Cite this: Chem. Commun., 2012, 48, 5922-5924

www.rsc.org/chemcomm

COMMUNICATION

Anhydrous proton conductivities of squaric acid derivatives[†]

Dipankar Basak,^{*a*} Craig Versek,^{*b*} Daniel T. Toscano,^{*a*} Scott Christensen,^{*c*} Mark T. Tuominen^{*b*} and D. Venkataraman^{*a}

Received 20th February 2012, Accepted 17th April 2012 DOI: 10.1039/c2cc31283b

In this communication, we introduce squaric acid derivatives as anhydrous proton conductors. We report the synthesis, characterization and proton conductivities of four squaric acid derivatives. The anhydrous proton conductivity of one of the derivatives was 2.3×10^{-3} S cm⁻¹ at 110 °C, comparable to the conductivity of molten 1*H*-1,2,3-triazole or 1*H*-imidazole.

There is a growing interest in developing new materials that can be used as proton exchange membranes (PEM) in fuel cells.^{1,2} The target proton conductivity for PEMs is $\sim 1 \times 10^{-1} \text{ S cm}^{-1}$ at 120 °C and 50% humidity.3 At the present time, membranes derived from perfluorosulfonic acid-based Nafion[®] or polybenzimidazole(PBI)/H₃PO₄ have high proton conductivities and are used in commercial fuel cells.^{4,5} In these systems, the proton transport is believed to occur through the diffusive mechanism wherein the proton is transported through the carrier molecules (water or H₃PO₄). Since the presence of such carriers is essential for high proton conductivity, the fuel cell operation conditions such as temperature are constrained by the physical properties of the carriers.⁶ Therefore, there is widespread interest in developing proton-transporting materials that have high intrinsic proton conductivity wherein the protons are transported through non-diffusive pathways (Grotthuss-type mechanism).

Any molecule that exists in multiple tautomeric forms, shows an extended hydrogen bonded network and has acidic protons is a potential candidate for Grotthuss-type proton transport. Thus far, the focus has been on nitrogen-based heterocycles such as 1H-1,2,3-triazole and 1H-imidazole.^{7–10} Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) exhibits an extended hydrogen bonded network similar to 1H-imidazole or 1H-1,2,3-triazole in its crystalline state (Fig. 1a) and exists in multiple tautomeric forms (Fig. 1b).¹¹ Furthermore, like water, the network consists of proton donor and acceptor sites. The amphoteric nature of squaric acid network is an attractive and important feature for translocation of protons over a long distance.

University of Massachusetts Amherst, MA 01003, USA



Fig. 1 1a. Crystal structure of squaric acid showing 2-D hydrogen bonded network (CSD code: KECYBUO3); 1b. Illustration of the re-organization of π bonds in squaric acid and the intermolecular proton transfer between the tautomers.

Although squaric acid has been studied for its antiferroelectric properties, its anhydrous proton transporting properties remain unexplored.^{12–14} In this communication, we report the synthesis, characterization, and proton conductivity under anhydrous conditions for squaric acid derivatives.

Four derivatives (compounds **4a–d**, Scheme 1) of squaric acid were synthesized using synthetic protocols reported in the literature.^{15–17} Addition of appropriate organolithium reagent to commercially available 3,4-diisopropoxycyclobut-3-ene-1,2-dione (1) furnished **2**, which was then converted to cyclobutenedione **3** in the presence of a catalytic amount of acid. Deprotection of isopropoxy group with 1:1 Conc.HCl/acetone (v/v) produced compounds **4a–d** in excellent yields.

Anhydrous proton conductivities of squaric acid and its derivatives (**4a–d**) were obtained by impedance spectroscopy. Vacuum dried samples were placed into a cavity (length: 0.1 cm, cross-sectional area: 0.079 cm^{-2}) between two custom brass electrodes, forming liquid seals at the ends of a PTFE tube. This set up was placed in a vacuum oven fitted with a variable temperature controller. Samples were heated to 120 °C, the highest temperature investigated for this study,



Scheme 1 Synthesis of of squaric acid derivatives.

