Supplementary information

Anhydrous proton conduction in liquid crystals containing benzimidazole moieties

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Structural Characterization

[1]H nuclear magnitude resonance (NMR) spectra of **4a** and **1a** are shown in Fig. S1. In the ^{1}H NMR spectrum of **4a**, the peak at 3.44 ppm was ascribed to the alkyl protons linked to the bromo atom. In the spectrum of **1a**, the peak was at 3.35 ppm arose from the alkyl protons linked to the sulfur atom[1,2]. The signal intensities of the peaks at 7.57, 7.51, 6.97 ppm corresponding to the chemical shifts of protons in aromatic rings increased in the ^{1}H NMR spectrum of **1a**. The results suggested the successful substitution reaction.
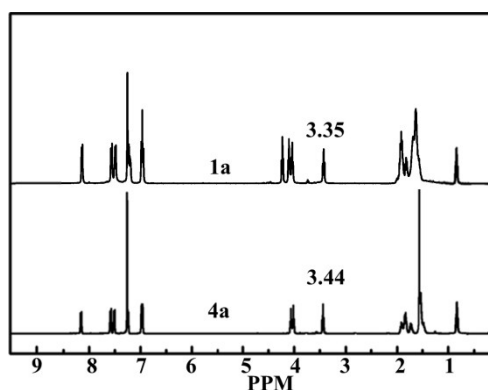

Fig. S1 ^{1}H NMR spectra of **1a** and **4a** in CDCl$_3$

Fourier transform infrared (FT-IR) spectra of **4a**, **1a, 1b and 1c** are shown in Fig. S2 and S3. The absorption band at 550cm^{-1} in the spectrum of **4a** was assigned to C-Br stretching[4]. In the spectrum of **1a**, the bands at 1346 and 600cm^{-1} were ascribed to the C=N stretching and N-H out-of plane blending vibrations of benzimidazole moieties, respectively[3]. The absorption band at 1440cm^{-1} was attributed to C-S stretching. A broad absorption centered at 3070cm^{-1} was attributed to the intermolecular hydrogen-bonded N-H stretching vibration between benzimidazole moieties[5].
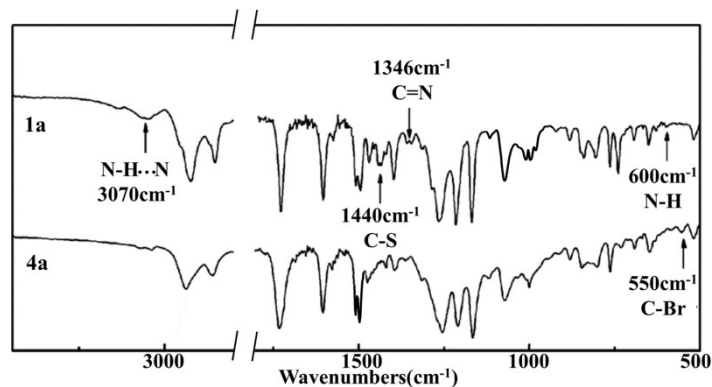
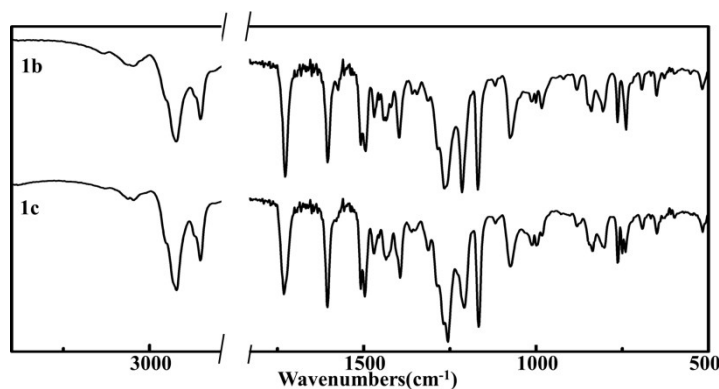Fig. S2 FT-IR spectra of **1a** and **4a** at room temperature

Fig. S3 FT-IR spectra of **1b** and **1c** at room temperature

Thermal characterization

The differential scanning calorimetry (DSC) traces of **1** during the first cooling and second heating scans are shown in Fig. S4. The multiple peaks indicated appearance of mesophases. XRD patterns of **1a**, **1b** and **1c** in the smectic phase during the cooling process are shown in Fig. S5.
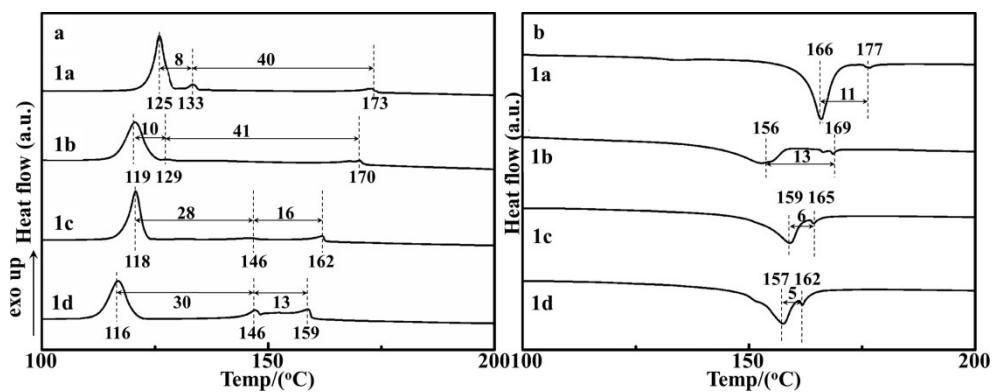

