benzothiadiazole (BT) units,¹³ which exhibit strong intermolecular interactions and form planar structures.^{14,15} The BT-based membranes exhibit lower water content and more effective proton conductivity compared with those of the parent SPES membranes, which indicates that the introduction of unique units, such as BT molecules, promotes effective proton transfer in PEMs.

This study focused on thiazolothiazole (TT) units, which exhibit strong interactions and a rigid conformation. Previous studies based on a single-crystal structure analysis have shown that monomers based on TT units adopt a planar conformation.¹⁶ In addition, the intermolecular distance of the monomers is short compared to its van der Waals radius.¹⁶ Specifically, the actual (d_{actual}) and van der Waals values ($d_{\text{v.d.W.}}$) of TT are 3.25 and 3.60 Å, respectively. In the BT unit, the d_{actual} and $d_{\text{v.d.W.}}$ are 3.19 and 3.35 Å, respectively.¹⁵ The ratio ($d_{\text{actual}}/d_{\text{v.d.W.}}$) of the TT unit is smaller than that of the BT unit, which indicates that the interaction between TT units is effective compared with that between the BT units. This closed structure is caused not only by the planar conformation, but also by intermolecular interactions (heteroatom interactions) between the atoms owing to their electrostatic bias. Therefore, TT units may be useful for tailoring the morphology and physical properties of molecular functional materials, such as organic semiconductors, in a similar manner to BT.^{17,18} These results encouraged us to investigate the effect of introducing TT units into a polymeric membrane on its morphology and physical properties, which include its water content and proton conductivity. Consequently, we designed a new aromatic copolymer based on the TT unit (Figure 1). The introduction of TT units to aromatic copolymers is expected to realize polymers with unique morphologies and high proton conductivities. This communication describes the simple synthesis of TT-based copolymers and the preparation of membranes from these copolymers. We also evaluated the physical properties and proton conductivity of the synthesized TT-based membranes.

EXPERIMENTAL PROCEDURES

Materials

Dithiooxamide (DOA), p-fluorobenzaldehyde (p-FBA), *N,N*-dimethylformamide (DMF) and potassium carbonate (K_2CO_3) were purchased from Wako Pure Chemical Industries. 4,4'-Biphenol (BP) and 4,4'-dichlorodiphenyl sulfone (DCDPS) were purchased from Tokyo Chemical Industry Co. 3,3'-Disulfonated-4,4'-dichlorodiphenyl sulfone sodium salt (SDCDPS) was purchased from NARD Institute Ltd, Osaka, Japan. Both DCDPS and SDCDPS were dried in a vacuum oven for 24 h at 80 °C before use.

General

¹H and ¹³C NMR spectra were recorded on a Bruker model AVANCE-500 spectrometer that operated at 500 MHz for ¹H and 125 Hz for ¹³C. The chemical shifts (δ in p.p.m.) were determined with respect to non-deuterated solvent residues as internal references. The sulfonation degree and ion exchange capacity (IEC) of the products were calculated via ¹H NMR integration.¹⁹ The weight-average and number-average molecular weights (M_w and M_n , respectively) of the product were determined using permeation chromatography (GPC, L-7100 Hitachi Co., Ltd, Tokyo, Japan; Shodex Oven A0-30, Showa Denko KK, Tokyo, Japan; Shodex RI-71, Showa Denko KK; UV L-7400, Hitachi Co., Ltd.; Shodex Asahipak GF-7MHQ columns, Showa Denko KK). The standard curve in the molecular weight determination was created from a polystyrene standard solution (TSK, Tosoh Corp., Tokyo, Japan). Ultraviolet (UV) spectroscopy (U-3310, Hitachi Co. Ltd.) was used to estimate the mole fraction of TT units in the copolymers based on the molar attenuation coefficient (ϵ) of its monomer. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer model Pyris 1 Thermogravimetric analyses, and the heating profile was recorded and analyzed using a Perkin-Elmer Pyris software system.