^a Department of Chemistry, University of Massachusetts Amherst, 710 N. Pleasant Street, Amherst, MA 01003, USA. E-mail: dv@chem.umass.edu; Fax: +14135454490;

Tel: +14135452028

^b Department of Physics, University of Massachusetts Amherst, MA 01003, USA

^c Department of Polymer Science and Engineering,

[†] Electronic supplementary information (ESI) available: general information, TGA, proton conductivity vs. time and cyclic voltametry data. See DOI: 10.1039/c2cc31283b

held for 12 h and subsequently cooled back to 40 °C (see ESI[†]). Conductivity vs. time was plotted to ensure integrity of the samples under applied experimental condition (Fig. S3, ESI⁺). The proton conductivity of squaric acid was found to be low ($<10^{-8}$ S cm⁻¹ at 120 °C) in our measurement, comparable to the conductivities of 1H-imidazole and 4,4-1H-1H-bi-1,2,3-triazole (bitriazole) in their crystalline state (melting point of squaric acid > 300 °C).^{18,19} This poor performance is attributed to a hindered molecular reorientation process, which is considered to be the rate-limiting step for anhydrous proton conduction.² Similarly, the phenyl derivative 4d (melting point 207-208 °C) did not show any measurable conductivity while compound 4a (melting point 160 °C) exhibited low conductivity (2.0 \times 10⁻⁸ S cm⁻¹ at 110 °C). Conversely, the conductivity of **4b** and **4c** were measured as 2.2×10^{-5} and 2.3×10^{-3} S cm⁻¹ at 110 °C, respectively (see Fig. 2). It is noteworthy that proton conductivity of 4c is comparable to the conductivity of molten 1*H*-imidazole at 90 °C ($\sim 10^{-3}$ S cm⁻¹) and higher than that of liquid 1*H*-1,2,3-triazole $(1.3 \times 10^{-4} \text{ S cm}^{-1})$ at room temperature.^{8,18} From the Arrhenius plot, the activation energy barrier for proton conduction was estimated as 40 kJ mol⁻¹ for **4c** and 62 kJ mol⁻¹ for **4b** by using the limiting slope at high temperature.

Thermogravimetric (TGA) analysis of **4a–d** under a nitrogen atmosphere showed minimal weight loss for **4a** until 310 °C, **4b** and **4d** until 200 °C, and **4c** until 150 °C (Fig. S1, ESI†); samples were kept at 60 °C *in vacuo* for 12 h before performing TGA to ensure removal of any adventitious water or volatile impurities.

As a result of the measured proton conductivities, we decided to focus our attention on molecules **4b** and **4c** and characterize them using differential scanning calorimetry (DSC), X-ray scattering and cyclic voltammetry. In DSC, upon first heating, **4b** shows a broad endotherm corresponding to a phase transition at 101.7 °C ($\Delta H_{\text{transition}} = 24.07 \text{ J g}^{-1}$) (Fig. S2 A, ESI†). A similar transition was observed for **4c** at 92.4 °C ($\Delta H_{\text{transition}} = 86.32 \text{ J g}^{-1}$) (Fig. S2 B, ESI†). Exotherms were not observed upon cooling, indicating that the initial crystalline phases are not recovered. Further, the second heating cycle reveals two weak endotherms at 35.98 °C and 115.87 °C for **4b**, but no such peak was observed for **4c**.

In order to investigate the morphology of these materials, wide angle X-ray scattering (WAXS) of **4b** and **4c** was



Fig. 2 Comparison of temperature dependent proton conductivities of 4a, 4b and 4c. Molecule 4c shows higher conductivity compared to 4a and 4b. Molecule 4d did not show any measurable conductivity and therefore is not shown in the figure.



Fig. 3 Wide-angle X-ray scattering of compounds 4b (A) and 4c (B); the samples were first measured at 25 °C, then heated to 130 °C and cooled to 50 °C. I(q) values have been shifted vertically for clarity. The X-ray scattering indicates the presence of a dimer for 4b (inset A) and a tetramer for 4c (inset B).

