Supplementary information

Use of a protic salt for the formation of liquid-crystalline proton-conductive complexes with mesomorphic diols

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1. $^1$H NMR spectra of protic salt 3

Protic salt 3 was identified by $^1$H NMR spectroscopy of the CDCl$_3$ (Fig. S3) and DMSO-d$_6$ solution (Fig. S4). The imidazole NH proton and sulfonic acid proton are not observed for the CDCl$_3$ solution (Fig. S3). In contrast, the DMSO-d$_6$ solution indicates a broad signal at 14.3 ppm, which is attributable to the imidazolium NH proton.

Figure S1. $^1$H NMR spectrum of protic salt 3 in CDCl$_3$.

Figure S2. $^1$H NMR spectrum of protic salt 3 in DMSO-d$_6$. 
2. XRD diffraction study of compound 1

The self-assembled structure of compound 1 was determined by XRD measurements. The wide-angle XRD pattern of 1 at 70 °C shows four peaks corresponding to the diffraction from the (100), (110), (200) and (300) planes of the hexagonal columnar structure. The two-dimensional transmission image of small-angle XRD pattern of 1 aligned homeotropically on a polyimide film at 70 °C shows diffraction spots with a six fold symmetry from the (100) plane.

Figure S3. (a) Wide-angle and (b) small-angle XRD patterns of compound 1 in the columnar phase at 70 °C.

3. The intercolumnar distance ($a$) and average number of molecules per cross-sectional slice of the columns ($n$)

Figure S4. Schematic illustration of the hexagonal columnar lattice.
The intercolumnar distance \( (a) \) of the single diol compound and the mixtures containing protic salt 3 is estimated as follows. The value of \( d_{100} \) is obtained from the wide-angle XRD patterns.

\[
a = \frac{2 \times d_{100}}{\sqrt{3}}
\]

The volume of the cross-sectional slice of the column \((V)\) is described as follows,

\[
V = A \times B \times \frac{1}{2} \times 12 \times h = \frac{\sqrt{3}}{2} a^2 h
\]

where \( h \) is the average spacing between benzene rings or molten alkyl chains in the direction of the column axis. The \( h \) value is estimated to be 4.5-4.6 Å from the halo around 20 ° in the wide-angle XRD patterns.

The density \((\rho)\) of the material is described as follows:

\[
\rho = \frac{n_1 M_1 + n_3 M_3}{\frac{\sqrt{3}}{2} a^2 h} = \frac{n_1 M_1 + n_3 M_3}{\sqrt{3} N_A a^2 h} = \frac{2 n_1 M_1 + n_3 M_3}{\sqrt{3} N_A a^2 h}
\]

where \( n_1 \) and \( n_3 \) are the average number of molecules of compound 1 and protic salt 3 per cross-sectional slice of the columns respectively, \( M_1 \) and \( M_3 \) are the molecular weight of 1 and 3 \((M_1 = 564.9 \text{ and } M_3 = 226.3)\). \( N_A \) is Avogadro’s number \((6.02 \times 10^{23} \text{ mol}^{-1})\).

Therefore, \( n_1 \) and \( n_3 \) can be obtained by solving the following simultaneous equations.

\[
\begin{align*}
\left\{ \begin{array}{l}
  n_1 : n_3 = (100 - x) : x \\
  n_1 M_1 + n_3 M_3 = \frac{\sqrt{3}}{2} N_A a^2 h \rho
\end{array} \right.
\]

where \( x \) is the mole% of 3 in the mixtures. The density of the diol compounds and the mixtures containing 3 is assumed to be 1.0 g cm\(^{-3}\).

The intercolumnar distance \( (a) \) of the mixtures 1/3(x) and 2/3(x) up to \( x = 40 \) are shown in Figure S5. The average number of diol molecules 1 \((n_1)\) and 2 \((n_2)\) and protic salt \((n_3)\) in the mixtures per cross-sectional slice of the columns are shown in Figure S6 and S7.
Figure S5. Intercolumnar distance of the mixtures in the Col₅ phase.

Figure S6. Average number of diol compound 1 ($n_1$: ●) and protic salt 3 ($n_3$: ■) per cross-sectional slice of the columns.
Figure S7. Average number of diol compound 2 ($n_2$: ●) and protic salt 3 ($n_3$: ■) per cross-sectional slice of the columns.
4. $^1$H NMR spectra of 1,3, and the mixture 1/3(50)

The interactions of diol compound 1 and protic salt 3 were examined by $^1$H NMR. The downfield shift of C(2) proton (H13) of imidazolium cation of 3 was observed.

