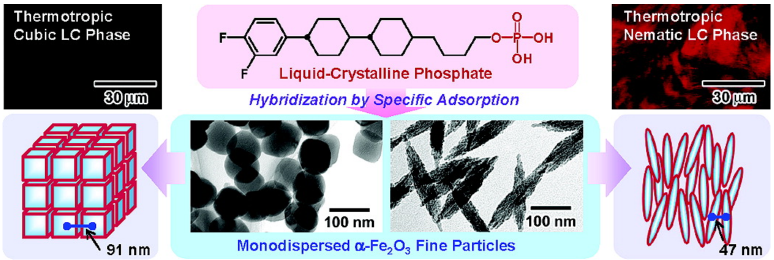
Communication

Organic–Inorganic Hybrid Liquid Crystals: Thermotropic Mesophases Formed by Hybridization of Liquid-Crystalline Phosphates and Monodispersed □-FeO Particles

Kiyoshi Kanie, and Atsushi Muramatsu

J. Am. Chem. Soc., **2005**, 127 (33), 11578-11579• DOI: 10.1021/ja054232f • Publication Date (Web): 28 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Organic−Inorganic Hybrid Liquid Crystals: Thermotropic Mesophases Formed by Hybridization of Liquid-Crystalline Phosphates and Monodispersed α-Fe_2O_3 Particles

Kiyoshi Kanie* and Atsushi Muramatsu*

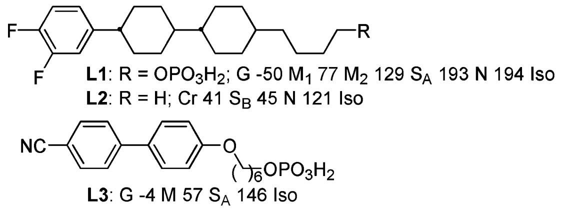
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

Received June 27, 2005; E-mail: kanie@tagen.tohoku.ac.jp; mura@tagen.tohoku.ac.jp

Nano-level hybridization of organic and inorganic materials has attracted a great deal of attention, especially in the fields of material science and nanotechnology, because it is not rare to find unexpected superadditive properties.[1] Organic liquid crystals (LCs) are anisotropic materials of an enormous variety of dynamic and self-assembling functions,[2] and thus the introduction of such functions into organic materials has been a useful technique in material science.[3−9] On the other hand, recent progress of particle deposition systems,[10] such as the gel−sol method,[11] enabled us to obtain monodispersed particles precisely controlled in size and morphology. By using the gel−sol method, we have reported a facile procedure for the preparation of monodispersed α-Fe_2O_3 particles with various shapes and sizes by the addition of shape controllers and seed particles.[12] For example, in the presence of PO_4^{3-} ions, monodispersed spindle-type α-Fe_2O_3 particles have been readily obtained. The morphological control was derived from the specific adsorption of the PO_4^{3-} ions on the crystal planes parallel to the *c*-axis, which retarded the particle growth toward perpendicular to the *c*-axis. Such strong adsorption of PO_4^{3-} ions gives us a possibility that we could obtain novel types of organic−inorganic hybrid LCs[13] by the adsorption of organic LC molecules with a phosphate moiety to the surfaces of α-Fe_2O_3 particles with different shapes.

We designed and synthesized **L1** and **L3** with a phosphate moiety, as shown in Chart 1. Phosphate-group-free **L2** was also prepared. The phase transition temperatures and LC phases of **L1**−**L3** were determined by polarized optical microscopy (POM) with a hot stage, differential scanning calorimetry (DSC), and X-ray diffraction. Also, α-Fe_2O_3 particles **H1**−**H6** with different sizes and morphologies were prepared (Figure 1). Monodispersed spindle-type **H1**−**H3** are expected to adsorb the phosphate moiety of **L1** because they were obtained with PO_4^{3-} ions as a shape controller.[14] Seeding technique[12] enabled us to control the particle mean size of **H1**−**H3**. Monodispersed cuboidal **H4**, polydispersed **H5**, and hexagonal platelet **H6**, prepared by using the specific adsorption of OH^- ions *perpendicular* to the *c*-axis,[12] were used in the present study. All particles were thoroughly washed with 1 M NH_3 and water by centrifugation to completely remove impurities and were freeze-dried. The resulting powders **H1**−**H6** were confirmed as α-Fe_2O_3 by X-ray diffraction analysis, and no difference in their surface conditions was observed by X-ray photoelectron spectroscopy.