performed at several different temperatures. Prior to any thermal treatment, pristine 4c at 25 °C exhibits multiple peaks, the first of which falls at $q = 3.86 \text{ nm}^{-1}$, corresponding to a length scale (d) of 16.3 Å (Fig. 3B; d is related to q by the equation $d = 2\pi/q$). Although the structure cannot be determined unambiguously from this data, Cerius 2 molecular modelling suggests that 4c exists as a chain of hydrogen-bonded tetramers with hydrogen bonding patterns similar to squaric acid (Fig. 3B inset). The centre-to-centre distance between two tetrameric units is ~ 16.3 Å, correlating very well with the observed distance in WAXS. Furthermore, the presence of numerous sharp peaks indicates that the material is indeed crystalline in nature, consistent with the large endotherm observed in DSC for the first heating cycle. Upon heating beyond the phase transition temperature to 130 °C, the majority of crystalline peaks disappear except for four distinct peaks. The position of the primary peak varies only slightly from the crystal phase (q =3.99 nm⁻¹ vs. q = 3.86 nm⁻¹), however it is significantly broadened, indicating a decreased average feature size of 4.3 nm (full-width at half maximum, $\Delta q = 1.46$ nm⁻¹). A broad peak at $q = 12.5 \text{ nm}^{-1}$ corresponds well with the numerous crystalline peaks evident at 25 °C, however the lack of sharp reflections again indicates decreased order in this phase when compared to the crystal state. Two additional small peaks at $q = 6.62 \text{ nm}^{-1}$ and $q = 7.17 \text{ nm}^{-1}$ also emerge, and lie reasonably close to peaks in the original crystal phase ($q = 6.14 \text{ nm}^{-1}$ and $q = 6.83 \text{ nm}^{-1}$). The combination of these reflections indicates that, upon heating, 4c forms a poorly ordered phase with a similar unit cell to the initial crystal structure. Upon cooling to

50 °C, the scattering pattern remains unchanged, indicating an irreversible phase transition at 92 °C, correlating well with DSC observation.

WAXS of **4b** prior to any thermal treatment (25 °C) exhibits fewer scattering peaks than **4c** in its pristine state, indicating a lower initial crystallinity, in agreement with DSC (Fig. 3A). The primary peak falls at $q = 4.00 \text{ nm}^{-1}$, corresponding to a length scale of 15.7 Å. We note that the end-to-end distance from the terminus of *n*-butyl chain to the C==O of squaric acid is ~8 Å (obtained from the energy minimized structure of **4b** using Chem3D MM2 level molecular modelling), suggesting a dimeric form (Fig. 3A inset). Heating the sample to 130 °C causes a slight shift and broadening of the primary peak to $q = 3.53 \text{ nm}^{-1}$ with an average feature size of 2.57 nm (full-width at half maximum, $\Delta q = 2.44 \text{ nm}^{-1}$). Furthermore, a broad halo region at $q = 15.0 \text{ nm}^{-1}$ was observed similar to **4c** at elevated temperature, again indicating the presence of a new phase with a similar unit cell as the initial crystal.

Based on the combination of DSC and WAXS data we conclude that upon heating, **4b** and **4c** both undergo an irreversible phase transition from a crystalline state to a poorly ordered phase with a similar unit cell to the original crystal. The presence of additional peaks with smaller full-width at half maximum in **4c** indicates that this phase is slightly more ordered than that in **4b**. The increased ordering of the new phase in **4c** likely indicates a higher concentration of squaric acid connected through a hydrogen-bonded network, which in turn facilitates anhydrous proton hopping. This observation is in agreement with a previous report wherein continuous nano-scale domains of proton transferring groups *via* self-organization yield high conductivity.²⁰

In order to probe the electrochemical stability of **4b** and **4c**, cyclic voltammograms (CVs) for these molecules were recorded in acetonitrile solution at 1×10^{-3} M under argon. The CV traces for both samples were similar, exhibiting a reversible oxidation peak at +0.6 V (*vs.* Ag/Ag+). CV traces remain nearly identical even after ten consecutive cycles, indicating little or no affinity of squaric acid derivatives towards the platinum electrode (Fig. S4, ESI†). In contrast, under identical electrochemical conditions, 1*H*-Imidazole exhibits irreversible oxidation and significant adsorption onto the platinum surface.^{8,21} This observation indicates that squaric acid derivatives do not poison platinum electrodes and show high electrochemical reversibility.

