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From smectic to columnar phase of polypedal liquid crystals based on tetrathiafulvalene/1,3-dithiol-2-thione and cholesterol

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ABSTRACT

Bipedal 1,3-dithiole-2-thiones attached two cholesteryl through a ω-thioalkanoyloxy spacer of varying length were synthesized. The bipedals were easily transformed to the appropriate tetrapedal tetrathiafulvalene derivatives by self-coupling reaction in net triethyl phosphite. All the synthesized compounds exhibit mesogenic phases in a wide temperature region, no crystallization but vitrifying to form glassy mesogens during cooling from the isotropic melt. The liquid crystals with shorter spacer (n=2–6) exhibited only a smectic A phase and those with the longest spacer (n=7) exhibited only a hexagonal columnar. In these series, the molecular packing depended on the length of spacers.

1. Introduction

Recently a lot of efforts have been made to basic and applied studies on ordered molecular organizations formed by relatively weak intermolecular interactions, such as liquid crystals, organogels, and Langmuir–Blodgett (LB) films, because they show new optical or electrical properties, which were not observed in the single molecule.[1–3] Since weak interactions are sensitively influenced by external stimuli, such as light, temperature, and electric field, properties of these molecules can be easily controlled.[4] In developing novel organic materials, liquid crystals (LCs) are currently viewed as highly potential candidate because the mesophases offer soft phases with lamellar, columnar or cubic arrangements, and a current goal is to use the fourth state of matter to achieve ordered functional systems.[5,6]

Tetrathiafulvalene (TTF) derivatives have played a pivotal role in the development of organic materials for optoelectronic application due to their excellent electron-donating properties.[7–9] The transport properties of these materials are clearly dependent on the molecular architecture in the solid state and so a wide variety of substituents have been introduced at the periphery of the TTF core in order to achieve a suitable solid-state organization.[10] In this respect, a possible approach is based on the preparation of mesogenic compounds. In particular, glassy liquid crystals (GLCs) hold a fast and good orientation, which can be readily processed into macroscopically ordered solid films.[11] However, most researches into TTF and its derivatives have been focused on their crystalline phase. Although a considerable number of TTF derivatives have so far been synthesized, there are only a few reports describing TTF derivatives with mesomorphic properties[12–20] and consequently, it is not yet possible to establish structure–property relationships for this family of compounds.

In order to study the effect of structure on the possible liquid crystal behavior of new TTF derivatives, we selected cholesteryl as side group, which has been successfully used in the preparation of chiral liquid crystals, and introduced it to the periphery of TTF unit through flexible spacers. Here, we report the synthesis and mesomorphic properties of TTF-based tetrapedals **1a**–**f** containing four cholesteryls and 1,3-dithiol-2-thione-baesd bipedals **4a**–**f** containing two cholesteryls, together with the electron donating property of tetrapedals **1a**–**f** with a TTF central core. Compounds **4f** and **1f** with the longest spacer showed a hexagonal columnar phase (Col_h) at a wide and low temperature region. The tetrapedal **1f** with a TTF central core showing a Col_h mesophase in a wide temperature range is reported for the first time to our knowledge although there is only one report of Col_h mesogenic compound based on TTF, which is short of X-ray diffraction data to confirm the Col_h structure.[21]

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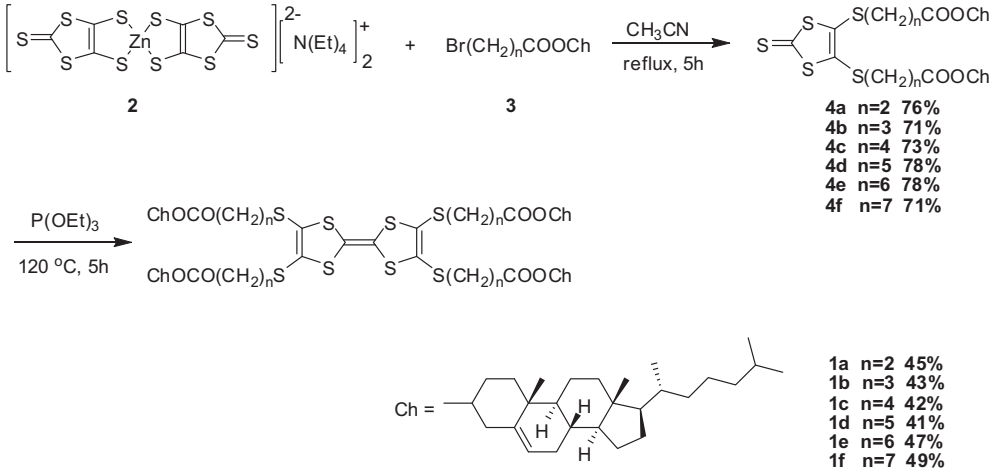
2. Results and discussion

