Synthetic polyelectrolytes, capable of fast transporting protons, represent a challenging target for membrane engineering in so many fields, for example, fuel cells, redox flow batteries, etc. Inspired by the fast advance in molecular machines, here we report a rotaxane based polymer entity assembled via host-guest interaction and prove that by exploiting the thermally triggered translational motion (although not in a controlled manner) of mechanically bonded rotaxane, exceptionally fast proton transfer can be fulfilled at an external thermal input. The relative motion of the sulfonated axle to the ring in rotaxane happens at ~60 °C in our cases and because of that a proton conductivity (indicating proton transfer rate) of 260.2 mS cm$^{-1}$, which is much higher than that in the state-of-the-art Nafton, is obtained at a relatively low ion-exchange capacity (representing the amount of proton transfer groups) of 0.73 mmol g$^{-1}$.
Fast proton transfer remains a big challenge in so many fields\textsuperscript{1,2}. For instance, highly conductive proton exchange membranes are vital in bumping up the power output of polymer electrolyte based H\textsubscript{2}/O\textsubscript{2} fuel cell (a typical example for clean energy production)\textsuperscript{3,4}. Fast proton transfer is also considered critical in vanadium flow batteries or organic redox flow batteries (representing the most recent advance in energy storage)\textsuperscript{5}. Conventionally, protons are transferred via negatively charged carriers (for instance, sulfonates) in either polymer electrolytes or proton exchange membranes and these carriers are covalently bonded to the polymer backbone\textsuperscript{6,7}, which has limited mobility due to large molecular weight. The limited mobility thereby results in low proton transfer rate, i.e., low proton conductivity and it remains the bottleneck to further enhance the efficiency of many energy conversion and energy storage processes, in which proton transfer is involved\textsuperscript{8,9}.

The external stimuli triggered motion in a molecular machine motivates us and sheds lights on how to further increase proton transfer rate/efficiency. A molecular machine, defined as an assembly of a distinct number of molecular components that are designed to perform machine-like movements as a result of an appropriate external stimulation\textsuperscript{10,11} has been successfully demonstrated and built, based on topological entanglement (mechanical bonds)\textsuperscript{12–14} or isomerisable unsaturated bonds\textsuperscript{15}. Controlled translational/rotational motion and controlled unidirectional rotation in such ingenious design represent the most intricate aspects in making a macroscopic prototype\textsuperscript{16,17}. Yet inspirations from such delicate design could lead to a giant leap forward in many fields.

We proved herein that by introducing the thermally triggered translational motion (although not in a controlled manner) of mechanically bonded rotaxane in a polymeric entity, exceptionally fast proton transfer could be attained at an external thermal supply. We implemented rotaxanes (based on a ring threaded over an axle with stops at both ends) in a polymer and proved that as a result of a thermal input (an increase in temperature), the relatively translational motion of the ring to the axle happens, which was however confined by the stoppers. The axle was modified with sulfonates (thereby negatively charged), which acted as proton transfer carrier. As a consequence, an proton conductivity (indicating proton transfer rate) of 260.2 mS cm\textsuperscript{−1}, which is much higher than that in the state-of-the-art Na\textsuperscript{+} transport membranes is sufficient to disrupt the host–guest interaction (a distinct endothermic peak over the temperature range of 65–75 °C, Supplementary Fig. 14). To render the axles with improved mobility, N-acetylation of sec-ammonium moieties was performed (Supplementary Figs. 12 and 13)\textsuperscript{21}. And we observed the disappear of the sec-ammonium proton signal and a new proton signal of the acetyl group at δ = 2.5 ppm appears (Fig. 2a and Supplementary Fig. 13) in the\textsuperscript{1}H NMR spectrum of the N-acetylated polyrotaxane. We proposed that by eliminating the positive charge in the center ammonium groups via N-acetylation, the host–guest interaction could be weakened, leading to enhanced axle mobility. As confirmed in the space correlation spectrum (NOESY), no strong host–guest interaction signal could be observed (as highlighted in the rectangle, Fig. 2c), suggesting that the axles are moving. This moving mechanism helps us better understand the\textsuperscript{1}H-NMR spectral changes before and after N-acetylation of polyrotaxane. Before N-acetylation, proton signals from the rotaxane moiety overlap in the range of 3.3–2.3 ppm. After N-acetylation, they shift significantly because of the shielding/deshielding effect of the crown ether ring, which is not flat and folds like the letter C\textsuperscript{22}. Partial of proton signals from the axles, which were trapped in the crown ether ring, is shielded, leading to upfield shifts, while others are de-shielded (shifting downfield).

