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Highly Conductive Anion Exchange Membranes from Microporous Tröger's Base Polymers

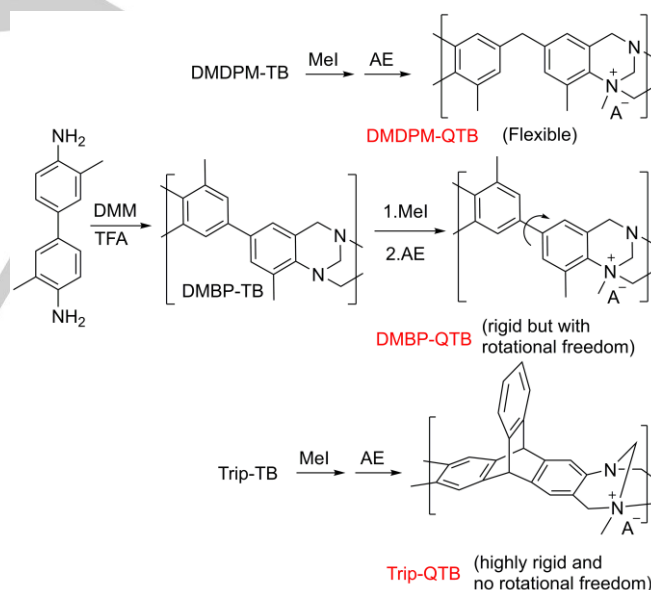
Zhengjin Yang^[a], Rui Guo^[a], Richard Malpass-Evans^[b], Mariolino Carta^[b], Neil B McKeown^{*[b]}, Michael D Guiver^{*[c]}, Liang Wu^[a] and Tongwen Xu^{*[a]}

Abstract: The development of polymeric anion exchange membranes (AEMs) combining high ion conductivity and long-term stability is a major challenge for materials chemistry. Here we report for the first time AEMs with regularly distributed fixed cationic groups, based on the formation of microporous polymers containing the V-shape rigid Tröger's Base units. Despite their simple preparation, involving only two synthetic steps from commercially available precursors, the polymers provide AEMs with exceptional hydroxide conductivity at relatively low ion exchange capacity, as well as high swelling resistance and chemical stability. An unprecedented hydroxide conductivity of 164.39 mS/cm is obtained at a relatively low ion exchange capacity of 0.82 mmol/g under optimal operating conditions. The exceptional anion conductivity appears related to the intrinsic microporosity of the charged polymer matrix, which facilitates rapid anion transport.

Anion exchange membranes (AEMs) contain fixed positively charged groups within the polymer matrix, allowing them to selectively conduct hydrated anions such as OH⁻, Cl⁻, HCO₃⁻ across the membrane^[1]. They are an important central component in many electrochemical and diffusion processes that require selective anion transport and high conduction combined with chemical stability. Their utilization is ubiquitous in industrial processes such as electrodialysis, diffusion dialysis, removal or recovery of metal ions from process streams^[2], and electrolysis^[3]. More recently, in the energy storage and generation field, there has been renewed interest in developing chemically stable and highly conductive AEMs for redox flow batteries^[4] and for anion exchange membrane fuel cells (AEMFC)^[5], the latter being primarily because the high pH operating conditions allow cost reductions through the use of non-precious metal catalysts. Advantages also include the faster electrode reaction kinetics and flexible fuel choices.^[6] However, the development of suitable AEMs for fuel cells remains a particularly demanding challenge for materials science, as the AEMs must combine high anionic conductivity with mechanical stability towards swelling in aqueous media and long-term chemical stability at high pH values. To date, many polymers have been investigated, mostly based on quaternised amines, with the aim of providing a high concentration of cationic

sites. However, only a few have demonstrated sufficient stability together with high ionic conductivity for practical application.^[7]

Recently, polymers prepared from diamine monomers using the highly efficient formation of Tröger's Base (TB), a V-shaped bridged bicyclic aromatic diamine, demonstrate exceptional potential for gas separation membranes due to the high rigidity and intrinsic microporosity imparted by the TB unit.^[8] The inefficient packing of the contorted polymer chains provides intrinsic microporosity that facilitates rapid transport of gases and their extreme rigidity provides selectivity for one gas over another. In addition, the efficient transport of ions has been demonstrated within these TB polymers allowing the fabrication of ionic diodes^[9] and protective membranes for electrodes.^[10] Here we report for the first time AEMs derived from quaternised TB polymers. Their intrinsic microporosity is anticipated to enable the rapid and efficient transport of anions. Despite the great diversity of cationic groups that have been incorporated into polymers with the objective of producing stable and high-performance AEMs, as far as we are aware, TB-containing polymers have not been investigated for this application.