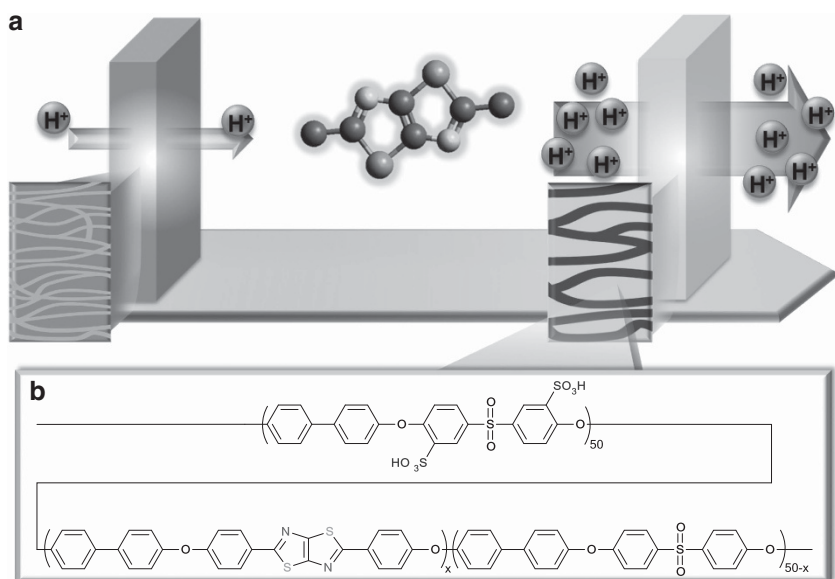


Figure 1 (a) Schematic illustration and (b) molecular structure of the designed random polymer based on thiazolothiazole (TT) units ($x=0.1$ and 1). A full colour version of this figure is available at the *Polymer Journal* journal online.

Structural analysis

The membrane surface morphology was investigated using tapping-mode atomic force microscopy (AFM, Cypher S, Oxford Instruments, Oxfordshire, UK). The AFM was performed using microfabricated cantilevers. Before the measurements, all samples were vacuum-dried at $50\text{ }^{\circ}\text{C}$ for 12 h.

Water content measurements

The water content at different RHs (30–95%) was measured as the amount of water adsorbed at $80\text{ }^{\circ}\text{C}$. The membranes were dried at $60\text{ }^{\circ}\text{C}$ in a vacuum oven for 15 min to obtain the dry weight (W_{dry}). Next, each membrane was suspended under atmospheric and relative humidity conditions at $80\text{ }^{\circ}\text{C}$ until swollen, and its wet weight (W_{wet}) was recorded. The water content of the membranes was calculated using equation 1.

$$\text{Water content} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{wet}} \times 100\%. \quad (1)$$

Proton conductivity measurements

The proton conductivity σ (S cm^{-1}) of the membranes was measured by an AC impedance method using a Solatron 1260 impedance analyzer, as reported in a previous study.¹⁹ Four platinum electrodes were placed on a membrane on a glass plate. The platinum electrodes and membrane were secured by another glass plate that was placed on the electrodes. The measurement conditions were controlled using a bench-top-type temperature and humidity chamber (SH-221,

ESPEC). The impedance spectra were then measured using ZPlot/ZView software (Scribner Associates) under an AC perturbation signal of 10 mV in the frequency range of 1 Hz to 10 000 KHz. The proton conductivity σ (S/cm) was calculated using equation 2.

$$\text{Proton conductivity} \quad \sigma = D / (R \times L \times T) \times 10^4 \text{ S/cm} \quad (2)$$

where R is the membrane resistance, D is the distance between two platinum electrodes and L and T are the membrane width and thickness, respectively.

