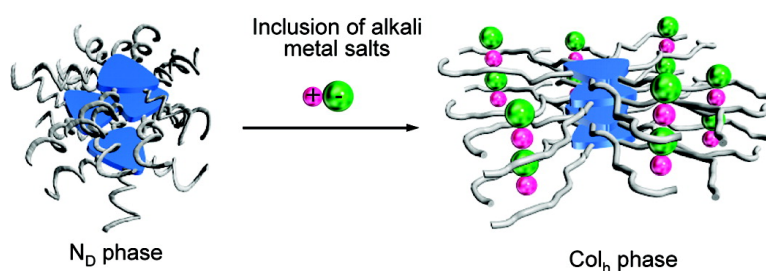


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# Room-Temperature Discotic Nematic Liquid Crystals over a Wide Temperature Range: Alkali-Metal-Ion-Induced Phase Transition from Discotic Nematic to Columnar Phases

Shigeo Kohmoto,\* Emiko Mori, and Keiki Kishikawa

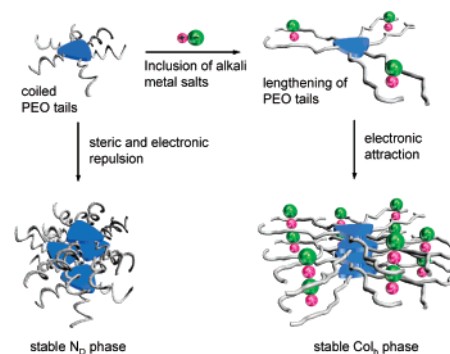
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Unlike a large number of calamitic nematic liquid crystals showing a room-temperature mesophase, only few disc-shaped molecules have been known to exhibit a discotic nematic phase ( $N_D$ ) at room temperature.<sup>1</sup> Even the number of compounds showing a  $N_D$  phase is rather limited. Several derivatives of triphenylene,<sup>2</sup> truxene,<sup>3</sup> thiotruxene,<sup>4</sup> naphthalene,<sup>5</sup> phenylene ethynylene macrocycles,<sup>6</sup> phenylethynylbenzene,<sup>7</sup> and hydrazone<sup>8</sup> are the typical examples to show stable  $N_D$  phases; however, most of them show  $N_D$  phases at high temperature and in a narrow range of temperature. In view of the demands for optical compensation films for wide-viewing-angle LCDs<sup>9</sup> and lubricant usage in a minute space,<sup>10</sup> room-temperature  $N_D$  liquid crystals are highly desired. In this communication, we report on our novel approach to triphenylene-based room-temperature  $N_D$  liquid crystals and their unique phase transition from a  $N_D$  phase to a hexagonal columnar ( $Col_h$ ) phase triggered by alkali metal ions. This is the rare example of room-temperature  $N_D$  liquid crystals and, to the best of our knowledge, the first example of the morphological transformation of discotic liquid crystal phases by complexation of ions.

Literature survey of triphenylene derivatives, the archetypal discotic liquid crystals, revealed that its benzoyl ester derivative with alkyl chain substituent<sup>11</sup> showed the  $N_D$  phase at high temperature ( $> 170$  °C). We considered that a replacement of alkyl chain parts to more flexible tails could result in a decrease of mesophase temperature. For this purpose, poly(ethylene oxide) (PEO) units have been introduced to the triphenylene core.<sup>12</sup> Figure 1 illustrates our concept for the formation of a stable  $N_D$  phase and its transformation to a  $Col_h$  phase triggered by the addition of alkali metal ions. It is known that poly(ethylene glycol) (PEG) and PEO adopt helical and coil conformations.<sup>13</sup> The average width of the single helix of PEO is reported to be 7.6 Å from its STM measurements.<sup>14</sup> The width is fairly larger than the thickness of the triphenylene  $\pi$  plane, which could prevent formation of the columnar array of the triphenylene cores. In addition to this steric factor, electronic repulsion among PEO tails could also promote the formation of a  $N_D$  phase. The PEO tails can complex alkali metal ions by ion–dipole interactions.<sup>15</sup> This complexation straightens the bent coiled PEO tails. As a result, triphenylene discs can self-assemble to form columnar arrays owing to the sequential ionic interactions among the alkali metal ions complexed with their counterions in the direction of columnar axis. Thus, hitherto unknown phase transition from a  $N_D$  phase to a  $Col_h$  phase can be triggered by alkali metal ions.

Three triphenylene derivatives **1a–1c** possessing di-, tri-, and tetraethylene oxide units as their side chains, respectively, were examined. Their liquid crystalline behaviors were investigated by polarized light optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffractions (XRD). Com-



**Figure 1.** Schematic representation of the formation of a  $N_D$  phase and the phase transition from the  $N_D$  phase to the  $Col_h$  phase triggered by the addition of alkali metal salts.