In conclusion, four different derivatives of squaric acid were synthesized and investigated for anhydrous proton conduction. The *tert*-butyl derivative of squaric acid exhibited proton conductivity as high as 2.3×10^{-3} S cm⁻¹ at 110 °C while its *n*-butyl analogue exhibited relatively poor conductivity. This variation is attributed to an increased order of the new phase present in *tert*-butyl derivative and a lower activation energy barrier for proton movement. Squaric acid derivatives also exhibit electrochemical stability compared to irreversible

oxidation of 1H-imidazole under identical experimental conditions. We believe that squaric acid derivatives are very promising candidates as new anhydrous proton conducting materials. Further studies regarding blends of squaric acid derivatives into polymer matrix and immobilization of squaric acid onto a polymer backbone by flexible linkers are currently under investigation.

This work was initiated through a support by Fueling the Future Center for Chemical Innovation (CHE 0739227), sponsored by National Science Foundation. This material is also based upon work supported in part by the U. S. Army Research Laboratory and the U. S. Army Research Office under grant number 54635CH, and by the National Science Foundation Materials Research and Science Center on Polymers (DMR 0820506). We sincerely thank Prof. Ryan C. Hayward for his valuable input in interpreting the X-ray data.

Notes and references

- 1 K. D. Kreuer, Chem. Mater., 1996, 8, 610-641.
- 2 K. D. Kreuer, S. J. Paddison, E. Spohr and M. Schuster, *Chem. Rev.*, 2004, **104**, 4637–4678.
- 3 M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla and J. E. McGrath, *Chem. Rev.*, 2004, **104**, 4587–4611.
- 4 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535–4585.
- 5 M. E. Schuster and W. H. Meyer, Annu. Rev. Mater. Sci., 2003, 33, 233–261.
- 6 L. Carrette, K. A. Friedrich and U. Stimming, *Fuel Cells*, 2001, 1, 5–39.
- 7 M. F. H. Schuster, W. H. Meyer, M. Schuster and K. D. Kreuer, *Chem. Mater.*, 2004, 16, 329–337.
- 8 Z. Zhou, S. W. Li, Y. L. Zhang, M. L. Liu and W. Li, J. Am. Chem. Soc., 2005, 127, 10824–10825.
- 9 S. Martwiset, R. C. Woudenberg, S. Granados-Focil, O. Yavuzcetin, M. T. Tuominen and E. B. Coughlin, *Solid State Ionics*, 2007, **178**, 1398–1403.
- 10 D. Basak, S. Christensen, S. K. Surampudi, C. Versek, D. T. Toscano, M. T. Tuominen, R. C. Hayward and D. Venkataraman, *Chem. Commun.*, 2011, **47**, 5566–5568.
- 11 D. Semmingsen, F. J. Hollander and T. F. Koetzle, J. Chem. Phys., 1977, 66, 4405–4412.
- 12 S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, 463, 789–U797.
- 13 K. Yoshimura and L. S. Liebeskind, *Macromol. Rapid Commun.*, 2010, **31**, 1725–1730.
- 14 H. Terao, T. Sugawara, Y. Kita, N. Sato, E. Kaho and S. Takeda, J. Am. Chem. Soc., 2001, 123, 10468–10474.
- 15 M. W. Reed, D. J. Pollart, S. T. Perri, L. D. Foland and H. W. Moore, J. Org. Chem., 1988, 53, 2477–2482.
- 16 L. S. Liebeskind, R. W. Fengl, K. R. Wirtz and T. T. Shawe, J. Org. Chem., 1988, 53, 2482–2488.
- 17 D. Bellus, J. Am. Chem. Soc., 1978, 100, 8026-8028.
- 18 A. Kawada, A. R. McGhie and M. M. Labes, J. Chem. Phys., 1970, 52, 3121–3125.
- 19 C. A. Alabi, Z. Chen, Y. S. Yan and M. E. Davis, *Chem. Mater.*, 2009, **21**, 4645–4652.
- 20 Y. Chen, M. Thorn, S. Christensen, C. Versek, A. Poe, R. C. Hayward, M. T. Tuominen and S. Thayumanavan, *Nat. Chem.*, 2010, 2, 503–508.
- 21 C. Yang, P. Costamagna, S. Srinivasan, J. Benziger and A. B. Bocarsly, J. Power Sources, 2001, 103, 1–9.