Synthesis of the hydrophobic monomer based on a thiazolothiazole unit

p-FBA (15.0 g, 121 mmol), DOA (3.64 g, 30.3 mmol) and 335 ml of DMF were added to a 500-ml round-bottom flask with a reflux condenser and stirring bar. The reaction was carried out for 6 h at $150\text{ }^{\circ}\text{C}$. After the reaction, the flask was cooled to room temperature and the reaction mixture was poured into a large quantity of water. Methanol was added to the crude product to remove the unreacted feed materials. The obtained solid was sublimated at $250\text{ }^{\circ}\text{C}$ overnight. Next, the product was dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 24 h to completely remove the solvent (yield: 50%). The obtained polymers were characterized using ^1H NMR and ^{13}C NMR (Supplementary Figure S1). ^1H NMR (500 MHz, DMSO d_6): (p.p.m.) 8.13–8.09 (H_a), 7.45–7.40 (H_b). ^{13}C NMR (125 MHz, DMSO d_6): (p.p.m.) 168.00 (H_a), 163.19 (H_c), 150.78 (H_f), 130.20 (H_d), 129.1 (H_c), 117.2 (H_b).

Synthesis of the TT-based random polymer

Target polymers with different mol% of TT units were prepared by changing the molar ratio of the TT monomer. Herein, 0.1 and 1 mol% TT were used; high TT content imparts low solubility that hinders high molecular weight polymer synthesis. Polymers with 0, 0.1 and 1 mol% TT units were labeled as SPES, 0.1% TT and 1% TT, respectively. A typical synthetic procedure that is illustrated by the preparation of 0.1% TT copolymer is described as follows (Supplementary Figure S2). SDCDPS (5.1077 g, 10.4 mmol), BP (3.8727 g, 20.8 mmol), DCDPS (2.9800 g, 10.4 mmol), TT (0.0069 g, 0.021 mmol), K_2CO_3 (9.0018 g, 65.1 mmol) and 100 ml of NMP were added to a three-necked 300-ml flask equipped with a reflux condenser, a dean-stark trap, a nitrogen inlet and a mechanical stirrer. The solution was heated at $135\text{ }^{\circ}\text{C}$ for 4 h to dissolve the monomer in NMP. Next, 20 ml of toluene was added to this solution and the mixture was heated at $155\text{ }^{\circ}\text{C}$ until the toluene was completely removed. The resulting solution was maintained at $185\text{ }^{\circ}\text{C}$ for 12 h. After cooling to room temperature, the mixture was filtered to remove the K_2CO_3 . The filtered solution was placed on a molecular porous membrane and dialyzed for 3 days while replacing the outside solvent. The solution was poured into a large quantity of 2-propanol. The crude product was washed with hot methanol several times and dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 24 h (yield: 68%). The obtained polymers were characterized using ^1H NMR (Supplementary Figure S3) and ^{13}C NMR (Supplementary Figure S4). ^1H NMR (500 MHz, DMSO d_6): (p.p.m.) 8.34 (H_e), 7.98–7.96 (H_i , H_m), 7.88 (H_d), 7.77–7.71 (H_b , H_g , H_k), 7.20–7.12 (H_a , H_f , H_h , H_j , H_l), 7.01 (H_t). ^{13}C NMR (125 MHz, DMSO d_6): (p.p.m.) 161.8 (H_j), 158.7–158.6 (H_e , H_s), 156.0–155.7 (H_k , H_u), 154.6–154.4 (H_a , H_o), 139.5 (H_y), 136.9–134.7 (H_d , H_b , H_n , H_r , H_a' , H_b'), 130.4 (H_g), 129.1–128.7 (H_c , H_i , H_m , H_q , H_v , H_w), 121.2–119.9 (H_t , H_f , H_l , H_p , H_z), 118.5 (H_z).

Membrane preparation

SPES and TT-based membranes were prepared by casting the polymer solution (20 wt%) onto glass plates and controlling the thickness with an applicator. The membranes were dried on a heater at $50\text{ }^{\circ}\text{C}$ for 12 h. The prepared membranes were suspended in a 1 M H_2SO_4 solution at $90\text{ }^{\circ}\text{C}$ for 1 h, which allowed sodium-ion exchange with protons, and was then washed with deionized hot ($80\text{ }^{\circ}\text{C}$) water.

