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COMMUNICATION

Proton conduction in discotic mesogens†

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In this communication, we show that liquid crystalline phases lower the activation energy barrier for proton transport. The liquid crystalline phases were obtained using a triphenylene core with alkyl chains bearing a triazole moiety at their termini.

Recently, there is widespread interest in developing molecules and macromolecules with high proton conductivities at moderate temperatures (120 °C) under low humidity conditions for proton exchange membranes in fuel cells.^{1–4} A common approach that has been pursued, albeit with limited success, is to design polymers with pendant nitrogen-containing heterocycles that can mimic the thin film nanoscale phase morphology of Nafion[®], which is the active component in many commercial proton exchange membranes.^{5–9} Nafion consists of hydrophobic (tetrafluoroethylene) and hydrophilic (sulfonic acid) groups which phase segregate to result in proton conducting channels with occluded water molecules. For efficient anhydrous proton transport, it is imperative that the proton conducting groups are organized into supramolecular structures that provide a continuous path for the proton.¹⁰ Moreover, the proton conducting groups should have sufficient flexibility for molecular reorientation to receive subsequent protons.^{11–14} Based on earlier reports on ion transport,^{15–17} we believe that liquid crystalline phases may offer a balance between the required supramolecular organization of the proton-conducting groups and the flexibility for molecular reorientation, thus providing a viable platform for developing efficient proton transporting materials. Herein we report the synthesis, structure and performance of liquid crystalline (LC) proton conductors based on a triphenylene core with alkyl chains, whose termini are covalently attached to the triazole moiety.

It is well known that triphenylene-based molecules self-assemble into structures that exhibit discotic LC phases.^{18–20} We reasoned that in the LC phase, the registry between the

triphenylene aromatic cores may provide structural alignment of the nitrogen heterocycles necessary for proton conduction. Furthermore, the alkyl spacer may provide enough flexibility for molecular reorientation. Therefore, we hypothesized that the activation energy barrier for proton transport may be lower in the LC phase compared to the liquid or crystalline phases.

2,3,6,7,10,11-Hexahydroxytriphenylene (**3**) was synthesized in two steps starting from veratrol using well-established literature procedures.^{21,22} Alkyl chains of varying length with a terminal alkyne group were attached to **3** via Williamson's ether synthesis. The terminal alkyne groups were then converted to pivaloyloxymethyl protected 1,2,3-triazole moieties through the azide-alkyne-Huisgen dipolar cycloaddition reaction.^{23,24} The deprotection of the pivaloyloxymethyl group was accomplished using NaOH to furnish **9a–9c** as sticky solids in 62–69% yield (Scheme 1).^{25, 28}

Thermogravimetric analysis (TGA) of the compounds **9a–9c** showed no mass loss up to 300 °C, indicating thermal stability of the triazole-functionalized triphenylene moieties (Fig. S1, ESI†). The mesomorphic behavior of **9a–9c** were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small and wide angle X-ray scattering. On the first heating cycle, each sample showed a broad endotherm in DSC, corresponding to a strong first order phase transition. This transition was irreversible for **9a** (64.3 °C, Fig. S2, ESI†) and **9b** (60.4 °C, Fig. S3, ESI†). It was quasi-reversible in **9c** (68 °C, $\Delta H_{\text{melt}} = 44 \text{ kJ mol}^{-1}$; Fig. 1). POM studies did not indicate any mesomorphic behavior or recrystallization for **9a** and **9b**, which is consistent with the DSC and X-ray scattering data. However, **9c** exhibits birefringence over a wide temperature range (25 °C to 140 °C), with needle-like birefringence between 75 °C and 140 °C (Fig. 2). Cooling of **9c** below 70 °C yielded crystallites in POM, indicating crystallization. However, no isotropic phase was observed in this temperature range. The persistence of a LC phase for such a wide temperature range for **9c** is similar to that observed for hexacarboxamidoheptatriphenylene.¹⁹

