

A columnar liquid crystal based on triphenylphosphine oxide—its structural changes upon interaction with alkaline metal cations†

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A triphenylphosphine oxide (TPPO) compound bearing 3,4,5-tridodecyloxybenzyloxy moieties exhibits a columnar liquid crystalline phase, and by changing its self-assembled structure, is responsive to alkaline metal cations due to cation–phosphine oxide interactions.

The fabrication of ordered nanostructures by using molecular self-organisation processes has attracted attention due to their potential as functional materials such as ion- and electron-active materials.¹ Columnar liquid crystals^{2–7} can be used for the one-dimensional (1D) transportation of charge, ions and energy.^{2,4–7} For 1D ion-active liquid crystals, an imidazolium group,⁴ crown ethers⁵ and oligo(ethylene oxide)s⁶ are incorporated into mesogenic molecules to form columnar structures. Recently, ion-responsive liquid crystals derived from folic acid have been prepared.⁷ The change in their hydrogen-bonded structures, induced by ion dipolar interactions between the pterin ring and metal cation, is key to the transition processes. Our intention in the present study is to prepare new ion-responsive liquid crystals to develop novel dynamically-functioned materials. Here we report on a thermotropic liquid crystalline compound consisting of a phosphine oxide group, as shown in Fig. 1. Phosphine oxide groups can bind various metal cations such as alkaline, alkaline earth, transition and lanthanide metal ions through ion dipolar

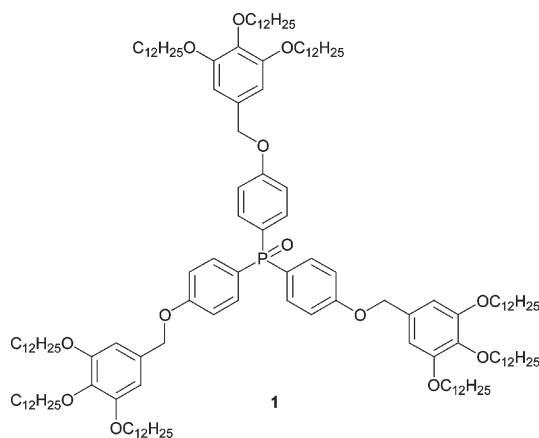


Fig. 1 Structure of phosphine oxide liquid crystal 1.

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interactions.⁸ Thus, we expected a new class of ion-active self-assembled columnar materials to be developed by employing triphenylphosphine oxide (TPPO) groups as the building blocks of liquid crystals. TPPO has a bowl-like shape that can self-assemble into 1D arrays.⁹ The P=O group can be used as a polar moiety for self-assembly.¹⁰ We have designed liquid crystalline molecule 1, with a TPPO group in the centre of the bowl and pyrogallol moieties with long alkyl chains at the periphery of the bowl, expecting that the binding of TPPO to metals will change its liquid crystalline behaviour. To the best of our knowledge, TPPO-based liquid crystals and their metal complexes have not yet been reported.

Compound 1 was synthesised by nucleophilic substitution of the hydroxyl groups of tris(4-hydroxyphenyl)phosphine oxide¹¹ with a benzyl chloride derivative.^{4,12} Compound 1 shows endothermic peaks at -3 and 56 °C in differential scanning calorimetry (DSC) thermograms upon heating. These peaks correspond to the crystalline–columnar and columnar–disordered isotropic transitions, respectively. The enthalpy change of the columnar–disordered isotropic transition is 4.0 kJ mol⁻¹. The focal conic texture typical of columnar phases (Col) is observed under a polarising optical microscope (Fig. 2). The X-ray diffraction (XRD) pattern of 1 presents two sharp peaks at 34.0 and 16.9 Å, and a broad peak at around 8 Å (Fig. 3). These sharp peaks correspond to the (100) and (200) reflections. The broad peak at 8 Å can be assigned to the (001) reflection, based on the finding that a packing distance of a TPPO derivative has been estimated to be *ca.* 6 Å from a single crystal structure.¹³

The oriented sample was prepared by the mechanical shearing of polydomain samples in sandwiched KBr crystals or glass plates. The polarising optical microscope image and small angle X-ray

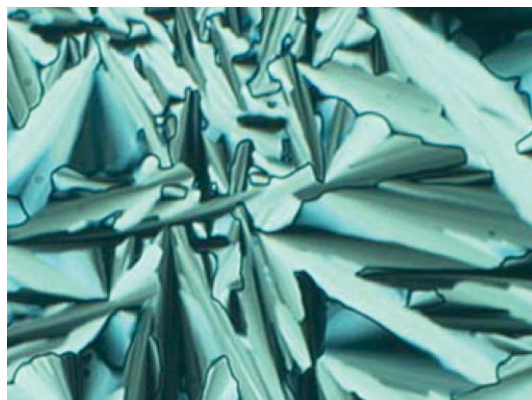


Fig. 2 Polarising optical microscopic image of 1 at 48 °C.