Figure S8. $^1$H NMR spectra of diol 1, protic salt 3, and the equimolar mixture of 1 and 3.
5. $^{13}$C NMR spectra of 1, 2, 3, 1/3(50), and 2/3(50)

The interactions of diol compound and protic salt were examined by $^{13}$C NMR. The carbonyl carbons of 1 and 2 appear at 167.2 ppm 169.2 ppm, respectively. No shifts of the carbonyl carbon are observed for the mixture s 1/3(50) and 2/3(50). These results suggest the carbonyl groups are not involved in specific interactions with protic salt 3.

![Figure S9. $^{13}$C NMR spectra of single compound 1 and 3 and equimolar mixture 1/3.](image)

![Figure S10. $^{13}$C NMR spectra of single compound 2 and 3 and equimolar mixture 2/3.](image)
6. IR spectra of single compounds 1-3 and the mixtures

The interactions of diol compounds 1, 2 and protic salt 3 were examined by FT-IR measurements. The IR spectra of single compounds 1, 2, and 3 are shown in Figure S11-S13, respectively. Figures S14-S17 indicate the IR spectra of the mixtures of 1, 2 with 3. The IR spectra of the mixtures containing 3 at the different concentration were also recorded (Fig. S18).

![Chemical structure of compound 1](image)

Figure S11. (a) Temperature dependent FT-IR spectra of compound 1 and (b) its enlarged view.
Figure S12. (a) Temperature dependent FT-IR spectra of compound 2 and (b) its enlarged view.

Figure S13. FT-IR spectra of protic salt 3 at room temperature.
For single compounds 1 and 2, the O-H stretching band around 3400 cm\(^{-1}\) is shifted to higher wavenumber as the temperature rises. The N-H and C=O bands are also slightly shifted to higher wavenumber.

Figure S14. (a) Temperature dependent FT-IR spectra of the mixture 1/3(30) and (b) its enlarged view.

Figure S15. (a) Temperature dependent FT-IR spectra of the mixture 2/3(30) and (b) its enlarged view.
Figure S16. (a) Temperature dependent FT-IR spectra of the mixture 1/3(50) and (b) its enlarged view.

Figure S17. (a) Temperature dependent FT-IR spectra of the mixture 2/3(50) and (b) its enlarged view.
Figure S18. FT-IR spectra of (a) the mixtures of compound 1 and protic salt 3 and (b) the mixtures of compound 2 and protic salt 3 at 70 °C.
7. POM images of the uniaxially oriented 2/3(20) in the Colₖ phase

A uniaxially parallel orientation of the columns of the mixture 2/3(20) has been achieved between the comb-shaped gold electrodes on a glass substrate by the application of mechanical shear force to the sample at 120 °C.

Figure S19. POM images of the uniaxially oriented mixture 2/3(20) under a crossed Nicols condition. (a) The shearing direction is parallel to the polarizer axis. (b) The sample of (a) is rotated by 45 °. Arrows indicate the directions of the shear force (S), analyzer (A) and polarizer (P) axes.
8. Vogel-Tamman-Fulcher plots of the ionic conductivities for mixtures 1/3(x) and 2/3(x)

The temperature dependence of the ionic conductivities for the mixtures 1/3(x) and 2/3(x), where x denotes the mole% of 3, are fitted by the Vogel-Tamman-Fulcher (VTF) equation:

\[ \sigma = \frac{A}{\sqrt{T}} \exp \left( \frac{-B}{T - T_0} \right) \]

where \( \sigma \) and T are the ionic conductivity and the absolute temperature. A, B and \( T_0 \) are fitting parameters. The parameter A (S m\(^{-1}\) K\(^{1/2}\)) is related to the carrier ion number. The parameter B (K) is related to the activation energy. The product of B (K) and the molar gas constant (8.31 J K\(^{-1}\) mol\(^{-1}\)) has the dimension of activation energy (J mol\(^{-1}\)). \( T_0 \) (K) is the ideal glass transition temperature at which the configurational entropy vanishes.

The temperature dependencies of ionic conductivities for the mixtures 1/3(x) and 2/3(x) are well fitted by the VTF equation. The VTF fitting parameters are summarized in Table S1. For example, the VTF fitting of the ionic conductivities for the mixture 2/3(20) in the Col\(_b\) phase is shown in Figure S20. The VTF plots of the ionic conductivities for the mixtures 1/3(x) and 2/3(x) shown in Figure S21 are depicted as straight lines.

![Figure S20. Arrhenius plots for the ionic conductivity of the mixture 2/3(20). The solid line is the fitting result of the value of ionic conductivity on the VTF equation.](image)
Table S1. VTF fitting parameters of the ionic conductivities for mixtures $1/3(x)$ and $2/3(x)$.