Scheme 1. The synthesis of the TB-polymer based AEM materials. The non-quaternised polymers DMDPM-TB and Trip-TB were prepared as described previously.^[8b, 11] Note that AE = Anion exchange, DMM = dimethoxymethane, TFA = trifluoroacetic acid and A⁻ = Cl⁻, HCO₃⁻ or OH⁻. The quaternised polymers (or membranes) were designated as DMDPM-QTB, DMBP-QTB and Trip-QTB, respectively.

The three polymers selected for this study can be defined by the structural components that are fused together by the TB unit to form the polymer chain: dimethyldiphenylmethane (DMDPM-TB), dimethylbiphenyl (DMBP-TB) and triptycene (Trip-TB). The synthesis of both DMDPM-TB^[12] and Trip-TB^[8b] was reported previously, with the latter being particularly

[a] CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, P.R. China
E-mail: twxu@ustc.edu.cn

[b] EaStCHEM School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, U.K.
Email: neil.mckeown@ed.ac.uk

[c] State Key Laboratory of Engines, School of Mechanical Engineering, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072, P.R. China
Email: michael.guiver@outlook.com

promising for gas separations. DMBP-TB was prepared specifically for this study to provide a new TB-polymer of intermediate overall rigidity between the relatively flexible DMDPM-TB and the highly rigid Trip-TB (Scheme. 1). The DMBP-TB is synthesised by the reaction of commercially available 4,4'-diamino-3,3'-dimethylbiphenyl with dimethoxymethane using trifluoroacetic acid as solvent (see SI for details). As expected, the intrinsic microporosity of the three TB polymers increases in correlation with the overall chain rigidity as demonstrated by their apparent BET surface areas that were calculated from nitrogen adsorption isotherms collected at 77 K (Table 1).

Robust and transparent films of each TB polymer, cast from chloroform solutions, were reacted with methyl iodide (MeI) in order to provide polycationic materials via quaternisation and the resulting quaternised films are designated as QTB. By analogy with the results from a previous study on the methylation of TB, this process is known to occur on only one of the two available tertiary amines via a S_N2 mechanism.^[13] If desired, simply adjusting the amount of MeI used or the reaction time readily controls the degree of quaternisation. Using an excess of MeI provides each polymer with a high degree of quaternisation as confirmed by both $^1\text{H-NMR}$ spectroscopy and AgNO_3 titration. The ion exchange capacity (IEC) of these films was calculated using Mohr's method, and found to be in the range of 0.8-0.9 mmol g^{-1} , which is a relatively low value compared with many reported AEMs (Table 1). Subsequent exchange of the I^- for OH^- (or HCO_3^- or Cl^-) could be achieved by simply treating the films with an aqueous solution of NH_4OH (or a suitable salt).

Mechanical robustness in its hydrated state is of crucial importance to the performance of a potential AEM and this property can be degraded due to the absorption of excessive water. Hence, water uptake (Wu) measurements on the OH^- anion exchanged films were performed showing uptake in the order $\text{DMDPM-QTB} < \text{DMBP-QTB} < \text{Trip-QTB}$ (Table 1) with the value for DMDPM-QTB being remarkably low ($Wu = 8.6$ weight %). This prompted a detailed study of the Wu values and swelling of a film of DMDPM-QTB at temperatures up to 80 °C, showing that its excellent structural resilience to water uptake is maintained even over the likely working temperature range of an AEMFC (Table S1). In contrast, Trip-QTB adsorbs more water, which is consistent with its higher intrinsic microporosity. Chemical stability of an AEM is also very important and this was evaluated by immersion of the OH^- exchanged films in 2 M NaOH aqueous solutions held at 60 °C for a prolonged period (240 h). For DMDPM-QTB and DMBP-QTB no degradation was detected by $^1\text{H NMR}$ (Fig. S8), which is unexpected given the well-established tendency for quaternary ammonium cations to degrade under such harsh conditions. However, for Trip-QTB (OH^-), degradation was apparent (Table S2). This difference in chemical stability may also be related to the far greater water uptake within this polymer.^[14] Finally, it is desirable that methanol, a potential fuel for AEMFCs, should have relatively low permeability through the AEM. This was confirmed for the OH^- exchanged films for DMDPM-QTB and DMBP-QTB but was significantly higher for Trip-QTB as expected from its greater intrinsic microporosity (Fig. S12).