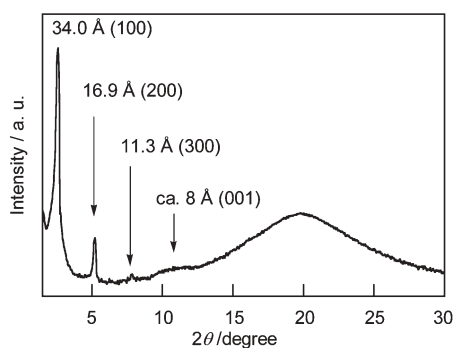


Fig. 3 X-Ray diffraction pattern of **1** at 30 °C.

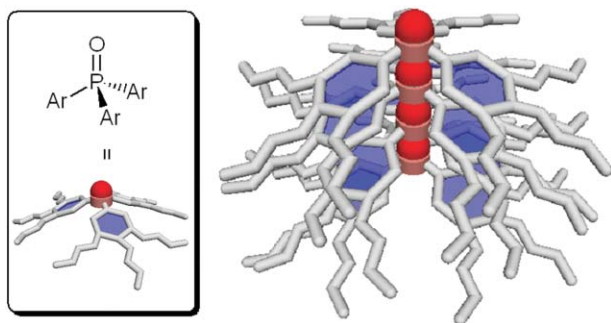


Fig. 4 Schematic illustration of an assembled structure of **1** in the columnar phase.

diffraction (SAXD) pattern support the alignment of **1**.[†] Polarised infrared (IR) spectra of this sample at 45 °C were obtained for two directions: parallel and perpendicular to the shear direction.[†] The absorbance of the P=O stretching in the spectrum parallel to the shear direction is larger in intensity than in the spectrum perpendicular to this same shear direction, indicating that 1D alignment of the P=O group parallel to the shear direction has been achieved.[†] These results suggest that the columnar phase formed by **1** is composed of stacks of TPPO, in which the phosphine oxide groups are pointing in the same direction in a single column (Fig. 4).

The phase transition behaviour of mixtures of **1** and lithium or sodium ions were examined. These mixtures were prepared by the slow evaporation of a THF solution of **1**, containing the requisite amount of lithium triflate (LiOTf) or sodium triflate (NaOTf), followed by 6 h of drying under vacuum. Fig. 5 shows the phase diagrams of **1** with LiOTf and NaOTf.[‡] The addition of LiOTf

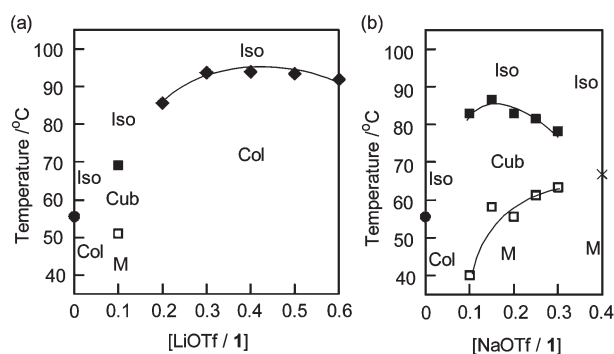


Fig. 5 Phase diagrams of **1** with (a) lithium and (b) sodium ions. M: mesophase, Cub: cubic phase, Col: columnar phase and Iso: disordered isotropic phase.

changed the assembled structure of **1**. A cubic phase (Cub) is observed for the mixture of LiOTf and **1** in the ratio of 0.1 : 1.0 from 51 to 69 °C.[†] Focal conic textures typical of columnar phases are observed for mixtures in the ratio of LiOTf to **1** from 0.2 to 0.6.[†] The transition temperatures from columnar to disordered isotropic phases are increased more than 30 °C by the addition of LiOTf. The stacking distance of the complexes increase from 8.0 to 9.5 Å upon addition of LiOTf.[†] These results suggest that LiOTf interacts with the TPPO groups and is maintained by a cation–phosphine oxide interaction.[†] In addition, the lithium cation has a coordination number of 2 and is in a linear arrangement.¹⁴ The columnar phase obtained from the mixture of LiOTf and **1** in the ratio of 0.5 : 1.0 shows the highest thermal stability, as shown in Fig. 5a. It is likely that this strong enhancement of the columnar phase is caused by the formation of a sandwich-like complex involving ion dipolar interactions, as schematically shown in Fig. 6 left.

