

Supplementary Information

A Columnar Liquid Crystal Based on Triphenylphosphine Oxide – Its Structural Changes upon Interactions with Alkaline Metal Cation

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Experimental

All reagents and solvents were purchased from Aldrich, Tokyo Kasei, and Wako and were used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates from E. Merck (silica gel F₂₅₄). Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (silica gel 60, spherical 40-50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. Elemental analyses were carried out on a Perkin-Elmer CHNS/O 2400 apparatus. ^1H NMR spectra were recorded on a JEOL JNM-LA400. Chemical Shifts of ^1H signals are expressed in parts per million (δ) using internal standards Me_4Si ($\delta = 0.00$). Mass spectra (MALDI) were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer.

DSC measurements were performed on a Mettler DSC 30 (scanning rate: $10\text{ }^\circ\text{C min}^{-1}$). Transition temperatures were taken as the maximum of the transition peaks on the second heating run. A polarising optical microscope Olympus BH-2 equipped with Mettler FP82HT hot stage was used for visual observation. IR measurements were conducted on a Jasco FT/IR-660 Plus spectrometer equipped with a Mettler FP82HT hot stage. Oriented samples were prepared by mechanically shearing polydomain

samples in sandwiched KBr crystals or glass plates.¹ X-Ray diffraction measurements were carried out on a Rigaku RINT-2500 diffractometer with a heating stage using Ni-filtered CuK α radiation.

Synthesis of tris[4-(3,4,5-dodecyloxybenzyloxy)phenyl]phosphine oxide (**1**)

To a DMF solution of tris(4-hydroxyphenyl)phosphine oxide (32 mg, 98 μ mol) and 3,4,5-tridodecyloxybenzyl chloride (200 mg, 0.29 mmol) was added K₂CO₃ (138 mg, 1.0 mmol). The reaction mixture was then stirred under Ar atmosphere at 70 °C for 6 h. To the reaction mixture water was added and extracted with hexane. The collected organic fraction was washed with water, dried over Na₂SO₄ and filtered. The solvent of the filtrate was removed under reduced pressure. Purification with GPC (JAIGEL 1H and 2.5H, CHCl₃, 3.8 ml min⁻¹) and column chromatography (silicagel, Hexane : Ethyl acetate : Methanol = 4 : 1 : 0.2) gave a white highly viscous oil (125 mg, 57%). ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (dd, J_{HH} = 8.4 Hz, J_{PH} = 11.2 Hz, 2H, Ph*H*), 7.03 (dd, J_{HH} = 8.8 Hz, J_{PH} = 2.2 Hz, 2H, Ph*H*), 6.61 (s, 2H, Ph*H*), 4.97 (s, 2H, OCH₂Ar), 3.92-3.98 (m, 6H, CH₂CH₂O), 1.72-1.81 (m, 6H, CH₂CH₂CH₂O), 1.41-1.49 (m, 6H, CH₂CH₂CH₂CH₂O), 1.29-1.31 (m, 48H, CH₂), 0.88 (t, J = 6.8 Hz, 9H, CH₃); m/z (MALDI-TOF) 2256.1 (calc. [M+H]⁺ = 2256.5).

Phase identification

The “Col” phase in Fig. 5

The columnar phases have been determined by the textures observed under the polarising optical microscope. However, details about columnar assemblies are unclear due to the absence of peaks such as the (110) peak.

The “Cub” phase in Fig. 5

The optically isotropic images have been observed under the polarising optical microscope for the mixtures of **1** and alkaline metal salt. The SAXD profile of the mixture of NaOTf and **1** in the ratio of 0.1 : 1.0 at 60 °C exhibits reflections at 31.8 (100), 22.6 (110), 18.4 (111), and 15.9 Å (200) (Fig. 7). The reciprocal d -spacing of $1 : 2^{1/2} : 3^{1/2} : 4^{1/2}$ is characteristic of primitive cubic lattice structures ($Pm3m$). The XRD profile of the mixture of LiOTf and **1** in the ratio of 0.1 : 1.0 at 60 °C exhibits only a few reflections in the low-angle area, which cannot be assigned to a cubic lattice structure. The cubic phase observed for the mixture of the LiOTf and **1** in the ratio of 0.1 : 1.0 is assigned to $Pm3m$ due to the presence of (111) reflections on the XRD pattern.