Table 1. The properties of the TB polymers and the quaternised (QTB) membranes.

Polymer (AEM)	DMDPM-TB	DMBP-TB	Trip-TB
M_w (g mol^{-1}) ^a (TB)	95 000	49 000	51 000
SA_{BET} ($\text{m}^2 \text{g}^{-1}$) ^b (TB)	38	339	899
IEC (mmol g^{-1}) ^c (QTB)	0.81	0.82	0.91
Wu (%; 30 °C) ^d (QTB)	8.6	36	81
P_{MeOH} ($\text{cm}^2 \text{s}^{-1}$) ^d (QTB)	3.9×10^{-8}	9.1×10^{-8}	1.7×10^{-6}

^aOf non-quaternised polymer from GPC against polystyrene standards. ^b N_2 adsorption isotherms at 77 K of powdered form of the non-quaternised polymers (note that quaternised polymers do not adsorb significant quantities of N_2). ^cOf quaternised polymers measured by $^1\text{H NMR}$ and AgNO_3 titration of Cl^- exchanged polymer. ^dOf OH^- exchanged polymers.

Due to their excellent structural and chemical stability, in addition to low methanol permeability, quaternised films of both DMDPM-TB and DMBP-TB were investigated further for their potential as AEMs by measuring their anionic conductivity (Cl^- , HCO_3^- and OH^-)^[15] using the four-point probe technique over the temperature range 30-80 °C (Figure 1). Due to its inferior stability towards aqueous NaOH, only the conductivity of Cl^- was measured for Trip-QTB. As expected from its greater mobility in pure water (Table S3), OH^- anion shows the highest conductivity (σ_{OH^-}) with values ranging for DMDPM-QTB from 43.4 mS cm^{-1} at 30 °C to 97.2 mS cm^{-1} at 80 °C and for DMBP-QTB from 23.5 mS cm^{-1} at 30 °C rising sharply to 164.4 mS cm^{-1} at 80 °C. DMBP-QTB demonstrates the highest value for σ_{OH^-} at 80 °C reported to date (Table S4). Indeed, these values of σ_{OH^-} for both DMDPM-QTB and DMBP-QTB are exceptional considering the relatively low values of IEC for these polymers. It can be concluded that the TB units provide a close and regular distribution of cation groups, which allows their coordination hydration shells to overlap sufficiently well to facilitate efficient transport^[6a]. The difference in conductivity regime over the measured temperature range can be attributed to a differences in transportation mechanism. The $\text{Cl}^-/\text{HCO}_3^-$ ions are mainly transported via a vehicular mechanism, while OH^- ions are transported by both vehicular and Grotthuss mechanisms, the latter being a thermal activated hopping, which would be preferred at higher temperatures^[16].

Comparing the effect of temperature on σ_{OH^-} of the two AEMs over the range 30-80 °C, it is clear that there is much greater temperature dependence for DMBP-QTB as compared to DMDPM-QTB, for which the weaker dependence is similar to that of previously reported polymers (Figure. 1).^[14, 17] This difference is likely to be related to the greater rigidity of the polymer chains of DMBP-TB, causing a higher energy barrier for hydroxide hopping, which therefore requires higher temperatures to undergo the thermal motions that appear to be required to form sufficiently overlapped hydration shells and to facilitate enhanced anion transport.