We assumed that the movable nature of the proton carrier, the negatively charged axles, would facilitate proton transfer. To demonstrate such capability, we converted the polyrotaxane polymers into membrane shape, which is commonly referred to as a proton exchange membrane, by solution casting the N-methyl-2-pyrrolidone (NMP, the solvent) solution of 5 (10 wt%) in a clean PTFE petri dish and a transparent membrane (with thickness of 90 ± 7.5 μm, mean ± SD (standard deviation), from five repeated measurements) was obtained after complete solvent evaporation. The counter-ions of the movable axles were then converted to H\textsuperscript{+} in 1 M aqueous HCl at 25 °C for 24 h prior to further characterizations. It should be noted that the acetylated sec-ammonium groups would

Thermally triggered motion of rotaxanes. Differential scanning calorimetry (DSC) curve suggests that the host–guest interaction between sec-ammonium moieties from the axles and the crown ether rings is sufficiently strong. A higher activation energy is required to disrupt the host–guest interaction (a distinct endothermic peak over the temperature range of 65–75 °C, Supplementary Fig. 14). To render the axles with improved mobility, N-acetylation of sec-ammonium moieties was performed (Supplementary Figs. 12 and 13)\textsuperscript{21}. And we observed the disappear of the sec-ammonium proton signal and a new proton signal of the acetyl group at δ = 2.5 ppm appears (Fig. 2a and Supplementary Fig. 13) in the\textsuperscript{1}H NMR spectrum of the N-acetylated polyrotaxane. We proposed that by eliminating the positive charge in the center ammonium groups via N-acetylation, the host–guest interaction could be weakened, leading to enhanced axle mobility. As confirmed in the space correlation spectrum (NOESY), no strong host–guest interaction signal could be observed (as highlighted in the rectangle, Fig. 2c), suggesting that the axles are moving. This moving mechanism helps us better understand the\textsuperscript{1}H-NMR spectral changes before and after N-acetylation of polyrotaxane. Before N-acetylation, proton signals from the rotaxane moiety overlap in the range of 3.3–2.3 ppm. After N-acetylation, they shift significantly because of the shielding/deshielding effect of the crown ether ring, which is not flat and folds like the letter C\textsuperscript{22}. Partial of proton signals from the axles, which were trapped in the crown ether ring, is shielded, leading to upfield shifts, while others are de-shielded (shifting downfield).

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not be affected by the ion exchange treatment. Titrations of the $\text{H}^+$ ions inside the membrane suggest a relatively low ion-exchange capacity (IEC, the amount of functional group content), which is in good accordance with elemental analysis results (0.73 mmol g$^{-1}$, Supplementary Table 2). Water uptake value (measured by the increased weight of dry membrane samples after immersion in DI water at certain temperature for 24 h) indicates that, in average, each sulfonated axle is surrounded by 14 water molecules at 30 °C or by 58 water molecules at 60 °C (Table 1). Despite the amount of water adsorbed, mechanical strength of the as-prepared polyrotaxane membrane is acceptable in the wet state for potential applications (Table 1 and Supplementary Table 3).

The thermally-triggered translational motion of the rotaxanes in the as-prepared membrane was observed in two distinct experiments. We first observed the transparency change of the as-prepared polyrotaxane membrane when the thermal stimulus was applied. As shown in Fig. 3a, the dry membrane samples were transparent in the first place, which gradually became opaque when they were treated in hot water for 2 h (60 °C). And the transparency of the membrane samples was recovered after the samples were dried. We have confirmed that disappear and recovery of transparency in these membrane samples is repeatable. Noting that treating the membrane samples in room temperature water does not cause transparency change and only
samples immersed in D2O as the temperature was increased from 40 to 60 °C, and spectrum recorded from the same NMR tube after removing the sample, hydrated membrane sample (treated in 60 °C water for 2 h) and re-dried membrane sample.

polyrotaxane membrane samples, showing the thermal responsive transparency change in membrane appearance, from bottom to top: dry membrane, (400 MHz, DMSO-d6, 298 K), the poly(crown ether) 1, (400 MHz, CDCl3, 298 K), polyrotaxane 4 (assembled from the 1 and 2 via host-guest interaction, 400 MHz, DMSO-d6, 298 K) and N-acetylated polyrotaxane, 5 (400 MHz, DMSO-d6, 298 K). b NOSEY spectrum of polyrotaxane 4 from the assembly of 1 and 2 (400 MHz, DMSO-d6, 298 K). c NOSEY spectrum of N-acetylated polyrotaxane, 5 (400 MHz, DMSO-d6, 298 K).