The cubic phase is also observed for mixtures of NaOTf and **1** in the ratios 0.1 to 0.3 (Fig. 5b). The SAXD profile for the cubic phases at 60 °C exhibits reflections of 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 ($Pm\bar{3}m$). The cubic phase obtained from a mixture of NaOTf and **1** in approximately the ratio 0.15 : 1.0 is stable at the highest temperature, as shown in Fig. 5b. This strong enhancement of the cubic phase may be caused by the formation of a polyhedral-like complex involving ion dipolar interactions, as schematically shown in Fig. 6 (right).¹⁵¶ It was previously reported that sphere-like complexes with polyhedral arrangements were yielded from alkaline and alkaline earth metal ions by cation–phosphine oxide interactions.¹⁵ These results suggest that the primitive cubic lattice

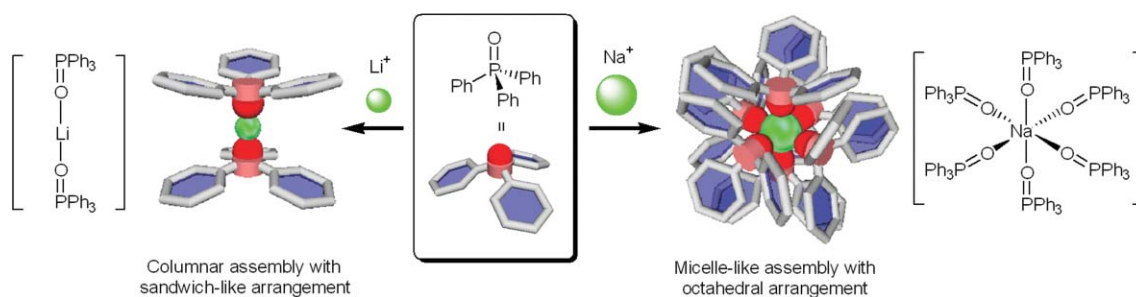


Fig. 6 Schematic illustration of the assembled structural changes of **1** initiated by the addition of alkaline metal ions.

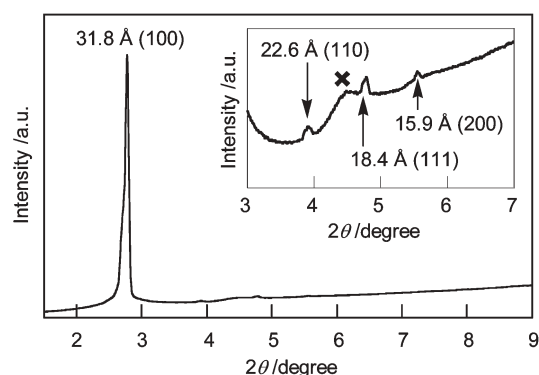


Fig. 7 Small angle X-ray diffraction pattern of the cubic phase obtained at 60 °C for the mixture of NaOTf and **1** in the ratio of 0.1 : 1.0. The inset is a magnified XRD pattern.†

structure of the octahedral complex can be formed in the cubic phase.

In conclusion, a columnar liquid crystal based on a TPPO moiety has been reported for the first time; the TPPO liquid crystal having metal binding ability. Structural changes are observed for the TPPO complex due to the interaction between TPPO and alkaline metal cations. The octahedral arrangement of **1** with sodium ions results in the formation of a cubic phase, while the linear arrangement of **1** with lithium ions induces a columnar phase. This liquid crystal material may be useful for the transportation, sensing and extraction of alkaline metal ions.

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Notes and references

† Macro-phase separation was observed for **1** with LiOTf and NaOTf in the ratio 1.0 : 0.7 and 1.0 : 0.5, respectively.

§ The halo at 4.5° originates from the X-ray scattering of the poly(imide) (Kapton) film used as the sample holder.

¶ The lattice constant of a single crystal (ref. 15) of a mixture of TPPO and Li cation in the ratio of 4 : 1 is between 14 and 17 Å. The size of the tridodecyloxybenzyloxy group close to 8 Å by interdigitation and/or bending of alkyl chains. The lattice constant (31.8 Å) is appropriate for the size of the micellar structure.