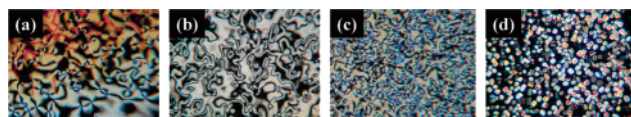
pounds **1b** and **1c** showed  $N_D$  phases at room temperature. Table 1 shows their phase transition temperatures. Figure 2a–c shows their optical textures observed by POM. As the number of ethylene oxide units increased, their phase transition temperatures from crystals to  $N_D$  phases were decreased. Triphenylene **1c** became glassy around 0 °C.

A unique phase transformation from a  $N_D$  phase to a  $Col_h$  phase was observed when alkali metal ions were added to triphenylene derivatives (entries 2, 3, and 6 in Table 1). Ionic interactions among alkali metal salts are the crucial attractive force for assembling<sup>16</sup> to form the columnar structure. Lithium salts of these compounds were prepared by evaporation of the THF solution of the triphenylenes with appropriate amounts of  $CF_3SO_3Li$  (LiOTf). Figure 2d shows the optical texture of **1a** with 2 molar equiv of LiOTf on cooling at 200 °C observed by POM. The XRD profile of **1a** showed one broad reflection peak corresponding to the  $d$  spacing of 19.7 Å, which was attributed to the average diameter of the disc-like molecule **1a** (Figure 3a). The addition of LiOTf caused the phase transformation from the  $N_D$  phase to the  $Col_h$  phase when the amount of LiOTf exceeded 1 molar equiv to **1a**. The lithium salt of **1a** with 1 equiv of LiOTf showed three reflection peaks in its XRD corresponding to the  $d$  spacings of 24.9, 14.4, and 12.6 Å, which were indexed in sequence as (100), (110), and (200) of a  $Col_h$  lattice (Figure 3b). The  $Col_h$  phases were also observed with increasing amounts of LiOTf, which caused an elongation of the diameter of the discs. The  $d$  spacings corresponding to the (100) reflections of the lithium salts of **1a** with 2, 3, and 6 equiv of LiOTf were increased to 25.3, 26.3, and 28.3 Å, respectively. These observations imply that the ethylene oxide units interwind under ion-free conditions and can be extended by the recognition of the additive alkali metal ions to lengthen their disc diameter. The strongest reflection for the (100) was observed for the lithium salt with 2 equiv of LiOTf. The addition of an excess amount of LiOTf brought about the decrease of its intensity. With 6 equiv of LiOTf,

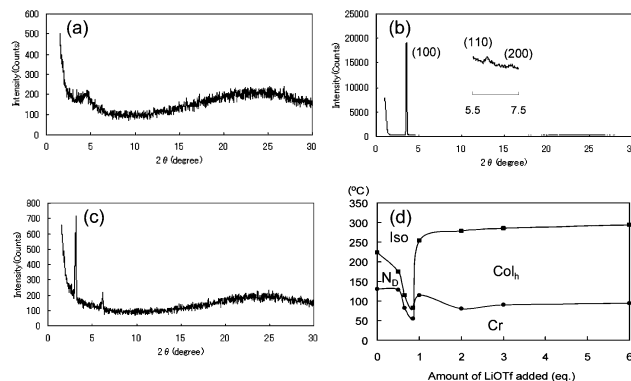
**Table 1.** Phase Transition Temperatures and Enthalpies (in Parentheses) for **1a–1c** Determined by DSC or POM<sup>a</sup>