RESULTS AND DISCUSSION

The molecular weights of the polymers were determined via GPC using polystyrene as the standard. The number-averaged molecular weight was at least 20 kDa for a polydispersity (M_w/M_n) value of 3.0 (Table 1). The TT mole

Table 1 Properties of TT-based polymers with various proportions of TT units

Samples	χ^a (%)	IEC_{dry}^b (meq g ⁻¹)	IEC_{cal}^c (meq g ⁻¹)	M_n^d (kg mol ⁻¹)	M_w^d (kg mol ⁻¹)	$M_w/M_n(-)$
SPES	44.5	2.01	2.0	30.6	60.3	2.0
0.1% TT	44.3	2.00	2.0	22.0	63.1	2.9
1% TT	44.4	2.01	2.0	21.5	65.5	3.1

^aSulfonation degree estimated from ¹H NMR measurements.

^bIEC in the dry condition calculated from the sulfonation degree.

^cIEC calculated from molecular structure.

^dNumber-averaged molecular weight and weight-averaged molecular weight calculated from the GPC measurements using polystyrene standard samples.

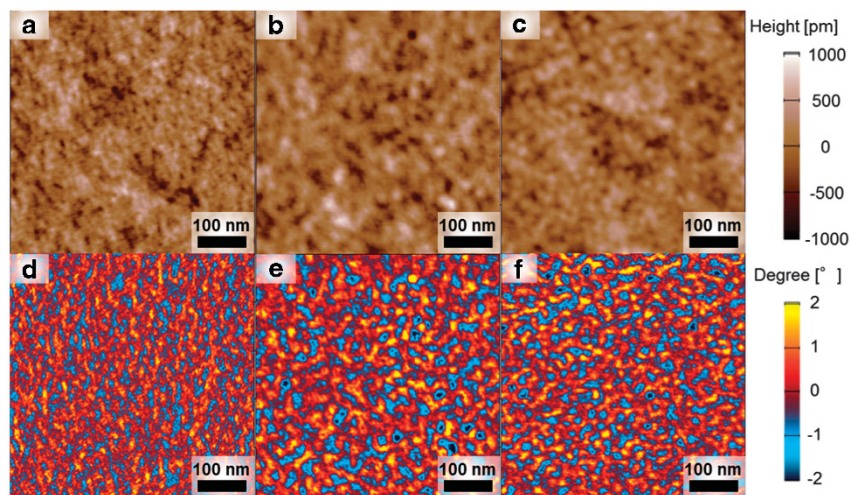


Figure 2 (a–c) Heights and (d–f) phases of tapping-mode microscopy (TM-AFM) images of a sulfonated [poly(arylene-ether-sulfone)] (SPES) membrane (left), a 0.1 mol% TT membrane (center) and a 1 mol% TT membrane (right). In the phase images, the hydrophobic and hydrophilic regions are in yellow and blue, respectively (scan size: 500 nm). Conditions: 22 °C, 87% RH.

fraction in the copolymers was estimated by a comparison with the UV spectra for BT-based copolymers (Supplementary Figure S5), whose BT mole fraction was defined by ¹H-NMR in a previous report¹³. It is estimated via Beer–Lambert law using attenuation coefficient (ϵ) of the monomer (Supplementary Table S1). For the BT-based copolymer, the BT mole fraction obtained from ¹H NMR ($x_{BT}^{1H\ NMR}$) is equal to charge ratio of the unit. In addition, the BT mole fraction in BT-based copolymers that was obtained using UV spectroscopy (x_{BT}^{UV}) was slightly larger compared with that of $x_{BT}^{1H\ NMR}$, which was 1.6 times larger than the charge ratio of the monomer (Supplementary Table S2). Furthermore, the TT mole fraction in the TT-based copolymers that was estimated using UV spectroscopy (x_{TT}^{UV}) was 1.7 times larger than the charge ratio of the monomer, which was similar to that of the BT unit (Supplementary Table S2). The deviation in the mole fraction that was estimated from ¹H NMR and UV spectroscopy may be derived from the difference in ϵ between monomers and copolymers due to changes in the conjugated structure for the units. The deviation between the charge ratio and mole fractions

