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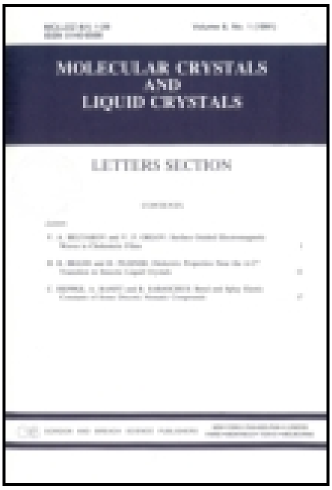

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# A Novel Photonic LC Material Combined with Rod-Like Azobenzenes and a Disc-Shaped Triphenylene

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# A Novel Photonic LC Material Combined with Rod-Like Azobenzenes and a Disc-Shaped Triphenylene

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*The homologous series of an alkoxyazobenzene-triphenylene system (**CnTEsAz**) in which six alkoxyazobenzenes are attached to triphenylene via propyleneester linkage were synthesized to study their mesomorphism. DSC and XRD measurements in addition to the optical texture observation clarified these homologues to be mesomorphic showing bimesomorphy of calamitic smectoic and discotic columnar mesophases in an enantioropic way.*

**Keywords** calamitic liquid crystal; discotic liquid crystal; photoisomerization; triphenylene; azobenzene

## Introduction

Calamitic and discotic liquid crystals are the categories of LCs on the anisotropic shape of molecules as rod-like and disc-like, respectively. Therefore, the orientational orders should give different characters based on both molecular anisotropy and its orders. The refractive index of liquid crystal is an optical property subjected to the orientaional order of mesogens as well as their anisotropic structure of molecules. As a chacteristic property of liquid crystals, one can change the director by an external electric field such as electrical one to control the anisotropy of refractive indices. Nematic liquid crystal and blue phases recently found to be useful [1] show this property, as the applications to flat panel display have been extensively studied.

Recently, it was found that a mesogen which has a triphenylene as its disc-shape core and peripherally-attached six alkyloxyazobenzenes (**C14TEsAz**) exhibit an enantiotropic bimesomorphism of discotic columnar and calamitic smectic phases accompanied with the reversible change of molecular anisotropy between rod and disc (Fig. 1) [2]. Moreover,

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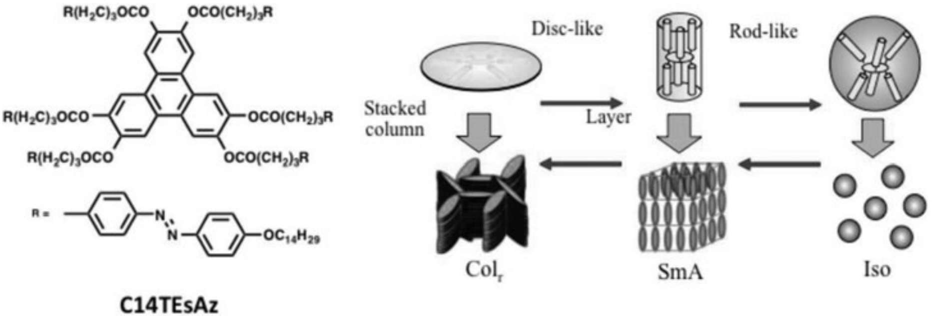


**Figure 1.** A schematic representation of the sequential bimesomorphy of calamitic smectic and discotic columnar mesophases exhibited by the tetradecyloxy homologue of hexaazobenzene-substituted triphenylene (**C14TEsAz**).

this phase transition sequence is maintained under the UV-irradiation (365 nm, 1 W cm$^{-2}$) which induces *trans* to *cis* photo-isomerization of the azobenzene moieties. The resultant situation is only the temperature decrease in the Iso-Sm, Sm-Col and Col-cryst phase transitions even under UV irradiation. This is the first example that a single molecular system exhibits a bimesomorphy of calamitic and discotic mesophases and particularly the molecular anisotropy changes between rod-like and disc-like ones in a photo-induced phase transitions of mesophase has been extensively studied, the results obtained is just to give only order to disorder phase transitions like typically liquid crystalline phase to isotropic one [3, 4]. Therefore, this compound is expected to show a novel type of functionality and both positive and negative signs of refractive index on the phase change could be controlled by not only thermal, but also photonic external fields.