1 For example: J. Alper, *Science*, 2002, **295**, 2397; R. F. Service, *Science*, 2002, **295**, 2399; T. Kato, *Science*, 2002, **295**, 2414; O. Ikkala and G. ten Brinke, *Chem. Commun.*, 2004, 2131; J. W. Goodby, G. H. Mehl,

- I. M. Saez, R. P. Tuffin, G. Mackenzie, R. Auzély-Velty, T. Benvenugu and D. Plusquellec, *Chem. Commun.*, 1998, 2057; M. L. Bushey, A. Hwang, P. W. Stephens and C. Nuckolls, *Angew. Chem., Int. Ed.*, 2002, **41**, 2828; F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; T. Kato and M. Yoshio, in *Electrochemical Aspects of Ionic Liquids*, ed. H. Ohno, Wiley-Interscience, New York, 2005, ch. 25, pp. 307–320.
- 2 R. J. Bushby and O. R. Lozman, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 569; A. F. Thünemann, D. Ruppelt, C. Burger and K. Müllen, *J. Mater. Chem.*, 2000, **10**, 1325; D. Guillon, *Struct. Bonding*, 1999, **95**, 41; T. Kato and N. Mizoshita, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 579; D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etbach, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141; R. C. Smith, W. M. Fischer and D. L. Gin, *J. Am. Chem. Soc.*, 1997, **119**, 4092; V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shivanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson and H. Duank, *Nature*, 2002, **419**, 384.
- 3 M. C. Artal, K. J. Toyne, J. W. Goodby, J. Barberá and D. J. Photinos, *J. Mater. Chem.*, 2001, **11**, 2801; P. Hindmarsh, M. J. Watson, M. Hird and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 2111.
- 4 M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994.
- 5 U. Beginn, G. Zipp, A. Mourran, P. Walther and M. Möller, *Adv. Mater.*, 2000, **12**, 513; C. F. van Nostrum, S. J. Picken, A.-J. Schouten and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1995, **117**, 9957.
- 6 V. Percec, J. A. Heck, D. Tomazos and G. Ungar, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2381.
- 7 K. Kanie, T. Yasuda, S. Ujii and T. Kato, *Chem. Commun.*, 2000, 1899; K. Kanie, M. Nishii, T. Yasuda, T. Taki, S. Ujii and T. Kato, *J. Mater. Chem.*, 2001, **11**, 2875; T. Kato, T. Matsuoka, M. Nishii, Y. Kamikawa, K. Kanie, T. Nishimura, E. Yashima and S. Ujii, *Angew. Chem., Int. Ed.*, 2004, **43**, 1969; Y. Kamikawa, M. Nishii and T. Kato, *Chem.-Eur. J.*, 2004, **10**, 5942.
- 8 L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme and G. Wipff, *J. Am. Chem. Soc.*, 2002, **124**, 7779; R. Selvaraju, K. Panchanatheswaran and V. Parthasarathi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 905; M. R. Cairn and B. J. Gellatly, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 1198; M. Baaden, G. Wipff, M. R. Yafian, M. Burgard and D. Matt, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1315; F. Arnaud-Neu, J. K. Browne, D. Byrne, D. Marrs, M. A. McKerverve, P. O'Hagan, M. J. Schwing-Weill and A. Walker, *Chem.-Eur. J.*, 1999, **5**, 175; P. Delangle, J.-P. Dutasta, J.-P. Declercq and B. Tinant, *Chem.-Eur. J.*, 1998, **4**, 100; H. Boerrigter, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 7148.
- 9 B. Xu and T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 1159; T. Komori and S. Shinkai, *Chem. Lett.*, 1993, **8**, 1455; S. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, **419**, 702; Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato and E. Nakamura, *J. Am. Chem. Soc.*, 2004, **126**, 432.
- 10 N. Malek, T. Maris, M.-É. Perron and J. D. Wuest, *Angew. Chem., Int. Ed.*, 2005, **44**, 4021.
- 11 B. P. Friedrichsen, D. R. Powell and H. W. Whitlock, *J. Am. Chem. Soc.*, 1990, **112**, 8931.
- 12 V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.*, 1997, **119**, 1539.
- 13 A. L. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **43**, 1233; O. B. Shawkataly, K. Ramalingam, S. Selvakumar, H.-K. Fun and A. R. Ibrahim, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1451.
- 14 X. Tian, R. Fröhlich and N. W. Mitzel, *Dalton Trans.*, 2005, 380; L. Bourget-Merle, P. B. Hitchcock and M. F. Lappert, *J. Organomet. Chem.*, 2004, **689**, 4357.
- 15 J. P. Fackler Jr, C. A. López and R. E. P. Winpenny, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 2218; M. B. Hursthouse, W. Levason, R. Ratnani, G. Reid, H. Stainer and M. Webster, *Polyhedron*, 2005, **24**, 121.