The “M” phase in Fig. 5

Sand-like textures are observed in the “M” phase by polarising optical microscopy. Moreover, only (100) and (200) reflections are seen in the low-angle area of XRD patterns. The “M” phase cannot be identified.

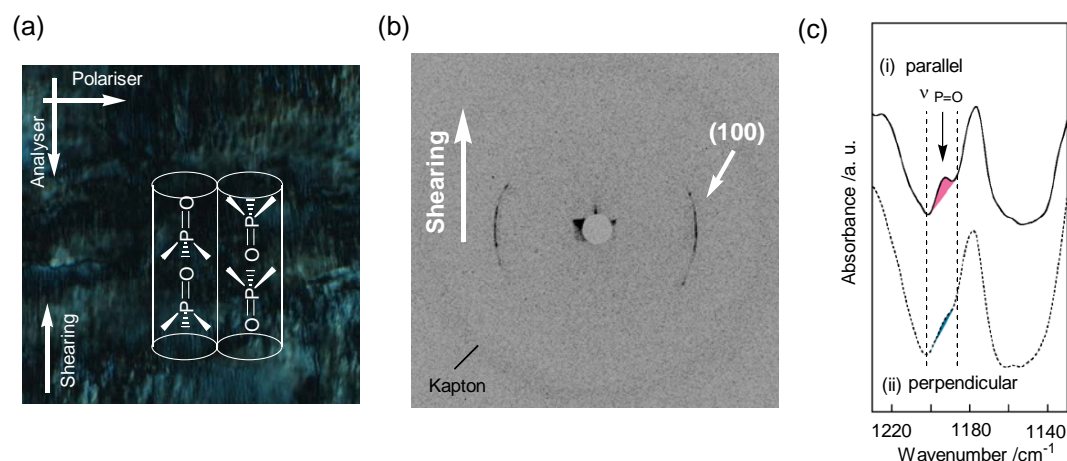


Fig. S1 (a) Polarising optical microscopic image of the oriented structures of **1** in the columnar state at 45 °C after shearing the material, (b) small angle X-ray diffraction pattern of the oriented sample of **1** by shearing at 41 °C and (c) polarised IR spectra of **1** (i) parallel (—) and (ii) perpendicular (---) to the shear direction at 45 °C.