Chart 1. Structures of Thermotropic LCs for Hybridization with α-Fe_2O_3 Particles[a]



[a] G: glass; Cr: crystal; M: mesomorphic; S_A: smectic A; N: nematic; Iso: isotropic phases. The figures between are transition temperatures in °C.

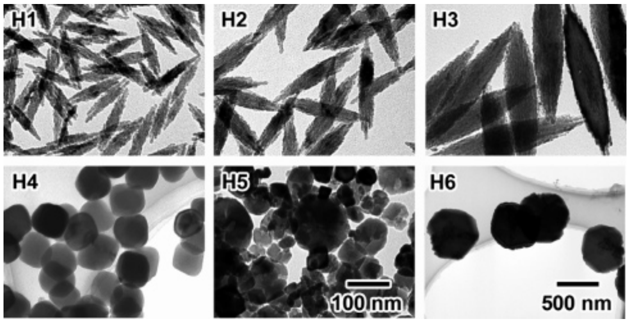


Figure 1. TEM images of α-Fe_2O_3 particles **H1**−**H6**. The scale bar in **H5** is common for **H1**−**H4**.

Hybridization of **L1** and **H1**−**H6** or **L2**−**L3** and **H2** was carried out as follows. Twenty milligrams of **L** and the same weight or 40 mg of **H** (**L**/**H** = 1/1 or 1/2) were mixed together and dispersed in 2 mL of methanol and 2 mL of $CHCl_3$ by ultrasonication for 30 min followed by removal of the solvents at 60 °C under flowing Ar. Figure 2 exhibits optical microscopic images of 1/2 hybrids of **L1**/**H2**, **L1**/**H5**, and **L1**/**H6** at 90 °C in the presence of a polarizer (a) and its absence (b). For the **L1**/**H2** hybrid, a marbled texture, as a characteristic of a nematic (N) phase with strong birefringence and fluidity, was observed. The mesomorphic phase was readily transformed to a uniaxially aligned monodomain by shearing (Figure 2 (i) (a), inset). DSC measurement on the second heating scan revealed that the hybrid showed the glass−mesophase transition at −35 °C. After an endothermic peak at 148 °C, the hybrid showed a highly fluidic state with strong birefringence observed by POM. The birefringence was kept up to 250 °C. Similar mesomorphic behavior was also seen for 1/2 hybrids of **L1**/**H1**,**H3** and 1/1 hybrids of **L1**/**H1**−**H3**. However, further increase of the **L1** component resulted in the partial phase separation of **L1** with **H1**−**H3**. On the other hand, 1/2 as well as 1/1 hybrids of **L1**/**H5** also formed a uniform fluidic material without phase segregation of **L1** with **H5** (Figure 2 (ii) (b)); however, no birefringence was found and formed was an optically isotropic state. The **L1**/**H4** = 1/2 and 1/1 hybrids, which consisted from monodispersed cuboidal α-Fe_2O_3 particles, also showed an optically isotropic state with fluidity. Thus, the aspect ratio of the α-Fe_2O_3 particles with different shapes was the decisive factor for the formation of the nematic LCs of the hybrids. Interestingly, birefringence, owing to the **L1** single component and coagulated **H6**, is seen for a 1/2 mixture of **L1**/**H6**, as shown in Figure 2 (iii). It shows phase segregation between **L1** and **H6** without hybridization. The platelet **H6** particles have a *c*-plane as

10.1021/ja054232f CCC: $30.25

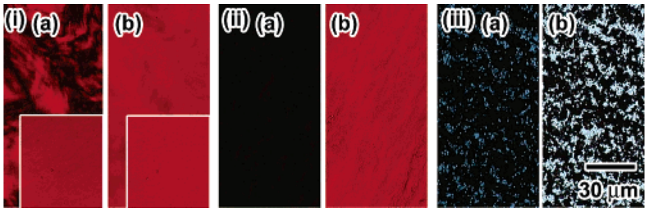


Figure 2. Optical photomicrographs of thermotropic hybrid LC phases of 1/2 hybrids of (i) **L1**/**H2**, (ii) **L1**/**H5**, and (iii) **L1**/**H6** at 90 °C (a) with a polarizer; (i)−(a) and (b) insets: sheared monodomain.