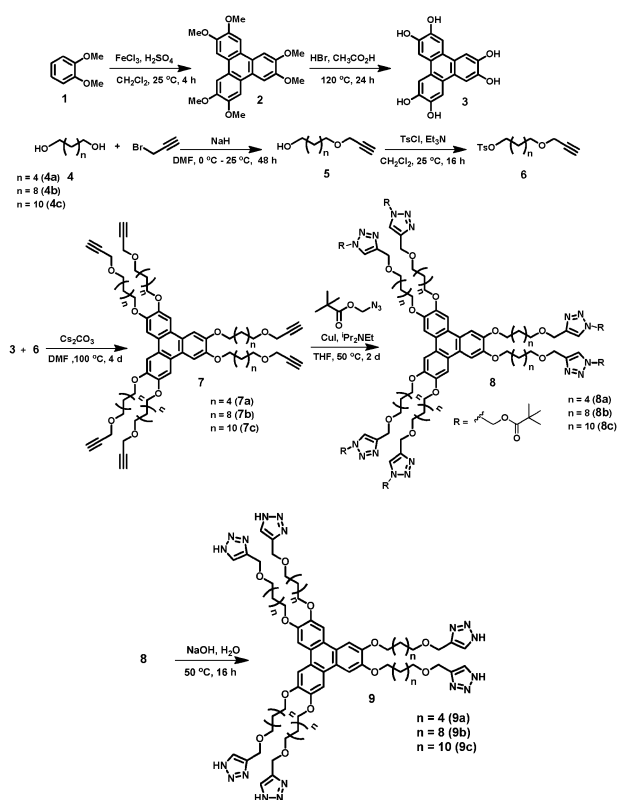
Wide angle X-ray scattering of **9c** at 25 °C exhibits peaks at q values $\sqrt{3}$ and $\sqrt{4}$ times the primary peak q^* , suggesting a hexagonal arrangement of columns in the crystalline state (Fig. 3). The characteristic spacing was found to be 23.5 Å, consistent with columnar packing of the triphenylene unit with partially interdigitated side chains. Upon heating to 100 °C, beyond the phase transition temperature, the primary peak at

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† Electronic supplementary information (ESI) available: Synthesis and characterization of all the molecules, TGA, DSC, and powder XRD data for **9a–9c**. See DOI: 10.1039/c1cc10509d



Scheme 1 Synthesis of the triphenylene-based molecules **9a–9c**.

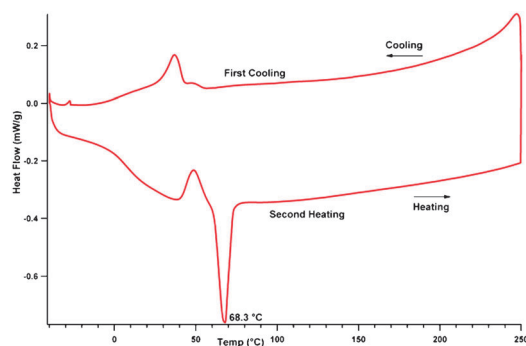


Fig. 1 Differential scanning calorimetric trace for compound **9c** from the first cooling/second heating cycle. The heating and cooling rates were $10^\circ\text{C min}^{-1}$ and 5°C min^{-1} , respectively.

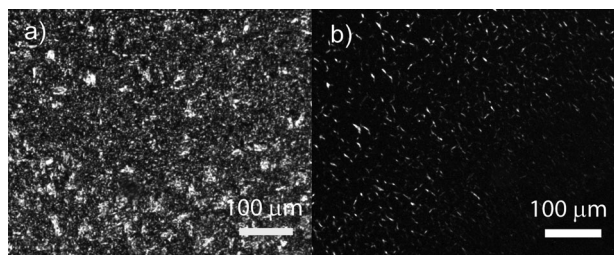


Fig. 2 Polarized optical microscopy images of **9c** showing (a) crystallization at 70°C and (b) the persistence of birefringence at 85°C even after 8 h.