that were estimated from UV spectroscopy of the BT and TT units are almost same. Therefore, we confirmed that the charge ratio of the TT unit is a proxy for polymer TT mole fraction. The ¹H NMR, GPC and UV spectroscopy measurements confirmed that the obtained products were the target polymers that were comprised of the TT unit. The IEC of the membranes was nearly 2.0 meq g⁻¹, as calculated from the ¹H NMR integration and was attributable to sulfonic acid groups (Table 1). The TT units provide excellent flexibility to the membranes (Supplementary Figure S6). In addition, large-area membrane preparation is easy, which indicates that the mechanical properties of the TT-based membrane are sufficient for PEMs. Moreover, the prepared membranes emitted clear blue fluorescence, which is derived from the TT unit under ultraviolet (UV) light (wavelength = 365 nm; Supplementary Figure S7). This result revealed that the prepared membranes comprised a newly synthesized TT-based copolymer. The thermal stabilities of the TT-based polymers were investigated using thermogravimetric analysis (Supplementary Figure S8). Both TT-based polymers exhibited excellent stability, which was similar to that of their

parent SPES. In addition, TT-based membranes have nearly the same oxidative stability as the corresponding SPES membranes, that is, a small TT mol fraction is not deleterious to membrane oxidative stability.

The surface morphologies of the prepared membranes were characterized using tapping-mode atomic force microscopy (TM-AFM). Figures 2a–c shows the height images of the membranes. These images confirmed that the membranes are sufficiently smooth for investigation in the phase mode. The phase-mode images are presented in Figures 2d–f. The membranes possess hard hydrophobic regions and soft hydrophilic regions that contain sulfonic acid groups or small amounts of water. The total areas and average sizes of the strongly hydrophobic and hydrophilic domains in the membrane surfaces were estimated from their phase images. The TT-based membranes exhibit more hydrophobic surface domains than their parent SPES membrane. The strongly hydrophobic parts are composed of condensed hydrophobic domains that contain TT units (attributable to their intermolecular interaction and planar conformation). The TT units also changed the total area and average size of the hydrophilic domains. We suggest that hydrophobic part of polymer chains strongly interacts with the TT unit and constructs hydrophobic domains, which induces aggregated hydrophilic domains in the polymer chain. Although the sizes and areas of the hydrophilic regions were similar in the BT-based and TT-based membranes, the strongly hydrophobic area was smaller in the TT-based membranes than in the BT-based membranes (Supplementary Table S3). These results suggest that the hydrophobic domain condition of the membranes depends on the property of the unit.

The water content of the TT-based membranes was determined as a function of relative humidity at 80 °C (Supplementary Figure S9). The water content of the TT-based membranes was nearly equal to that of the parent SPES membranes. Therefore, unlike the BT unit, the TT unit does not influence the swelling behavior of the membrane. The TM-AFM investigation suggests that different water

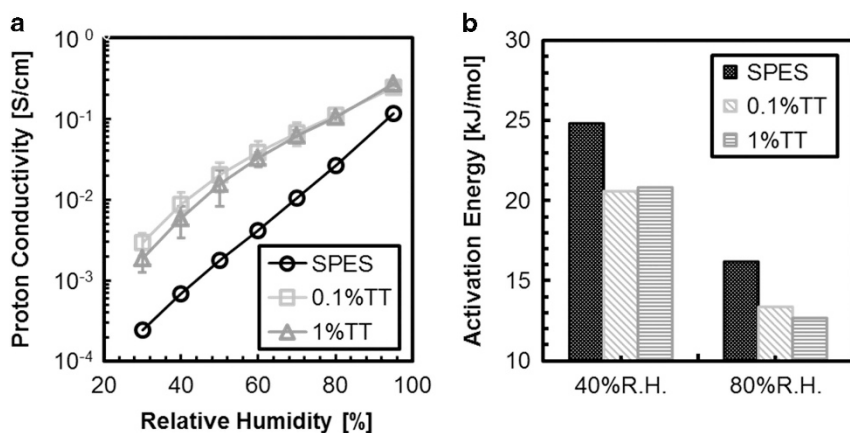


Figure 3 Effect of TT units on (a) proton conductivity and (b) activation energy (RH=40 and 80%) of proton exchange membranes (PEMs). A full colour version of this figure is available at the *Polymer Journal* journal online.

content behaviors between BT-based and TT-based membranes are caused by the changing total area occupied by strongly hydrophobic domains in the membrane surface.