Fig. S4 DSC traces of **1** during the first cooling (a) and second heating (b)
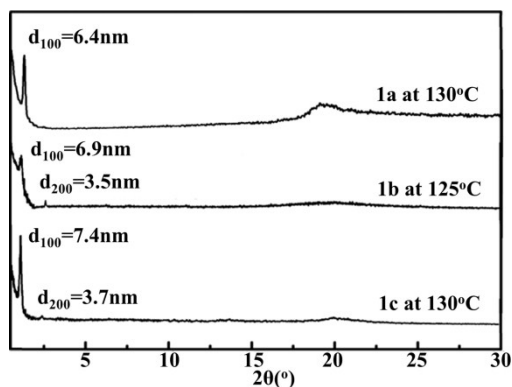
Fig. S5 XRD patterns of **1a**, **1b** and **1c** in the smectic phase during the cooling process

Electrochemical characterization

Samples were dried under vacuum overnight and sandwiched between two indium tin oxide (ITO) glass slides. The sample thickness (d) and cross sectional area (A) were controlled by a 150μm thick Teflon spacer with a 0.2 cm diameter hole. The impedance spectrum of **1d** at 140°C is shown in Fig. S6. The bulk resistance was derived from the low intersection of the high-frequency semicircle on a complex impedance plane with the real components axis. Multiple measurements were performed for each sample and the relative standard deviation of the resultant bulk resistance was less than 5%.
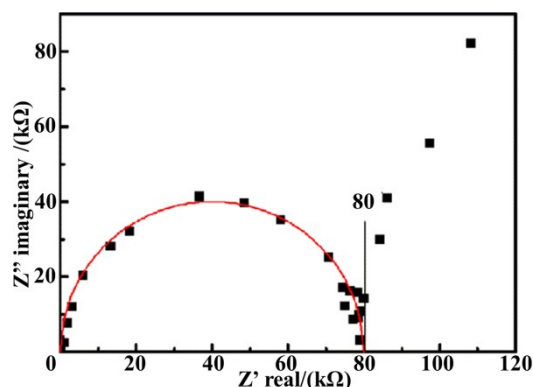

Fig. S6 Impedance spectrum for **1d** at 140°C

The transference numbers corresponding to ion and electron transfer were calculated using Wagner's DC polarization technique with ITO electrodes[7]. Current relaxation curve of **1d** at 140°C during potentionstatic polarization is shown in Fig. S7. The ion transference numbers (t_p) were calculated from the curve using the following equation:

$$t_p = \frac{I_s - I_f}{I_s} \tag{S1}$$

Where I_S is the initial current (μA) and I_f is the steady state current (μA). For all the samples, the ionic transference numbers were found to be in the range of 0.98~0.99.
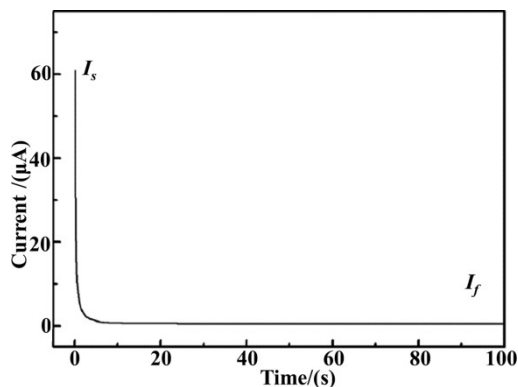
Fig. S7 Current relaxation curve of **1d** at 140°C

Proton conductivity σ (S cm^{-1}) was obtained from the following equation:

$$\sigma = d \cdot R_b^{-1} \cdot A^{-1}$$ (S2)

where R_b, d and A are the bulk resistance (Ω), the sample thickness (cm), and the sample area (cm^2), respectively.

The activation energies (Ea) for proton conduction were estimated from the Arrhenius plots.

$$\ln \sigma = \ln A - E_a \cdot R \cdot (T + 273)^{-1}$$ (S3)

where A is the pre-exponential factor (S cm^{-1}); R is known as molar gas constant (J° K^{-1} mol^{-1}); Ea is the activation energy (kJ mol^{-1}).

References

1. A. K. Khalil, Phosphorus Sulfur., 2007, **182**, 815.

2. J. P. Jayachandran, M. Wang, Synth. Commun., 1999, **29**, 4087.

3. V. LUPTÁKOVÁ, G. PLESCH, Clay Miner. 40(2005)295-302.

4. J. Coates, Interpretation of Infrared Spectra, A Practical Approach, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester, 2000, pp. 10815.

5. A. Kawada, A. R. McGhie, M. M. Labes, J. Chem. Phys., 1970, 52, 3121.

6. C. Perchard, A. Novak, J. Chem. Phys., 1968, **48**, 3079.

7. S. Selvasekarapandian, R. Baskaran, M. Hema, Phys. B., 2005, **357**, 412.