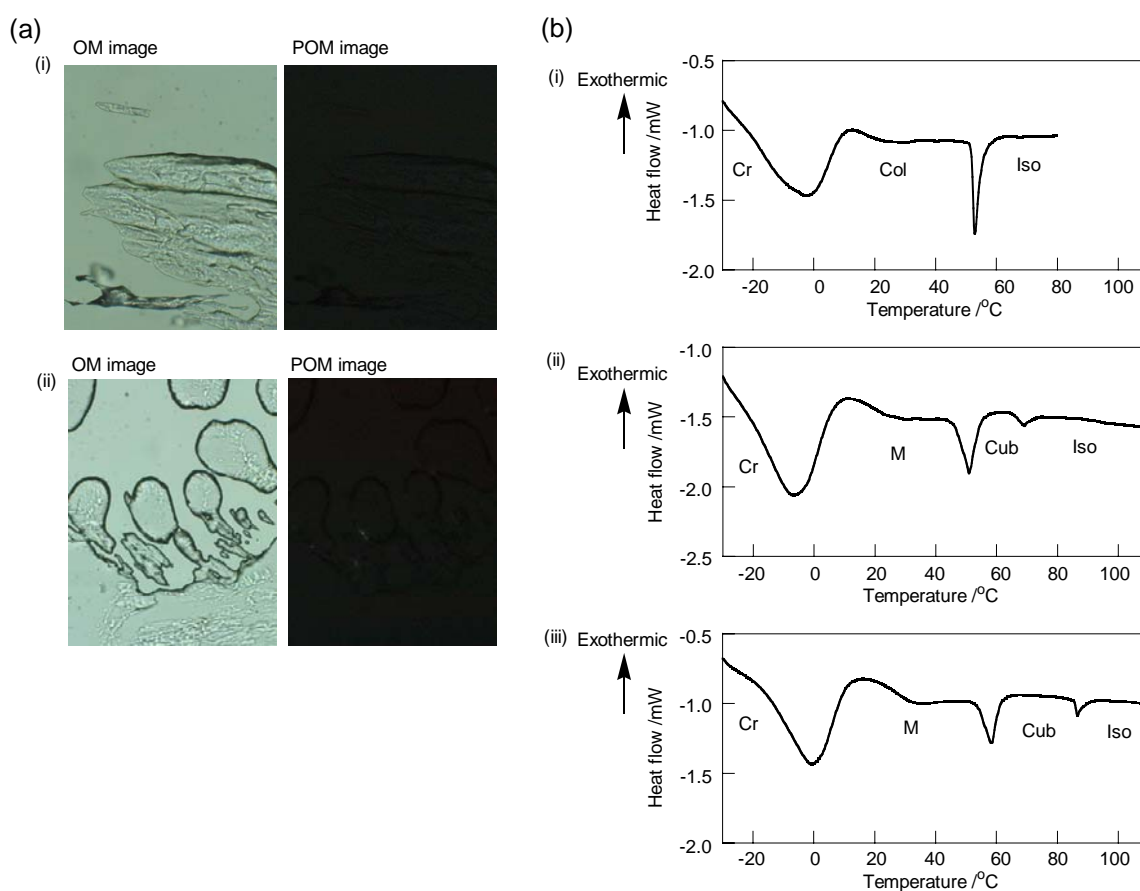


Fig. S2 (a) Optical microscopic (OM) and polarising optical microscopic (POM) images of

(i) the mixture of LiOTf and **1** in the ratio of 0.1 : 1.0 at 60 °C and (ii) the mixture of NaOTf and **1** in the ratio of 0.1 : 1.0 at 70 °C and (b) DSC thermogram of (i) **1**, (ii) the mixture of LiOTf and **1** in the ratio of 0.1 : 1.0 and (iii) the mixture of NaOTf and **1** in the ratio of 0.15 : 1.0. Cr: crystal; Col: columnar phase; M: mesophase; Cub: cubic phase; Iso: disordered isotropic phase.

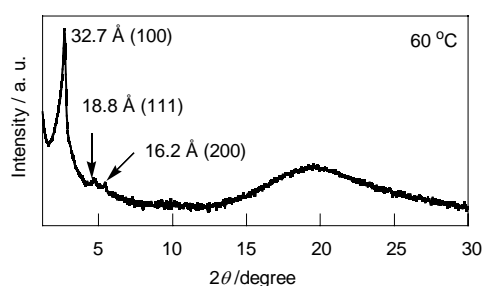


Fig. S3 XRD pattern of the mixture of LiOTf and **1** in the ratio of 0.1 : 1.0 at 60°C.

