Supporting Information for:

Proton Conduction in Discotic Mesogens

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I. General Information

II. Experimental Procedure

III. Thermal Gravimetric Analysis (TGA)

IV. Differential Scanning Calorimetry (DSC)

V. Polarized Optical Microscopy (POM)

VI. Powder X-ray Diffraction

VII. NMR Spectra

I. General Information

All reactions were carried out in oven-dried glassware (160 °C). The chemicals were purchased from major chemical suppliers and were used without further purification unless otherwise noted. Tetrahydrofuran was redistilled over sodium-benzophenone ketyl. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 40-63 μm). Analytical thin layer chromatography was performed on pre-coated silica gel glass plate with visualization under UV light or staining in potassium permanganate solution. All $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. Chemical shift (δ) and coupling constant (J) are reported in parts per million and Hertz, respectively. The abbreviations for splitting patterns are s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets, and m, multiplet.

TGA was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 500 °C under nitrogen.

Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 822e difference scanning calorimeter, where temperature and enthalpy were
calibrated with In (430 K, 3.3 J/mol) and Zn (692.7 K, 12 J/mol) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR® software system.

Optical microscopy was performed on a Nikon model OPTIPHOT optical polarizing microscope equipped with a Mettler FP–82HT hot–stage.

X-Ray scattering was done using an in-house setup from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000). It uses a 30 W microsource (Bede) with a 30×30 \( \mu \text{m}^2 \) spot size matched to a Maxflux® optical system (Osmic) leading to a low-divergence beam of monochromatic CuK\( _\alpha \) radiation (wavelength \( \lambda = 0.1542 \text{ nm} \)). After passing beam defining and guard pinholes, the beam of about 0.4 mm diameter enters the sample chamber. Samples were placed within a hot stage connected to an Omega CN76000 temperature controller. WAXS is performed using an image plate (maximum resolution 50 \( \mu \text{m} \)) positioned in the sample chamber at a distance of 139 mm. The whole system is evacuated. The actual scattering angles are calibrated using the accurately known reflection from tricosane.

Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry facility, which is supported, in part, by the National Science Foundation.

Impedance data were obtained using a Solartron 1260 frequency response analyzer in the range 0.1 Hz to 32MHz with a sinusoidal excitation voltage of 0.1 V root-mean-square amplitude. Vacuum dried samples were placed into a cavity (L= 0.1 cm long by A = 0.07917 cm\(^2\) cross-sectional area) between two custom brass electrodes, forming liquid seals at the ends of a PTFE tube. The sample's resistance to proton transport, \( R \), was estimated by fitting a constant value to the plateau of impedance magnitude, which occurred within this frequency range. Conductivity was computed as \( \sigma = \frac{L}{(R * A)} \). Measurements were conducted in an ESPEC SH-241 temperature control chamber between 40 °C and 150 °C with a sweep rate of 1 °C /min.

II. Experimental Procedure
5a: To a suspension of sodium hydride (7.4 g, 308.5 mmol) in anhydrous DMF (90 mL) was added dropwise to a solution of 1,6-hexanediol (39.7 g, 336.3 mmol) in anhydrous DMF (45 mL) at 0 °C. After being stirred for 0.5 h at 0 °C, a solution of propargyl bromide (10 g, 84.1 mmol) in 45 mL of anhydrous DMF was added dropwise. The reaction mixture was allowed to stir at room temperature for 24 h while the solution turned brown. The mixture was filtered off, washed with ether (300 mL). The collected filtrate was further washed with water (3x100 mL), brine (2x50 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (2:1 hexanes/ethyl acetate) to afford 9.3 g (65 %) of 5a as clear liquid.

5a: $^1$H NMR (CDCl₃, 400 MHz)  4.13 (d, $J = 2.4$ Hz, 2H), 3.63 (t, $J = 6.8$ Hz, 2H), 3.51 (t, $J = 6.4$ Hz, 2H), 2.42 (t, $J = 2.4$ Hz, 1H), 1.7-1.54 (m, 4H), 1.46-1.42 (m, 4H); $^{13}$C NMR (CDCl₃, 101 MHz) 79.9, 74.3, 69.9, 62.3, 57.8, 32.5, 29.3, 25.8, 25.5.

5b: Slightly yellow oil. Yield: 77%. $^1$H NMR (CDCl₃, 400 MHz)  4.06 (d, $J = 2.4$ Hz, 2H), 3.54 (t, $J = 6$ Hz, 2H), 3.44 (t, $J = 6.4$ Hz, 2H), 2.38 (t, $J = 2.4$ Hz, 1H), 2.11 (bs, 1H), 1.56-1.45 (m, 4H), 1.28-1.17 (m, 12H); $^{13}$C NMR (CDCl₃, 101 MHz) 79.7, 74.2, 69.9, 62.1, 57.7, 32.5, 29.4, 29.4, 29.3, 29.3, 25.9, 25.7.