a principal one and also a phosphate-favored plane as an extremely narrow side surface, formed by the specific adsorption of OH^- on the basal plane.[12] It shows that the factor for the hybridization might be brought by the specific adsorption of the phosphate group of **L1** on a plane parallel to the *c*-axis. None of the mesomorphic phenomena were seen with **L3**/**H2** hybrids, and it was decomposed at ca. 260 °C. Hence, in this case, the original liquid crystallinity of **L3** was lost by the hybridization with **H2**. Furthermore, since the phase separation was observed only with **L2**/**H2** hybrids through POM, the phosphate group of **L1** played an essential role for the formation of the hybrid LC of **L1**. The definite interaction between the phosphate group of **L1** and the surfaces of **H1**−**H5** was confirmed by temperature variable infrared spectroscopy, and no free PO_3H_2 vibration was observed by the hybridization.

The mesomorphic phase structures of the **L1**/**H1**−**H5** hybrids were examined by small-angle X-ray scattering (SAXS) measurements. The profiles of the **L1**/**H2** = 1/2 hybrid at 90 and 170 °C suggested the existence of periodic particle interactions at intervals of 49.7 and 46.5 nm, respectively, corresponding to the total width of an **H2** covered with the **L1** molecules toward the short axis of the spindle-type particles. Therefore, the mesomorphic phase seems to have a nematic-like one-dimensional order in the direction of the long axis of the spindle-type particles. Such a periodic scattering was not observed for the single components of **H1**−**H6** and the **L1**/**H5** hybrids. On the other hand, peaks of 45.6, 30.4, and 22.8 nm at 170 °C were observed for the hybrid of **L1**/**H4** = 1/1, which corresponded to d_{200}, d_{300}, and d_{400} planes, respectively, of a superlattice structure with a simple cubic LC structure. The lattice parameter could be assigned as $a = 91.2$ nm, which was consistent with the particle mean sizes of **H4** covered with the **L1** molecules by the adsorption on their surfaces.

Wide-angle X-ray diffraction measurements of **L1** at 90 °C revealed the presence of a peak at 2.7 nm, corresponding to the formation of a smectic bilayer structure of **L1**. On the other hand, such a periodic multilayer structure of **L1** was not observed on the **L1**/**H1**−**H5** hybrids at 90 °C. These results indicated that a kind of N order was formed with the **L1**/**H1**−**H3** hybrids, in place of the original smectic multilayer order of **L1**, as a result of the adsorption of **L1** to the surfaces of **H1**−**H3** through the phosphate group of **L1**. Since the BET surface area of **H2** was 48 m^2/g, the surface density of **L1** on **H2** for the **L1**/**H2** = 1/2 hybrid was calculated as 14.6 molecules/nm^2 on the assumption of the saturated adsorption. This adsorption density was somewhat greater than the occupation area of an **L1** molecule standing perpendicular to the surfaces of **H1** particles, which was estimated from the single-crystal structure of an **L1** analogue (ca. 0.16 nm^2/molecule). However, since there was no sign of the LC formation of independent **L1** molecules, it seemed that most of the **L1** molecules were densely adsorbed perpendicular to the surfaces of **H1**−**H5** particles. As a consequence, the spindle-type or cuboidal α-Fe_2O_3 particles were deemed to be bridged together through the hydrophobic interaction between the mesogenic cores of the **L1** molecule layers on their surfaces, leading to an N or a cubic thermotropic LC structure of the α-Fe_2O_3 particles.