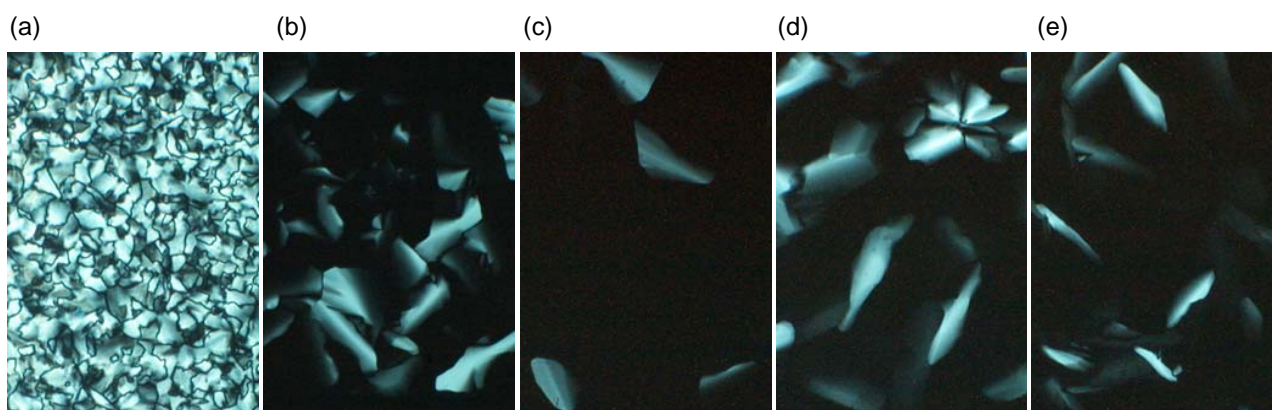


Fig. S4 Polarising optical microscopic images of the mixtures of LiOTf and **1** in the ratio of (a) 0.2 : 1.0, (b) 0.3 : 1.0, (c) 0.4 : 1.0, (d) 0.5 : 1.0, and (e) 0.6 : 1.0 at 70 °C.

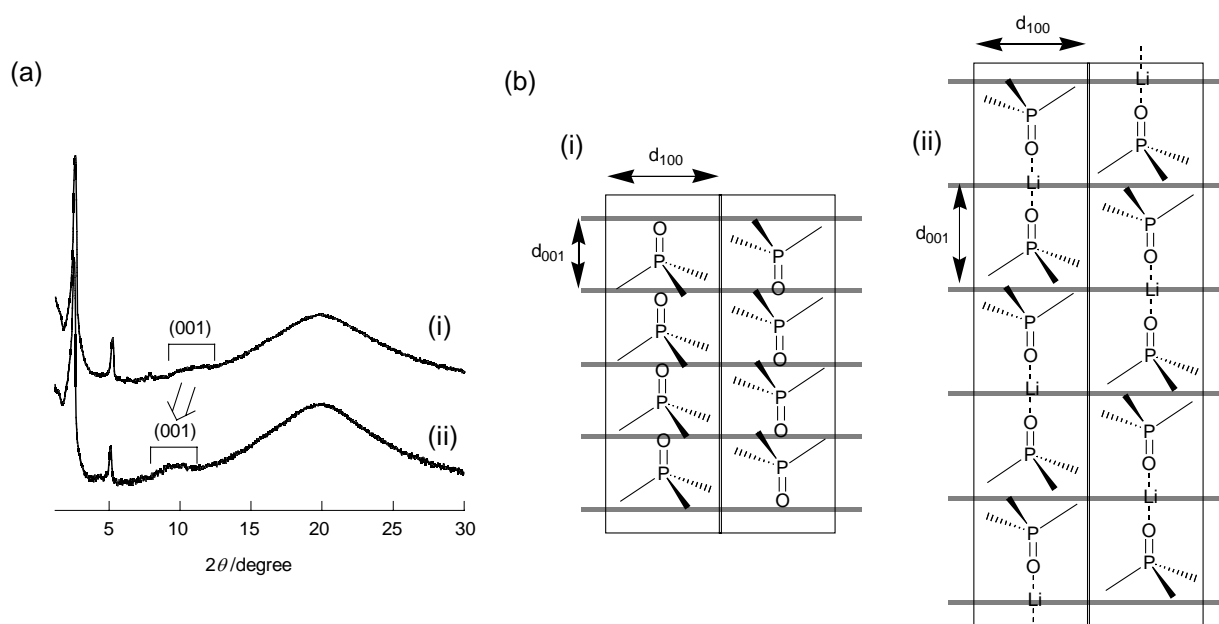


Fig. S5 XRD patterns of (a) (i) **1** and (ii) the mixture of LiOTf and **1** in the ratio of 0.2 :1.0 at 30 °C and (b) schematic illustration of the proposed assembled structure of (i) **1** and (ii) the mixture of LiOTf and **1**.

1) M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994.