5c: Slightly yellow oil. Yield: 82%. $^1$H NMR (CDCl₃, 400 MHz)  4.11 (d, $J = 2.4$ Hz, 2H), 3.61 (t, $J = 6$ Hz, 2H), 3.49 (t, $J = 6.8$ Hz, 2H), 2.40 (t, $J = 2.4$ Hz, 1H), 1.61-1.51 (m, 4H), 1.35-1.26 (m, 16H); $^{13}$C NMR (CDCl₃, 101 MHz) 80.0, 74.1, 70.3, 63.0, 57.9, 32.8, 29.6, 29.5, 29.4, 29.4, 26.1, 25.7.
6a: To a solution of **5a** (9.3 g, 54.4 mmol) in 300 mL of dichloromethane was added 37.9 mL of triethylamine (271.9 mmol) and stirred for 0.5 h at room temperature. 20.7 g (108.8 mmol) of TsCl was added to the solution and the resulting mixture was allowed to stir at room temperature for additional 16 h while the mixture turned brownish color. The reaction mixture was washed with water (3x150 mL), brine (2x100 mL) and dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified using column chromatography (4:1 hexanes/ethyl acetate) to afford 11.1 g (66 %) of **6a** as clear oil.

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 4.11 (d, J = 2.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.47 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.41 (t, J = 2.4 Hz, 1H), 1.67-1.51 (m, 4H), 1.33-1.31 (m, 4H), $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 144.7, 133.0, 129.9, 127.8, 80.0, 74.3, 70.6, 69.9, 57.9, 29.2, 28.6, 25.4, 25.1, 21.6.

**6b**: Clear oil. Yield: 68%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 4.13 (d, J = 2.4 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.50 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.41 (t, J = 2.4 Hz, 1H), 1.66-1.54 (m, 4H), 1.34-1.28 (m, 12H), $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 144.6, 133.1, 129.8, 127.8, 80.0, 74.1, 70.7, 70.2, 57.9, 29.5, 29.3, 29.3, 28.8, 28.7, 26.0, 25.3, 21.6.

**6c**: Clear oil. Yield: 73%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.13 (d, J = 2.4 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.50 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.41 (t, J = 2.4 Hz, 1H), 1.66-1.55 (m, 4H), 1.35-1.24 (m, 16H), $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 144.6, 133.2, 129.8, 127.8, 80.0, 74.1, 70.7, 70.2, 57.9, 29.5, 29.4, 29.4, 29.3, 28.9, 28.7, 26.0, 25.2, 21.6.
7a: Cs₂CO₃ (20.07 g, 61.6 mol) was taken in a three-necked round bottom flask, equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel. After three consecutive evacuation and backfilling with argon, 250 mL dry DMF was added and the white suspension was stirred at 100 °C for 1 h. The dropping funnel was charged with a solution of 2,3,6,7,10,11-hexahydroxytriphenylene (1.0 g, 3.08 mmol) and 6a (7.18 g, 23.13 mmol) in 200 mL of dry DMF and added dropwise to the suspension over 24 h. The mixture immediately turned blue in color and over the progress of the reaction finally turned gray. The resulting mixture was stirred at 100 °C for further 3 d. The reaction was cooled down to room temperature, filtered off, washed with chloroform (250 mL). The filtrate was concentrated and the resulting black solution was re-dissolved in chloroform (200 mL) and washed with 10% K₂CO₃ solution (3x150 mL) and brine (2x200 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated in reduced pressure. The crude product was purified by column chromatography (2% acetone/dichloromethane) to afford 2.6 g (68%) of 7a as a white solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.82 (s, 6H), 4.23 (t, J = 6.4 Hz, 12H), 4.14 (d, J = 2.4 Hz, 12H), 3.55 (t, J = 6.4 Hz, 12H) 2.42 (t, J = 2.4 Hz, 6H), 1.98-1.92 (m, 12H), 1.71-1.48 (m, 36H); ¹³C NMR (CDCl₃, 101 MHz) δ 148.9, 123.6, 107.3, 80.0, 74.2, 70.2, 69.6,
58.0, 29.6, 29.5, 26.0; HRMS (FAB) calcd. for $\text{C}_72\text{H}_{96}\text{O}_{12}$: 1152.7266; found: 1152.7206.