$q = 2.67\ \text{nm}^{-1}$ shifted to $q = 3.14\ \text{nm}^{-1}$ (corresponding to a spacing of $20.0\ \text{\AA}$) and broadened. Together with the birefringence observed in POM, this clearly indicates the

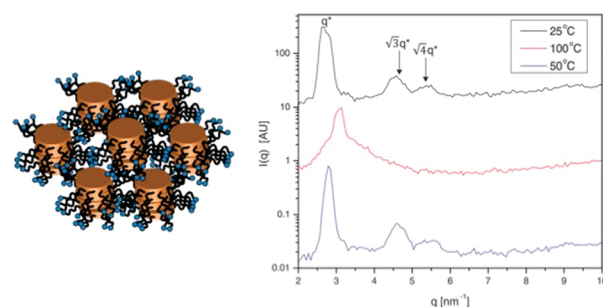


Fig. 3 (left) A schematic representation of the speculated columnar arrangement of **9c** in the liquid crystalline phase and (right) WAXS data for **9c** showing the crystalline phase at 25°C , liquid crystalline phase at 100°C and the recovery of the crystalline phase at 50°C . The y-axis has been shifted for clarity.

formation of a liquid crystalline phase, although the absence of higher order peaks in the X-ray scattering pattern suggests it is poorly organized. An additional peak at $2.9\ \text{\AA}$ also sharpened upon heating; while the origin of this peak is unknown, we note it is at too short of a distance to represent π - π stacking. Upon cooling, the original peaks reappeared indicating the reemergence of the initial morphology. Based on DSC, POM and X-ray scattering data we conclude that **9c** exists in the crystalline phase below 68°C and in the LC phase above the melting point and until a temperature of at least 140°C . Given the birefringence observed in the LC phase, the indication of hexagonal packing in the crystalline phase and prior literature,¹⁹ we speculate that there may be a columnar arrangement of **9c** in the LC phase. Samples **9a** and **9b**, upon heating also showed a single peak around $20\ \text{\AA}$, similar to that seen in **9c** at elevated temperatures. Thus all three samples exhibit some degree of mesomorphic organization, but the ordering is too poorly defined in **9a** and **9b** for birefringence to be observed in POM.

The proton conductivities of **9a–9c** were obtained by AC impedance spectroscopy.^{25–27} Vacuum dried samples were placed into a cavity (length: $0.1\ \text{cm}$, cross-sectional area: $0.079\ \text{cm}^2$) between two custom brass electrodes, forming liquid seals at the ends of a PTFE tube. This setup was placed in a chamber equipped with a variable temperature controller. Conductivities were obtained after two heating and cooling cycles (25 – 140°C at a rate of 1°C min^{-1}) to ensure homogeneity of the sample. In general, **9c** showed higher conductivity compared to **9a** and **9b** over the entire temperature range (Fig. 4). The conductivity of **9c** at 140°C was $1 \times 10^{-5}\ \text{S cm}^{-1}$ which was two orders of magnitude higher than the conductivity at 25°C ($6 \times 10^{-7}\ \text{S cm}^{-1}$). A plot of $\log(\sigma)$ vs. $1/T$ of **9c** showed three distinct features: a linear increase in conductivity up to 68°C , a sharp change in slope from 68 – 78°C , and a linear increase in conductivity beyond 78°C . DSC data also showed a phase transition at 68°C . Therefore, the discontinuity in the slope from 68 – 78°C can be attributed to structural reorganization due to melting and recrystallization. The conductivity before 68°C emanated from the crystalline phase and the conductivity after phase transition emanated from the LC phase. The activation energy barrier for proton conduction was calculated to be $46\ \text{kJ mol}^{-1}$ in the crystalline phase and $11\ \text{kJ mol}^{-1}$ in the LC phase.

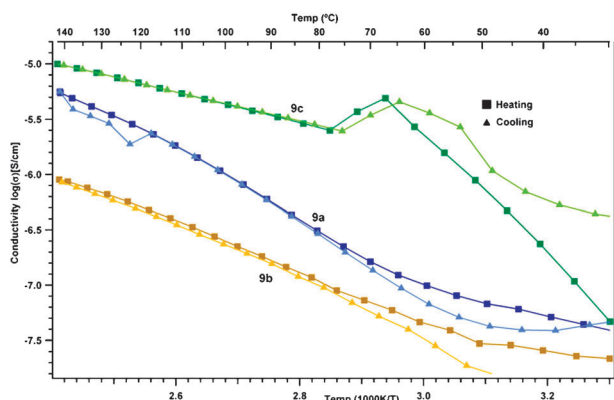


Fig. 4 Comparison of temperature dependent proton conductivity of molecules **9a**, **9b** and **9c**. Molecule **9c** shows a slope change around 68 °C indicating a change in the activation energy. This temperature also corresponds to a crystalline–LC phase transition. Molecules **9a** and **9b** show continuous increase in conductivity with temperature.