<table>
<thead>
<tr>
<th></th>
<th>$A$ (S m$^{-1}$ K$^{1/2}$)</th>
<th>$B$ (K)</th>
<th>$T_0$ (K)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/3(20)$</td>
<td>0.032</td>
<td>625.9</td>
<td>238.8</td>
<td>0.9983</td>
</tr>
<tr>
<td>$1/3(30)$</td>
<td>0.121</td>
<td>751.3</td>
<td>229.7</td>
<td>0.9991</td>
</tr>
<tr>
<td>$1/3(50)$</td>
<td>13.10</td>
<td>2161.1</td>
<td>124.82</td>
<td>0.9972</td>
</tr>
<tr>
<td>$2/3(20)$</td>
<td>0.049</td>
<td>877.71</td>
<td>242.34</td>
<td>0.9984</td>
</tr>
<tr>
<td>$2/3(30)$</td>
<td>0.173</td>
<td>847.73</td>
<td>239.43</td>
<td>0.9996</td>
</tr>
<tr>
<td>$2/3(50)$</td>
<td>14.35</td>
<td>2480.1</td>
<td>128.02</td>
<td>0.9986</td>
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</table>

Figure S21. VTF plots of the ionic conductivities for (a) the mixture $1/3(x)$ and (b) the mixture $2/3(x)$ in the liquid-crystalline phases. The mixtures $1/3(20)$, $1/3(30)$, $2/3(20)$, and $2/3(30)$ form the Col$_h$ phases. The mixtures $1/3(50)$ and $2/3(50)$ exhibit the S$_A$ phases.
9. DSC thermograms of 1, 2 and their mixtures with 3

Figure S22. DSC thermograms of (a) compound 1, (b) mixture 1/3(10), (c) mixture 1/3(20), (d) mixture 1/3(30), (e) mixture 1/3(40), and (f) mixture 1/3(50) at the scanning rate of 10 K/min.
Figure S23. DSC thermograms of (a) compound 2, (b) mixture 2/3(10), (c) mixture 2/3(20), (d) mixture 2/3(30), (e) mixture 2/3(40), and (f) mixture 2/3(50) at the scanning rate of 10 K/min.
Figure S24. DSC thermograms of (a) the mixtures $1/3(x)$ and (b) the mixtures $2/3(x)$ on cooling at the scanning rate of 10 K/min.

Figure S25. DSC thermograms of protic salt 3 at the scanning rate of 10 K/min.
10. Wide-angle XRD diffraction patterns of the mixtures

Figure S26. Wide-angle XRD patterns of (a) compound 1, (b) mixture 1/3(10), (c) mixture 1/3(20), (d) mixture 1/3(30), (e) mixture 1/3(40), and (f) mixture 1/3(50) at 70 °C.
Figure S27. Wide-angle XRD patterns of (a) compound 2, (b) mixture 2/3(10), (c) mixture 2/3(20), (d) mixture 2/3(30), (e) mixture 2/3(40), and (f) mixture 2/3(50) at 70 °C.
Table S2. The values of \(d\)-spacing for the mixtures 1/3(x) at 70 °C.

<table>
<thead>
<tr>
<th></th>
<th>(100) [Å]</th>
<th>(200) [Å]</th>
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<tbody>
<tr>
<td>1</td>
<td>39.41</td>
<td>19.71</td>
</tr>
<tr>
<td>1/3(10)</td>
<td>45.04</td>
<td>21.02</td>
</tr>
<tr>
<td>1/3(20)</td>
<td>46.95</td>
<td>21.96</td>
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<tr>
<td>1/3(30)</td>
<td>47.97</td>
<td>22.87</td>
</tr>
<tr>
<td>1/3(40)</td>
<td>50.73</td>
<td>23.99</td>
</tr>
<tr>
<td>1/3(50)</td>
<td>49.04</td>
<td>22.75</td>
</tr>
</tbody>
</table>

Table S3. The values of \(d\)-spacing for the mixtures 2/3(x) at 70 °C.

<table>
<thead>
<tr>
<th></th>
<th>(100) [Å]</th>
<th>(200) [Å]</th>
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<tbody>
<tr>
<td>2</td>
<td>37.72</td>
<td>18.87</td>
</tr>
<tr>
<td>2/3(10)</td>
<td>44.14</td>
<td>20.63</td>
</tr>
<tr>
<td>2/3(20)</td>
<td>47.97</td>
<td>22.29</td>
</tr>
<tr>
<td>2/3(30)</td>
<td>50.73</td>
<td>23.36</td>
</tr>
<tr>
<td>2/3(40)</td>
<td>55.17</td>
<td>25.66</td>
</tr>
<tr>
<td>2/3(50)</td>
<td>49.04</td>
<td>22.87</td>
</tr>
</tbody>
</table>

Figure S28. Wide-angle XRD pattern of protic salt 3 at 25 °C.