7b: White solid. Yield: 72%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.83 (s, 6H), 4.22 (t, $J = 6.4$ Hz, 12H), 4.13 (d, $J = 2.4$ Hz, 12H), 3.50 (t, $J = 6.4$ Hz, 12H) 2.41 (t, $J = 2.4$ Hz, 6H), 1.97-1.89 (m, 12H), 1.61-1.53 (m, 24H), 1.41-1.33 (m, 60H); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 148.9, 123.6, 107.4, 80.0, 74.1, 70.3, 69.7, 58.0, 29.6, 29.5, 29.4, 26.2, 26.1; HRMS (FAB) calcd. for $\text{C}_{96}\text{H}_{144}\text{O}_{12}$: 1489.0658; found: 1489.0748.

7c: White solid. Yield: 65%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.83 (s, 6H), 4.22 (t, $J = 6.4$ Hz, 12H), 4.13 (d, $J = 2.4$ Hz, 12H), 3.50 (t, $J = 6.4$ Hz, 12H) 2.41 (t, $J = 2.4$ Hz, 6H), 1.97-1.89 (m, 12H), 1.62-1.53 (m, 24H), 1.41-1.29 (m, 84H); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 148.9, 123.6, 107.4, 80.1, 74.1, 70.3, 69.7, 58.0, 29.7, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 26.2, 26.1; HRMS (FAB) calcd. for $\text{C}_{108}\text{H}_{168}\text{O}_{12}$: 1657.2360; found: 1657.2352.
8a: In a single-necked round bottom flask a mixture of 7a (0.5 g, 0.40 mmol) and CuI (0.27 g, 1.41 mmol) were taken under argon. To the mixture a solution of N,N-diisopropylethylamine (1.41 mL, 8.08 mmol), 0.64 g (4.04 mmol) of pivoly azide in 70 mL of deoxygenated THF were added and stirred at 50 °C for 24 h. The brown reaction mixture was cooled down to room temperature and 70 mL of water was added. The organic layer was extracted with ethyl acetate (3x100 mL), washed with water (2x100 mL), brine (2x100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (4:1 dichloromethane/acetone) to afford 0.51 g of 8a (58%) as a sticky liquid.

¹H NMR (CDCl₃, 400 MHz) δ 7.81 (s, 6H), 7.79 (s, 6H), 6.19 (s, 12H), 4.63 (s, 12H), 4.21 (t, J = 6.4 Hz, 12H), 3.55 (t, J = 6.4 Hz, 12H), 1.97-1.89 (m, 12H), 1.70-1.44 (m, 48H), 1.17 (s, 54H); ¹³C NMR (CDCl₃, 101 MHz) δ 177.7, 148.9, 146.0, 123.8, 123.6, 107.3, 70.9, 69.6, 69.5, 64.1, 38.8, 29.7, 29.5, 26.8, 26.0, 26.0; HRMS (FAB) calcd. for C₁₀₈H₁₆₂N₁₈O₂₄: 2095.2009; found: 2095.2478.

8b: Sticky liquid. Yield: 62%. ¹H NMR (CDCl₃, 400 MHz) δ 7.80 (s, 6H), 7.76 (s, 6H), 6.19 (s, 12H), 4.59 (s, 12H), 4.19 (t, J = 6.4 Hz, 12H), 3.48 (t, J = 6.4 Hz, 12H), 1.94-1.87 (m, 12H), 1.58-1.50 (m, 24H), 1.38-1.29 (m, 60H), 1.15 (s, 54H); ¹³C NMR (CDCl₃, 101 MHz) δ 177.7, 148.9, 146.0, 123.8, 123.6, 107.3, 71.0, 69.7, 69.6, 64.1, 38.8, 29.7, 29.6, 29.5, 26.8, 26.2, 26.1; HRMS (FAB) calcd. for C₁₃₂H₂₁₀N₁₈O₂₄: 2431.5765; found: 2431.5427.

8c: Sticky liquid. Yield: 68%. ¹H NMR (CDCl₃, 400 MHz) δ 7.87 (s, 6H), 7.78 (s, 6H), 6.21 (s, 12H), 4.62 (s, 12H), 4.21 (t, J = 6.4 Hz, 12H), 3.50 (t, J = 6.4 Hz, 12H), 1.94-1.89 (m, 12H), 1.59-1.50 (m, 24H), 1.38-1.28 (m, 60H), 1.18 (s, 54H); ¹³C NMR (CDCl₃, 101 MHz) δ 177.8, 148.9, 146.2, 123.8, 123.6, 107.3, 71.1, 69.7, 69.7, 64.1, 38.8, 29.7, 29.7, 29.6, 29.5, 26.8, 26.2, 26.1. HRMS (FAB) calcd. for C₁₄₄H₂₃₄N₁₈O₂₄: 2600.7722; found: 2600.5107.
9a: In a single-necked round bottom flask 8a (0.4 g, 0.19 mmol) was dissolved in 10 mL of 1M NaOH/THF (1:1 v/v mixture) and the mixture was heated at 50 °C for 16 h. The bluish reaction mixture was cooled down to room temperature, 10 mL water was added to it and pH was adjusted to 7.0 by dropwise addition of HCl solution. The mixture was filtered off, washed with water and dried under vacuum to afford 9a as a bluish sticky solid (0.25 g, 94%).