We have shown that the LC phase can lower the activation energy barrier for proton conduction. We believe that LC materials are viable platforms for creating next generation PEMs. Further studies to attach different proton transporting functional groups and compare their proton conductivities are currently under investigation.

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Notes and references

- 1 K. D. Kreuer, S. J. Paddison, E. Spohr and M. Schuster, *Chem. Rev.*, 2004, **104**, 4637–4678.
- 2 M. E. Schuster and W. H. Meyer, *Annu. Rev. Mater. Res.*, 2003, **33**, 233–261.
- 3 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535–4585.
- 4 L. Carrette, K. A. Friedrich and U. Stimming, *ChemPhysChem*, 2000, **1**, 162–193.
- 5 K. D. Kreuer, *Chem. Mater.*, 1996, **8**, 610–641.
- 6 J. C. Persson and P. Jannasch, *Chem. Mater.*, 2006, **18**, 3096–3102.
- 7 J. C. Persson and P. Jannasch, *Chem. Mater.*, 2003, **15**, 3044–3045.
- 8 Z. Zhou, S. W. Li, Y. L. Zhang, M. L. Liu and W. Li, *J. Am. Chem. Soc.*, 2005, **127**, 10824–10825.
- 9 R. C. Woudenberg, O. Yavuzetin, M. T. Tuominen and E. B. Coughlin, *Solid State Ionics*, 2007, **178**, 1135–1141.
- 10 Y. B. Chen, M. Thorn, S. Christensen, C. Versek, A. Poe, R. C. Hayward, M. T. Tuominen and S. Thayumanavan, *Nat. Chem.*, 2010, **2**, 503–508.
- 11 M. Iannuzzi, *J. Chem. Phys.*, 2006, **124**, 204710.
- 12 S. Scheiner and M. Y. Yi, *J. Phys. Chem.*, 1996, **100**, 9235–9241.
- 13 H. Hen, T. Y. Yan and G. A. Voth, *J. Phys. Chem. A*, 2009, **113**, 4507–4517.
- 14 B. S. Hickman, M. Mascal, J. J. Titman and I. G. Wood, *J. Am. Chem. Soc.*, 1999, **121**, 11486–11490.
- 15 M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994–995.
- 16 T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38–68.
- 17 C. F. Chow, V. A. L. Roy, Z. Ye, M. H. W. Lam, C. S. Lee and K. C. Lau, *J. Mater. Chem.*, 2010, **20**, 6245–6249.
- 18 J. Motoyanagi, T. Fukushima and T. Aida, *Chem. Commun.*, 2005, 101–103.
- 19 R. I. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barbera, M. G. Debye, J. Piris and Y. H. Geerts, *Adv. Mater.*, 2003, **15**, 1614–1618.
- 20 S. Sergeyev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, **36**, 1902–1929.
- 21 R. Zniber, R. Achour, M. Z. Cherkaoui, B. Donnio, L. Gehringer and D. Guillon, *J. Mater. Chem.*, 2002, **12**, 2208–2213.
- 22 F. C. Krebs, N. C. Schiodt, W. Batsberg and K. Bechgaard, *Synthesis*, 1997, 1285–1290.
- 23 R. Huisgen, *Proc. Chem. Soc., London*, 1961, 357.
- 24 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
- 25 T. E. Springer, T. A. Zawodzinski, M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, 1996, **143**, 587–599.
- 26 P. D. Beattie, F. P. Orfino, V. I. Basura, K. Zychowska, J. F. Ding, C. Chuy, J. Schmeisser and S. Holdcroft, *J. Electroanal. Chem.*, 2001, **503**, 45–56.
- 27 X. Z. Yuan, H. J. Wang, J. C. Sun and J. J. Zhang, *Int. J. Hydrogen Energy*, 2007, **32**, 4365–4380.
- 28 J. C. Loren, A. Krasinski, V. V. Fokin and K. B. Sharpless, *Synlett*, 2005, **18**, 2847–2850.