**Table 1 Properties of the polyrotaxane proton exchange membranes**

| Membrane     | Grating ratio (GR)a | Ion exchange capacity (IEC) | Water uptake (WU) | Water content ratio| Mechanical properties (60 °C, wet)c |
|--------------|---------------------|-----------------------------|-------------------|-------------------|-----------------------------------|
| Polyrotaxane | 79.9%               | 0.73 (mmol g−1)             | 18.2%             | 76.6%             | 12.01 20.69                       |

aGrating ratio, calculated from the content of the sulfonated axles and crown ether moieties based on the elemental analysis results
bWater content ratio, a molar ratio of water molecules to the sulfonated axles, calculated from WU and IEC
cTS, tensile strength measured in the stress-strain curve; Eb, elongation at break

could slight water swelling be found. We have proved via NMR that the transparency change we observed is not caused by the loss or dissolution of the movable axles since no signals were detected in D2O when the membrane sample was removed (top spectrum in Fig. 3b). We, therefore, conclude that the transparency change in membrane samples is caused by the thermally-triggered motion of rotaxanes. And the thermally triggered translational motion of rotaxanes in the membrane samples was also reflected in the temperature dependent 1H NMR spectra (Fig. 3b). Although in the membrane state, we have detected the proton signals of the hydrated axles in the 40 °C 1H NMR spectrum, which is extremely weak as expected. As the temperature continues to rise, from 50 to 60 °C, the corresponding signals get stronger and stronger, because sufficient energy is provided to activate fast axle movements.

**Accelerated proton transfer.** Because of the thermally triggered motion of rotaxanes, the negatively charged axles (bearing sulfonated functional groups as proton carrier) are now movable at a thermal stimulus. One benefit from the movable proton carriers...
membrane shows almost linearly increasing trend, rising from the anhydrous proton conductivity of the polyrotaxane remains unclear since we currently do not have the facility to water molecules on the thermally triggered motion of rotaxanes witnessed the same thermal responsive behavior of the polyrotaxane membrane and we observed the same trend in independent (Fig. 4a). Proton conductivity measurements under varied temperature demonstrate that only by freeing the linear axes, could accelerated proton transfer be obtained at external thermal stimuli (Fig. 4c). It should be further noted that replacing the linear axes with K⁺ results a membrane that is not capable of transferring protons (Supplementary Fig. 11).

Discussion
In summary, we have assembled a rotaxane based polymer entity via host–guest interaction and demonstrated that at an external thermal stimulus, translational motion of the axes to the rings in rotaxane moieties happens. By exploiting the translational motion of rotaxanes, movable proton carriers (the negatively charged axes) can therefore be implemented. We found that the thermally triggered movement of proton carriers help proton transfer at a much faster rate than that in traditional proton exchange membranes and this striking feature would benefit various fields in energy conversion and energy storage process where proton transfer is involved.

Methods
Chemicals. Hydrobromic acid (HBr) and magnesium sulfate (MgSO₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. Methanesulfonic acid (98%), diphenyl ether (99%), sebacic acid (98%), methyl-4-formylbenzoate (99%), ammonium hexafluorophosphatate (98%), and methyl-4-((aminomethyl)benzoate hydrochloride were purchased from Shanghai Energy-Chemical Co. Ltd. Dibenzo-24-crown-8 and 1-naphthol-3-sulfonic acid sodium salt were purchased from Tokyo Chemical Industry (TCI). Lithium aluminum hydride (LiAlH₄) (97%), phosphorus pentoxide (P₂O₅) and sodium sulfate decahydrate were purchased from Aladdin Industrial Corporation, China. All reagents were used as received.

Synthesis of graft polyrotaxane and preparation of membrane. The synthesis procedures used to prepare 1, 2c, 2d, 2, 4, and 5 are shown in Supplementary Figs. 1–13. Analytical thin-layer chromatography (TLC) was performed on glass sheets pre-coated with the silica gel 60-F254. The ¹H NMR spectra are recorded in ppm.