The densities of the sulfonic acid groups in the hydrophilic parts of SPES and TT-based membranes were investigated using Fourier transform infrared (FT-IR) measurements. In the spectrum of the TT-based membrane, the absorption peak that was related to the O–S–O asymmetric stretching vibration appeared at higher wavenumbers than in the SPES membrane spectrum (Supplementary Figure S10). In previous research, this peak shift was attributed to weaker H-bonds in a membrane structure with highly interacting sulfonic acid groups, which enhance proton conduction through the sulfonic acid groups.²⁰ The investigation implies that the introduced TT units create a structure that favors proton transfer through the sulfonic acid groups by increasing their density.

Finally, the proton conductivity of the TT-based membranes was evaluated using impedance measurements. The proton conductivities of the TT-based and SPES-based membranes as a function of relative humidity at 80 °C are shown in Figure 3a. Clearly, the inclusion of TT improves the proton conductivity of the membrane. At 30% RH, the proton conductivity is eight times higher in both TT-based membranes than in the parent SPES membranes. The proton conductivity of the TT-based membranes is as high as that of the BT-based membranes. The activation energy of proton conductivity at 80% RH and 40% RH was calculated from the Arrhenius plot (Figure 3b). The activation energy was lower in the TT-based membranes than in the parent SPES membranes and almost matched that of BT-based membranes over a wide range of RH. This

difference indicates that the TT unit (like its BT counterpart) expresses a unique morphology, which further encourages proton transfer in the PEM. We speculate that effective proton transfer was induced by the formation of a favorable conformation for proton conduction in the TT-based membranes.

In summary, we successfully synthesized TT-containing polymers using a simple method. Even a few TT units affected the hydrophobic and hydrophilic domains on the membrane surface by increasing the proton conductivity and lowering its activation energy compared to the parent SPES membranes. Moreover, the hydrophobic domain property of the membrane likely depends on the unit introduced to the polymer. Therefore, we expect that by introducing a unique unit with specific interaction behavior (such as a BT or TT unit), we can control the physical properties of membranes.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

This study was supported by the Kanagawa Academy of Science and Technology. We would like to thank Mr Motoya Suzuki (Material Analysis Suzukake-dai Center, Tokyo Institute of Technology) for the AFM measurements and discussion.

Shuntaro Amari¹, Shinji Ando^{1,2} and Takeo Yamaguchi^{1,2}

¹Laboratory for Chemistry and Life Science Institute of Innovative Research, Tokyo Institute of Technology, Kanagawa, Japan and ²Kanagawa Academy of Science and Technology, Kanagawa, Japan