entry	Compd.	T (°C) and $\Delta H_f$ (Jg <sup>-1</sup> )
1	<b>1a</b>	Cr $\xrightleftharpoons[100.3 (-12.6)]{129.9 (13.7)}$ N <sub>D</sub> $\xrightleftharpoons[222.2 (-0.4)]{223.5 (0.2)}$ Iso
		Cr $\xrightleftharpoons[103]{115}$ Col <sub>h</sub> $\xrightleftharpoons[227]{254}$ Iso
2	<b>1a</b> + LiOTf (1eq)	Cr $\xrightleftharpoons[103]{115}$ Col <sub>h</sub> $\xrightleftharpoons[227]{254}$ Iso
		Cr $\xrightleftharpoons[152]{153}$ Col <sub>h</sub> $\xrightleftharpoons[259]{273}$ Iso
3	<b>1a</b> + NaOTf (1eq)	Cr $\xrightleftharpoons[152]{153}$ Col <sub>h</sub> $\xrightleftharpoons[259]{273}$ Iso
		Cr $\xrightleftharpoons[78]{132}$ N <sub>D</sub> $\xrightleftharpoons[221]{224}$ Iso
4	<b>1a</b> + LiCl (1eq)	Cr $\xrightleftharpoons[78]{132}$ N <sub>D</sub> $\xrightleftharpoons[221]{224}$ Iso
		Cr $\xrightleftharpoons[23]{25}$ N <sub>D</sub> $\xrightleftharpoons[146.2 (-0.3)]{147.4 (0.3)}$ Iso
5	<b>1b</b>	Cr $\xrightleftharpoons[23]{25}$ N <sub>D</sub> $\xrightleftharpoons[146.2 (-0.3)]{147.4 (0.3)}$ Iso
		G $\xrightleftharpoons[247]{253}$ Col <sub>h</sub> $\xrightleftharpoons[247]{253}$ Iso
6	<b>1b</b> + LiOTf (4eq)	G $\xrightleftharpoons[247]{253}$ Col <sub>h</sub> $\xrightleftharpoons[247]{253}$ Iso
		N <sub>D</sub> $\xrightleftharpoons[65]{76}$ Iso
7	<b>1c</b>	N <sub>D</sub> $\xrightleftharpoons[65]{76}$ Iso

<sup>a</sup> Cr, crystal; G, glass; N<sub>D</sub>, nematic discotic; Col<sub>h</sub>, hexagonal columnar; Iso, isotropic. No indication of enthalpy means that it is too small to be measured.



**Figure 2.** Optical textures of N<sub>D</sub> phases of **1a** (a), **1b** (b), and **1c** (c) on cooling at 217, 110, and 12 °C, respectively, observed by POM (×600). The Col<sub>h</sub> phase of **1a** triggered by the addition of 2 molar equiv of LiOTf on cooling at 200 °C observed by POM (×600) (d).



**Figure 3.** XRD of **1a** at 200 °C (a) and the lithium salt of **1a** with 1 (b) and 6 molar equiv of LiOTf (c), respectively, at 200 °C. Phase diagram of **1a** with variable amounts of LiOTf. Cr, crystal; N<sub>D</sub>, nematic discotic; Col<sub>h</sub>, hexagonal columnar; Iso, isotropic (d).

its intensity decreased significantly (Figure 3c). Excess LiOTf destabilizes the mesophase. This might be caused by the excess of bulky counterions supposed to be located between the discs, which expanded the layer distance and disturbed the ordered columnar structure. Figure 3d shows the phase diagram of **1a** with a variable amount of LiOTf. As the amount of LiOTf was increased, the temperature range for the N<sub>D</sub> phase became narrow. With ca. 1 equiv of LiOTf, the N<sub>D</sub> phase started to be transformed to the columnar phase.

Similarly, phase transformation from a N<sub>D</sub> phase to a columnar phase was also observed for **1b** and **1c** upon addition of LiOTf. They required larger amount of LiOTf (4–6 equiv) than that for **1a** (entry 6 in Table 1). Their XRD patterns showed the relatively weak reflection corresponding to that of the (100), and the assignment of the type of columnar phases was difficult. Moreover, due to their columnar orientation parallel to the surface normal direction, no optical texture was observed for **1c** by POM.

Similar alkali-metal-ion-induced phase transformation of triphenylenes from a N<sub>D</sub> phase to a Col<sub>h</sub> phase was also triggered by addition of NaOTf (entry 3 in Table 1). The counterions play an important role in these transformations since lithium chloride was an ineffective additive for this purpose (entry 4 in Table 1). In this case, only a minor portion of the salts might be transformed to a columnar mesophase as indicated by its XRD pattern. However, a majority of them remained as the N<sub>D</sub> phase since only the N<sub>D</sub> phase was observed by POM for the lithium salt of **1a** with up to 12 molar equiv molar of LiCl. This is a remarkable counterion selective transformation from a N<sub>D</sub> phase to a Col<sub>h</sub> phase.

In summary, triphenylene derivatives possessing PEO as side chains exhibited N<sub>D</sub> phases at room temperature. Unique phase transformation from a N<sub>D</sub> phase to a Col<sub>h</sub> phase was observed when alkali metal ions were added. This transformation was dependent on the type of counterions of the additive alkali metal salts. Details of the effect of the counterion on the phase transition are in progress in our laboratory.

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**Supporting Information Available:** Preparation information, spectral data of the compounds, and phase transition temperatures and XRD of the complexes, **1a**/LiCl and **1a**/NaOTf (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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