Synthesis of compound 1. Dibenzo-24-crown-8 (1 mmol), sebacic acid (4 mmol) and diphenyl ether (3 mmol) were dissolved in Eaton’s reagent (12.8 mL), and the mixture was heated to 40 °C and stirred for 24 h. After the reaction was stirred for 24 h, it was poured into water. The slightly yellow fibers that formed were filtered off and washed with water. After the fibers were dried, compound 1d was obtained as a white fiber-like polymer, 2a (98%). ¹H NMR (400 MHz, CDCl₃,
298 K) δ 7.97 (dd, J = 19.5, 8.1 Hz, 8H), 7.54 (dd, J = 17.4, 6.3, 6.8 Hz, 4H), 7.40 (t, J = 7.9 Hz, 3H), 7.20 (t, J = 7.3 Hz, 2H), 7.07 (dd, J = 8.6, 3.8 Hz, 8H), 7.03–6.97 (m, 2H), 6.90 (dd, J = 8.8, 4.7 Hz, 2H), 4.74–4.56 (m, 4H, 4.40–4.12 (m, 12H), 3.94–3.70 (m, 10H), 3.20 (m, J = 5.0 Hz, 1H), 3.05–2.79 (m, 12H), 2.33 (t, J = 7.4 Hz, 2H), 1.88–1.62 (m, 14H), 1.36 (s, 32H).

Synthesis of compound 4c. Compound 2a (1 mmol, 1 equiv) and compound 2b (1 equiv) were dissolved in dry toluene (60 mL), and the mixture was heated under reflux in an argon oven for 24 h using a Dean–Stark apparatus. After the reaction mixture cooled, the solvents were removed under vacuum, and the remaining components were washed with ethanol (3 × 30 mL). Compound 2c was isolated as a white solid (90%). \( ^1H \) NMR (400 MHz, DMSO-d\(_6\), 298 K) δ 8.46 (d, J = 1.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 4.90 (d, J = 1.3 Hz, 2H), 3.93 (d, J = 9.6 Hz, 6H).

Synthesis of compound 2d. A solution of compound 2c (1 equiv) in dry THF was cooled to 0 °C, and powdered LiAlH\(_4\) (6 equiv) was added to the solution to the period of 1 h. The mixture was then warmed to room temperature and heated under nitrogen in an argon atmosphere overnight. After the reaction was stirred overnight, it was cooled to 0 °C. Sodium sulfate decylate (2 equiv) was then carefully added to the flask. The mixture was stirred for 1 h, filtered, and washed with THF. The filtrate was collected and dried (with MgSO\(_4\)), and the solvent was removed under vacuum to give compound 2d as a yellow liquid (80%). \( ^1H \) NMR (400 MHz, DMSO-d\(_6\), 298 K) δ 7.45–7.21 (m, 8H), 5.24 (t, J = 5.7 Hz, 2H), 4.52 (d, J = 4.8 Hz, 4H), 3.68 (s, 4H), 3.56–3.41 (m, 1H).

Synthesis of compound 2. Compound 2d (1 mmol) was dissolved in 30 mL of HBr (48%), and the resulting mixture was heated under reflux for 24 h. After the reaction was stirred for 24 h, it was cooled to room temperature, filtered, and washed with water. The yellow solid was dissolved in a saturated, aqueous NH\(_4\)PF\(_6\) solution and stirred for 2 h. The reaction mixture was then filtered and washed with water to yield a white solid, compound 2 (82%). \( ^1H \) NMR (400 MHz, DMSO-d\(_6\), 298 K) δ 2.69 (s, 2H), 4.21–4.10 (m, J = 7.0–7.8 Hz, 9H), 4.53 (s, 4H), 4.15 (t, J = 5.7 Hz, 4H), 4.07 (d, J = 9.0 Hz, 12H).

Synthesis of compound 3. Compound 1 (1 mmol) was dissolved in chloroform (100 mL), and then, 2 (1.2 equiv) was added to the reaction system. The resulting mixture was stirred at room temperature for 6 h. 1-Naphthyl-3-sulfonic acid sodium salt (3 equiv) and K\(_2\)CO\(_3\) (18 equiv) were dissolved in dry DMF (15 mL), and the resulting mixture was placed under a nitrogen atmosphere at 60 °C for 3 h. Then, the reaction system procedure was cooled to room temperature, and we used a syringe filter to quickly remove the unreacted K\(_2\)CO\(_3\), which was a white solid and added the supernatant to the first reaction system. After the mixture was stirred for 72 h under a nitrogen atmosphere at room temperature, it was poured into diethyl ether and stirred. The yellow fibers that were formed were filtered off, washed with ethyl ether and dried under an air flow to give 4 as a yellow, fiber-like polymer. \( ^1H \) NMR (300 MHz, DMSO-d\(_6\), 298 K) δ 10.17 (s, 2H), 8.26–7.74 (m, 20H), 7.11–7.29 (m, 24H), 7.28–6.89 (m, 24H), 5.19 (s, 2H), 4.66 (d, J = 7.29 Hz, 4H), 4.48–3.97 (m, 18H), 3.97–3.13 (m, 34H), 2.81 (d, J = 4.76 Hz, 40H), 2.56–2.28 (m, 24H), 1.41 (d, J = 9.0 Hz, 62H).

