Supplementary information

Anhydrous proton conduction in liquid crystals containing benzimidazole moieties

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Structural Characterization

¹H nuclear magnitude resonance (NMR) spectra of 4a and 1a are shown in Fig. S1. In the ¹H 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. 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 ¹H NMR spectrum of 1a. The results suggested the successful substitution reaction.

![Fig. S1 ¹H NMR spectra of 1a and 4a in CDCl₃](image)

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. 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. 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.
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.
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%.

The transference numbers corresponding to ion and electron transfer were calculated using Wagner’s DC polarization technique with ITO electrodes. 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:

\[ t_p = \frac{I_s - I_f}{I_s} \]  \hspace{1cm} (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.
Proton conductivity $\sigma$ (S cm$^{-1}$) was obtained from the following equation:

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

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

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

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

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

References