Surface modification of rare-metal nanospheres by a thiol derivative of an LC compound has been examined.[15] However, the details were unknown, and the optical anisotropy characteristic of LCs was not observed either. Furthermore, LC behaviors for some inorganic particles are only limited in dilute lyotropic systems.[16−19] On the other hand, we have recently developed the organic−inorganic hybrid LC with thermotropic LC behavior.[13] In this system, only an N phase formed by the hybridization of a calamitic amine with monodispersed acicular TiO_2 particles has been demonstrated. Hence, the present paper is the first report on new thermotropic N and cubic LC phases via specific adsorption of the phosphate group on the α-Fe_2O_3 specific surfaces. Furthermore, monodispersed α-Fe_2O_3 particles used in the present study are readily converted into Fe_3O_4 and γ-Fe_2O_3 as magnetic materials, precisely keeping their morphology without sintering.[20] In this regard, the nano-level hybridization of inorganic nanoparticles with fair magnetic properties and LCs with good electric response will make them one of the most advanced functional materials with excellent multi-responsiveness.

Acknowledgment. We are indebted to Prof. E. Matsubara for helpful advice for SAXS measurements, performed at COE Laboratory, IMR, Tohoku University. We also acknowledge Dainippon Ink & Chemicals for the kind offer of LC substrates. This work was financially supported by JSPS (Grant-in-aid for young scientific research (A) No. 16685018) and The Ogasawara foundation for the promotion of science & engineering.

Supporting Information Available: Experimental details for the preparation of **L1**−**L3** and **H1**−**H6**, and characterization of hybrid LC behavior. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Handbook of Organic−Inorganic Hybrid Materials and Nanocomposites*; Nalwa, H. S., Ed.; American Scientific Publishers: California, 2002.
(2) *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998.
(3) Lee, S.-W.; Mao, C.; Flynn, C. E.; Belcher, A. M. *Science* **2002**, *296*, 892−895.
(4) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702−705.
(5) Oh, S.-Y.; Akagi, K.; Shirakawa, H.; Araya, K. *Macromolecules* **1993**, *26*, 6203−6206.
(6) Hulvat, J. F.; Sofos, M.; Tajima K.; Stupp, S. I. *J. Am. Chem. Soc.* **2005**, *127*, 366−372.
(7) Kanie, K.; Nishii, M.; Yasuda, T.; Taki, T.; Ujiie, S.; Kato, T. *J. Mater. Chem.* **2001**, *11*, 2875−2886.
(8) Kato, T. *Science* **2002**, *295*, 2414−2418.
(9) Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 1485−1508.
(10) Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. *Chem. Rev.* **2004**, *104*, 3893−3946.
(11) Sugimoto, T. *Monodispersed Particles*; Elsevier: Amsterdam, 2001.
(12) (a) Sugimoto, T.; Khan, M. M.; Muramatsu, A.; Itoh, H. *J. Colloids Surf. A* **1993**, *79*, 233−247. (b) Sugimoto, T.; Wang, Y. *J. Colloid Interface Sci.* **1998**, *207*, 137−149.
(13) Kanie, K.; Sugimoto, T. *J Am. Chem. Sc.* **2003**, *125*, 10518−10519.
(14) (a) Ozaki, M.; Kratohvil, S.; Matijevic, E. *J. Colloid Interface Sci.* **1984**, *102*, 146−151. (b) Sugimoto, T.; Muramatsu, A. *J. Colloid Interface Sci.* **1996**, *184*, 626−638.
(15) (a) Kanayama, N.; Tsutsumi, O.; Kanazawa, A.; Ikeda, T. *Chem. Commun.* **2001**, 2640−2641. (b) Yoshikawa, H.; Maeda, K.; Shiraishi, Y.; Xu, J.; Shiraki, H.; Toshima, N.; Kobayashi, S. *Jpn. J. Appl. Phys.* **2002**, *41*, L1315−L1317.
(16) Gabriel, J.-C. P.; Davidson, P. *Adv. Mater.* **2000**, *12*, 9−20.
(17) Gabriel, J.-C. P.; Camerel, F.; Lemaire, B. J.; Desvaux, H.; Davidson, P.; Batail, P. *Nature* **2001**, *413*, 504−508.
(18) Miyamoto, N.; Nakao, T. *Adv. Mater.* **2002**, *14*, 1267−1270.
(19) Li, L.-S.; Walda, J.; Manna, L.; Alivisatos, A. P. *Nano Lett.* **2002**, *2*, 557−560.
(20) Itoh, H.; Sugimoto, T. *J. Colloid Interface Sci.* **2003**, *265*, 283−295.

JA054232F