Synthesis of compound 4. Compound 1 (1 mmol) was dissolved in chloroform (100 mL) and was stirred at room temperature for 6 h, 1-Naphthol-3-sulfonic acid sodium salt (3 equiv) and K\(_2\)CO\(_3\) (18 equiv) were dissolved in dry DMF (15 mL), and the resulting mixture was placed under a nitrogen atmosphere at 60 °C for 2 h. The mixture was then cooled to room temperature, to which was added compound 4b and 4c. A solution of compound 4b and 4c was stirred under a nitrogen atmosphere at room temperature. Similar purification procedure was conducted, and we finally obtained a yellowish fiber-like polymer (polymer 4-1). With the same casting procedure, we obtained a control membrane. We measured the proton conductivity of the control membrane. Unfortunately, no proton conductivity was detected, suggesting no proton transfer capability if the cavity of the crown ether was occupied by K\(^+\).

Synthesis of compound 5. A mixture of compound 4 (1 mmol), Et\(_3\)N (5 mmol), and Ac\(_2\)O (3 mmol) in N,N-dimethylformamide (DMF, 0.69 mL) was stirred at 40 °C for 24 h. Then, it was poured into diethyl ether and stirred. The yellow fibers that were formed were filtered off, washed with diethyl ether and dried under flowing air to give 5 as a yellow, fiber-like polymer\(^(3)\). \( ^1H \) NMR (400 MHz, DMSO-d\(_6\), 298 K) δ 8.21–7.77 (m, 20H), 7.68–7.37 (m, 20H), 7.07 (d, J = 32.0 Hz, 20H), 5.18 (d, J = 18.6 Hz, 4H), 4.64–3.59 (m, 22H), 3.69 (d, J = 58.3 Hz, 22H), 3.45–3.27 (m, 30H), 3.06 (s, 12H), 2.70 (s, 18H), 2.48 (d, J = 12.7 Hz, 20H), 2.32 (s, 6H), 2.18 (t, J = 8.1 Hz, 12H), 1.91 (q, J = 7.6 Hz, 12H), 1.65–0.93 (m, 62H).

Preparation of polyrotaxane membrane. Compound 5 was dissolved in NMP to form a 10 wt% casting solution that was cast onto a glass plate. The cast films were then heated at 80 °C to remove the solvent. After the drying process, flexible, transparent PEMs were obtained. All the membranes were fully converted to the H\(^+\) form via immersion in aqueous HCl (1 mol L\(^{-1}\)) solution at room temperature for 24 h, and this was followed by thorough washing and storage in sealed sample bottles (full of deionized water). The resulting membrane was treated with 1 M aqueous HCl at 25 °C for 24 h to convert the termini into the H\(^+\) form for proton transport. This membrane was then denoted polyrotaxane membrane.

With the same casting procedure, we obtained a control membrane from compound 4-1. We measured the proton conductivity of the control membrane. Unfortunately, no proton conductivity was detected, suggesting no proton transfer capability if the cavity of the crown ether was occupied by K\(^+\).

**Instruments and characterizations.** NMR and nuclear overhauser effect spectroscopy (NOESY) spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Chemical shifts are reported relative to the signals corresponding to the residual non-deuterated protons in NMR solvents (CDCl\(_3\): δ 7.26 ppm, DMSO-d\(_6\): δ 2.53 ppm, D\(_2\)O: δ 1.56 ppm).

**Data availability.** The authors declare that all data supporting the findings of this study are available within the paper and its supplementary information. They are also available from the corresponding authors upon reasonable request.

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Received: 16 January 2018 Accepted: 16 May 2018
Published online: 12 June 2018
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Acknowledgements
This research was supported by the National Natural Science Foundation of China (Nos. 91534203, 21490581, 21252607, 21706247) and the Fundamental Research Funds for the Central Universities.

Author contributions
L.W. and T.W.X. conceived the project. L.W. and Z.I.Y. designed the experiment. X.L.G. synthesized all chemical compounds, collected and analyzed the data; Y.B.H. and X.L. prepared the membrane and helped with data analyses; Y.Z. and M.H. performed membrane characterizations. L.W., Z.I.Y., and T.W.X. wrote the paper.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-04733-4.

Competing interests: The authors declare no competing interests.

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