The performance and stability of the TB polymer-derived AEMs are all the more remarkable due to the simplicity of their preparation from cheaply available starting materials, which involves only two simple synthetic steps (TB polymerisation and quaternisation). In contrast, current state-of-the-art AEM

materials are prepared using multi-step procedures to provide relatively complex macromolecular structures that phase separate into hydrophobic regions for stability and hydrophilic regions for anion transport.^[17b, 18] The design of such materials draws inspiration from the example of Nafion® where phase separation is responsible for its excellent performance as a PEM. For the TB polymers, DMDPM-QTB and DMBP-QTB, the anion conducting pathways appear to be provided on a smaller scale by the inefficient packing of the polymer chains caused by the rigid V-shape of the quaternised TB unit. Analogous to gas permeability through PIMs, the transport of hydrated anions within the amorphous TB polymers will be facilitated by hopping between subnanometre free volume voids between the polymer chains, although for the anions these voids will be occupied by

water molecules to provide a sponge-like structure. Interestingly, the closely related ultra-rigid polymer with a higher degree of intrinsic microporosity (Trip-TB) performed relatively poorly due to excessive water uptake and chemical instability. In contrast, DMBP-TB, which is a rigid polymer that possesses some rotational freedom along its chain, provided DMBP-QTB having exceptional σ_{OH^-} . However, the highest σ_{OH^-} values were achieved only at elevated temperature indicating that enhanced anionic transport requires activation via thermal-induced motion. The structural diversity offered by TB polymers^[11] and their relatively simple method and broad applicability of the synthetic approach provide many opportunities for further optimization of their performance as AEMs, and investigations towards this objective are in progress.

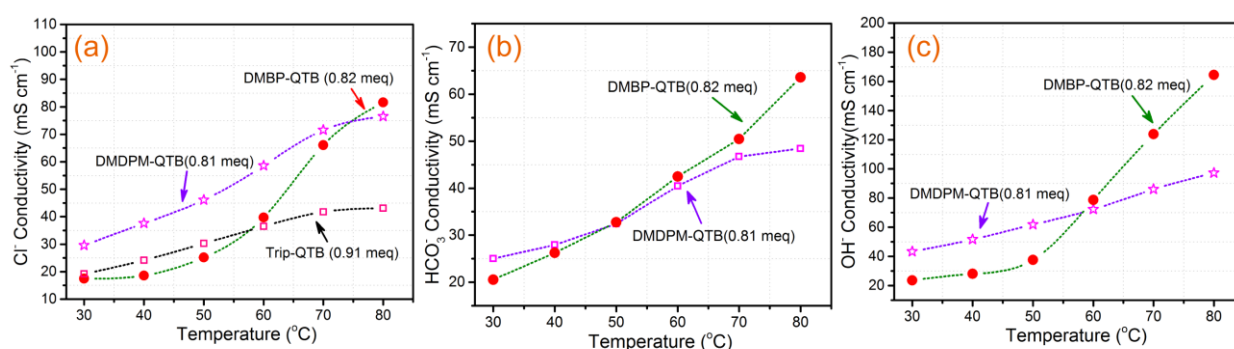


Figure 1. The conductivity of (a) Cl^- , (b) HCO_3^- and (c) OH^- in the quaternised TB polymers over the temperature range 30–80 °C.

Acknowledgements

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Keywords: Tröger's Base • anion exchange membrane • hydroxide conductivity • polymers of intrinsic microporosity • electrochemical membrane processes

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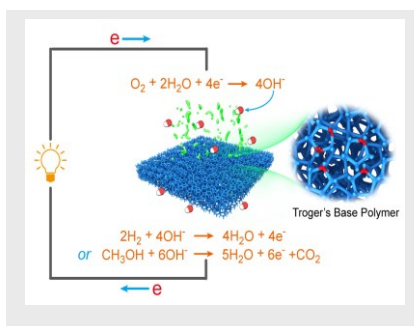
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Entry for the Table of Contents (Layout 1)

Layout 1:

COMMUNICATION

Quaternised Tröger's Base polymers provide highly conducting and stable anion exchange membranes with potential for energy conversion applications. The V-shaped Tröger's Base unit stops the polymer chains from packing efficiently resulting in subnano-sized intrinsic microporosity, which provides a sponge-like morphology that facilitates rapid anion transport.



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