$^1$H NMR (DMSO-d$_{6}$, 400 MHz) $\delta$ 14.85 (bs, 6H), 7.99 (s, 6H), 7.78 (s, 6H), 4.55 (s, 12H), 4.25 (bs, 12H), 3.46 (t, $J = 6.4$ Hz, 12H), 1.83-1.72 (m, 12H), 1.56-1.43 (m, 36H); $^{13}$C NMR (DMSO-d$_{6}$, 101 MHz) $\delta$ 149.0, 144.9, 133.4, 123.4, 122.2, 107.6, 70.1, 69.1, 63.6, 29.6, 29.4, 26.0, 25.9; HRMS (FAB) calcd. for $C_{72}H_{102}N_{18}O_{12}$: 1410.7925; found: 1410.8411.

9b: bluish sticky solid. Yield: 93%. $^1$H NMR (DMSO-d$_{6}$, 400 MHz) $\delta$ 14.86 (bs, 6H), 7.77 (s, 6H), 7.66 (s, 6H), 4.62 (s, 12H), 4.19 (bs, 12H), 3.37 (t, $J = 6.4$ Hz, 12H), 1.78 (m, 12H), 1.47-1.34 (m, 12H), 1.34-1.10(m, 72H); $^{13}$C NMR (DMSO-d$_{6}$, 101 MHz) $\delta$ 148.9, 146.2, 134.5, 123.4, 107.5, 76.2, 70.3, 69.1, 63.5, 29.6, 29.5, 29.4, 26.2, 26.1; HRMS (FAB) calcd. for $C_{96}H_{150}N_{18}O_{12}$: 1747.1681; found: 1747.1851.
**9c:** bluish sticky solid. Yield: 97%. $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 14.86 (bs, 6H), 7.75 (s, 6H), 7.57 (s, 6H), 4.48 (s, 12H), 4.0 (bs, 12H), 3.36 (t, $J = 6.4$ Hz, 12H), 1.71 (m, 12H), 1.45-1.36 (m, 24H), 1.36-1.20 (m, 84H); $^{13}$C NMR (DMSO-d$_6$, 101 MHz) $\delta$ 148.5, 143.3, 130.0, 123.1, 106.8, 70.1, 68.8, 63.5, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2; HRMS (FAB) calcd. for $C_{108}H_{174}N_{18}O_{12}$: 1915.3559; found: 1915.3667.

**III. Thermal Gravimetric Analysis (TGA)**

![Thermogravimetric Analysis (TGA) of 9a-9c (heating rate 10 °C/min)](image)

**Fig. S1** Thermogravimetric Analysis (TGA) of **9a-9c** (heating rate 10 °C/min)

**IV. Differential Scanning Calorimetry (DSC)**

**9a:**
Fig. S2 DSC trace of 9a (heating rate 10 °C/min, cooling rate 5 °C/min. Enthalpy variation for first heating was 46.6 J/mol

9b:

Fig. S2 DSC trace of 9b (heating rate 10 °C/min, cooling rate 5 °C/min. Enthalpy variation for first heating was 36.6 J/mol

V. Polarized Optical Microscopy (POM)
9a and 9b: Consistent with DSC results, both samples showed melting behavior and did not recrystallize on the length scale of the experiment.

9c: When heated at 1 °C/min, birefringence persists in this sample over a wide temperature range before finally disappearing at 140 °C, indicating a very slow phase transition (Fig. S4).

![Polarized Optical Microscopy of 9c, heating rate of 1°C/min](image)

**Fig. S4** Polarized Optical Microscopy of 9c, heating rate of 1°C/min

**VI. Powder X-ray Diffraction**

Both 9a (Fig S6) and 9b (Fig S7) exhibited a quasi-reversible phase transition on the experimental time scale, in agreement with DSC. In all cases, at elevated temperatures the samples were not truly isotropic, but exhibited a peak on the length scale of 17-20 Å.
VII. NMR Spectra