E-mail: yamag@res.titech.ac.jp

- Kirubakaran, A., Jain, S. & Nema, R. K. A review on fuel cell technologies and power electronic interface. *Renew. Sustain. Energy Rev.* **13**, 2430–2440 (2009).
- Ghassemi, H. & McGrath, J. E. Synthesis and properties of new sulfonated poly(p-phenylene) derivatives for proton exchange membranes. *Polymer* **45**, 5847–5854 (2004).
- Zhang, X., Sheng, L., Higashihara, T. & Ueda, M. Polymer electrolyte membranes based on poly(m-phenylene)s with sulfonic acid via long alkyl side chains. *Polym. Chem.* **4**, 1235–1242 (2013).
- Saito, J., Miyatake, K. & Watanabe, M. Synthesis and properties of polyimide ionomers containing 1H-1,2,4-triazole groups. *Macromolecules* **41**, 2415–2420 (2008).
- Xing, P. X., Robertson, G. P., Guiver, M. D., Mikhailenko, S. D., Wang, K. P. & Kaliaguine, S. Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. *J. Membr. Sci.* **229**, 95–106 (2004).
- Padmavathi, R. & Sangeetha, D. Design of novel SPEEK-based proton exchange membranes by self-assembly method for fuel cells. *Ionics* **19**, 1423–1436 (2013).
- Wang, F., Hickner, M., Kim, Y. S., Zawodzinski, T. A. & McGrath, J. E. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. *J. Membr. Sci.* **197**, 231–242 (2002).
- Feng, S. N., Shen, K. Z., Wang, Y., Pang, J. H. & Jiang, Z. H. Concentrated sulfonated poly(ether sulfone)s as proton exchange membranes. *J. Power Sources* **224**, 42–49 (2013).
- Park, C. H., Lee, C. H., Guiver, M. D. & Lee, Y. M. Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs). *Prog. Polym. Sci.* **36**, 1443–1498 (2011).
- Bae, B., Miyatake, K. & Watanabe, M. Effect of the hydrophobic component on the properties of sulfonated poly(arylene ether sulfone)s. *Macromolecules* **42**, 1873–1880 (2009).
- Gao, Y., Robertson, G. P., Guiver, M. D., Mikhailenko, S. D., Li, X. & Kaliaguine, S. Low-swelling proton-conducting copoly(aryl ether nitrile)s containing naphthalene structure with sulfonic acid groups meta to the ether linkage. *Polymer* **47**, 808–816 (2006).
- Wang, G., Lee, K. H., Lee, W. H., Kang, N. R., Shin, D. W., Zhuang, Y. B., Lee, Y. M. & Guiver, M. D. Soluble sulfonated polybenzothiazoles containing naphthalene for use as proton exchange membranes. *J. Membr. Sci.* **490**, 346–353 (2015).
- Amari, S., Ando, S. & Yamaguchi, T. Development of novel polymer electrolyte membranes based on a benzothiadiazole unit. *RSC Adv.* **6**, 99433–99436 (2016).
- Mataka, S., Takahashi, K., Imura, T. & Tashiro, M. Reduction of 4,7-Diphenyl-1,2,5-Thia(Oxa)Diazolo[3,4-C]pyridines affording 2,5-Diphenyl-3,4-diaminopyridines and ring-closure of the diamines to fluorescent azaheterocycles. *J. Heterocyclic Chem.* **19**, 1481–1488 (1982).
- Akhtaruzzaman, M., Kamata, N., Nishida, J., Ando, S., Tada, H., Tomura, M. & Yamashita, Y. Synthesis, characterization and FET properties of novel dithiazolylbenzothiadiazole derivatives. *Chem. Commun.* **25**, 3183–3185 (2005).
- Ando, S., Nishida, J. I., Tada, H., Inoue, Y., Tokito, S. & Yamashita, Y. High performance n-type organic field-effect transistors based on pi-electronic systems with trifluoromethylphenyl groups. *J. Am. Chem. Soc.* **127**, 5336–5337 (2005).
- Ando, S., Nishida, J., Fujiwara, E., Tada, H., Inoue, Y., Tokito, S. & Yamashita, Y. Characterization and field-effect transistor performance of heterocyclic oligomers containing a thiazolothiazole unit. *Chem. Lett.* **33**, 1170–1171 (2004).

- 18 Ando, S., Kumaki, D., Nishida, J., Tada, H., Inoue, Y., Tokito, S. & Yamashita, Y. Synthesis, physical properties and field-effect transistors of novel thiazolothiazole-phenylene co-oligomers. *J. Mater. Chem.* **17**, 553–558 (2007).
- 19 Hara, N., Ohashi, H., Ito, T. & Yamaguchi, T. Rapid proton conduction through unfreezable and bound water in a wholly aromatic pore-filling electrolyte membrane. *J. Phys. Chem. B* **113**, 4656–4663 (2009).
- 20 Ogawa, T., Aonuma, T., Tamaki, T., Ohashi, H., Ushiyama, H., Yamashita, K. & Yamaguchi, T. The proton conduction mechanism in a material consisting of packed acids. *Chem. Sci.* **5**, 4878–4887 (2014).

Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)