UV–vis spectra were recorded on a Hitachi U-3010 spectrophotometer in CH_2Cl_2 ($c=1\times10^{-5}$ M). Cyclic voltammetric studies were carried out on a Potentiostat/Galvanostat 273A instrument in CH_2Cl_2 ($c=1\times10^{-3}$ M) and 0.1 M Bu_4PF_6 as the supporting electrolyte. Counter and Working electrodes were made of Pt and Glass–Carbon, respectively, and the reference electrode was calomel electrode (SCE). A Perkin–Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks, the heating and cooling rates were controlled to 10 °C/min. An Olympus BX51-P optical polarized microscope (magnification: 40×), equipped with a Mettler FP82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. The thermal stability of target compounds were characterized by Shimadzu DTG-60H thermogravimetric analyzer. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea.

2.1. Synthesis

The structures and synthetic route of target tetrapedals were shown in Scheme 1. The reaction of bis(tetraethylammonium) bis (1,3-dithiole-2-thione-4,5-dithiol) zincate salt (**2**) with cholesteryl ω-bromoalkyanoates (**3**) in acetonitrile gave bipedal 1,3-dithiol-2-thione derivatives **4** in good yields (70–78%), and phosphite-mediated self-coupling of **4** eventually obtained the desired tetrapedal liquid crystal compounds **1a**–**f** (41–47%).

(n=5) exhibited a liquid crystalline phase at a melting state (17.7 °C), which was transformed to an isotropic phase at 97.4 °C (Fig. 1a and Table 1). On slow cooling of **4d** from the isotropic liquid to liquid crystalline phase, a banded focal conic fan texture was observed by POM experiment, which was transformed to glassy state during cooling (Fig. 2a). The DSC curves together with optical texture preliminarily confirmed the presence of a 1-D smectic A phase (S_A). The SAXS of **4d** measured at cooling to 80 °C displayed three sharp reflections with d spacings of 4.95, 2.47, and 1.65 nm, which were in the ratio of 3:2:1 and agreed well with (100), (200), and (300) reflections of a lamellar packing structure (Fig. 3a). Considering the layer thickness (4.95 nm) obtained from the X-ray diffraction pattern is much larger than the estimated molecular length (2.5 nm by Corey–Pauling–Koltun (CPK) model) and the S···S interaction between the 1,3-dithiole-2-thione segments, bimolecule arrangement in lamellar structure is expected, in which the 1,3-dithiole-2-thione segments interdigitate to fill the space (Fig. 4a). The small-angle X-ray diffraction pattern of **4b** (n=3) also displayed similar Bragg diffraction peaks corresponding to the long spacing or layer reflections in the small-angle region (Table 2 and Fig. S4) and thus also index to a lamellar structure. Considering the similarity of the optical textures with those of **4b** and **4d**, **4a**, **4c**, and **4e** could also be indexed to lamellar arrangement (Fig. S2). The compound **4f** (n=7) with the longest spacer is unique in that it displays two mesophases at 10.7 °C and 77.5 °C, followed by transformation to an isotropic phase at 89.2 °C (Table 1 and Fig. 1b). Upon cooling from the isotropic liquid, a cholesteric-like texture was observed by POM experiment (Fig. 2b). The DSC curves together with optical texture preliminarily considered to be a cholesteric phase. To identify the detailed phase structure, SAXS studies were performed. The X-ray diffractogram of **4f** taken at 85 °C shows



Scheme 1. The synthetic route of **1a**–**1f**.

2.2. Characterization of liquid crystal phase

The phase sequences and phase structures of key precursor bipedals **4a**–**f** and target tetrapedals **1a**–**f** were investigated by polarized-light optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scatterings (SAXS). All the synthesized compounds exhibit mesophases and no crystallization but vitrifying to form glassy mesogen during cooling from the isotropic melt. The bipedals **4a**–**e** exhibited only one mesophase in a wide temperature region. Only compound **4f** with the longest spacer showed two phase transitions in heating as well as in cooling cycle (Table 1, Fig. 1 and Fig. S1). For example, compound **4d** a strong diffuse halo in the wide-angle X-ray regions, but no sharp peak in the lower Bragg angle region was observed, indicating the presence of a cholesteric phase (Fig. 3b). On further cooling to 75.5 °C, the cholesteric phase gradually transformed to another mesophase, the typical fine mosaic texture appeared and its disordered systems induce vitrification rather than crystallization during cooling (Table 1, Figs. 1b and 2c). The detailed mesophase structure is also confirmed by SAXS experiments. The X-ray diffraction pattern of **4f** measured at cooling to 60 °C displays three sharp reflections corresponding to spacing of 5.01, 2.85, and 1.87 nm in the small-angle region as shown in Fig. 3c. They are in the ratio of 1:√3:√7 and could be indexed as (100), (110), and (210)