In this work, in order to investigate the mesomorphic phase transition behavior of the homologues, **CnTEsAz** (n = 11, 12, 13, 15 and 16) were synthesized and it was found

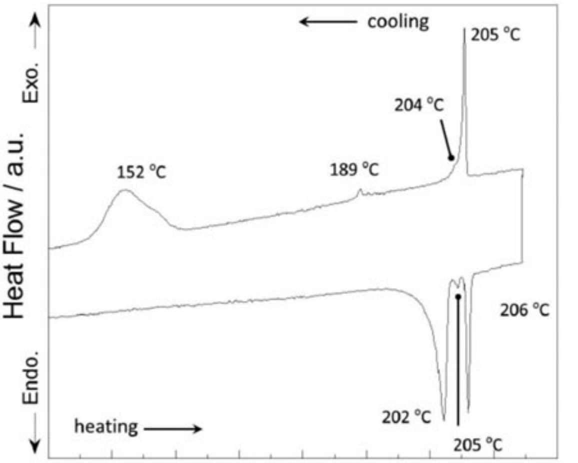
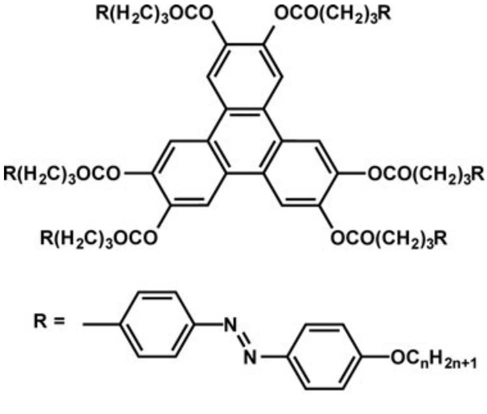


**Figure 2.** DSC thermogram of **C12TEsAz** at 1°C min$^{-1}$ of heating and cooling rates.

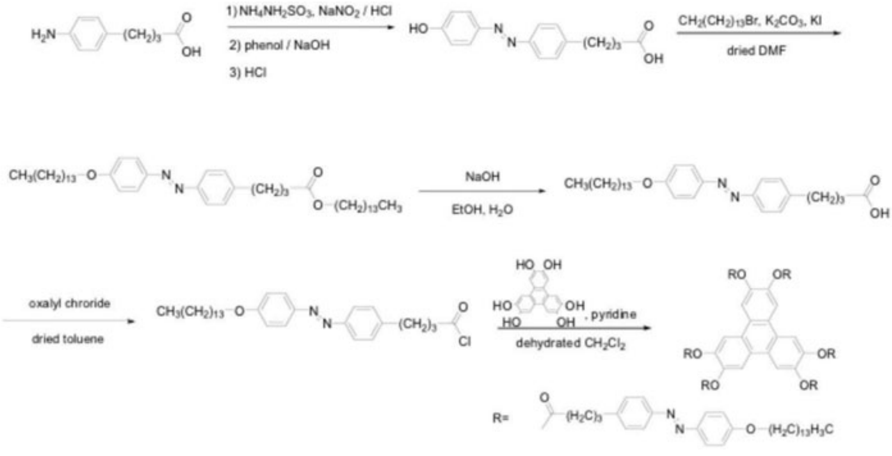
that the homologues with the longer chains (n ≥11) exhibit enantiotropic phase transitions involving both smectic and columnar mesphases.



**CnTEsAz**
**(n=11, 12,..., 16)**

## Experimental

The syntheses of **CnTEsAz** (n = 11–16) were carried out following the method previously described [2]. The synthetic route is shown in Scheme 1 (exemplified by n = 14). The phase transition properties were studied by DSC (TA Instruments DSC2920) and XRD (Rint2000, Rigaku, with temperature-controllable hot stage) in addition to the optical texture observation on temperature change with a polarizing microscope (Olympus BH-2) equipped with a temperature controllable hot stage (Mettler FP82HT and Lincam MK600). An optical cut filter (O-58) was used for the protection of UV and visible light exposure ($\lambda < 580$ nm) under texture observation.



**Scheme 1.**

## Results and Discussion

Figure 2 shows a DSC thermogram of **C12TEsAz** at 1°C min$^{-1}$ of heating and cooling rate. One can see three endothermic peaks on heating at 202°C, 205°C and 206°C. On cooling, on the other hand, three exothermic peaks and one shoulder could be observed at 205°C, 204°C (as a shoulder), 189°C and 152°C. These are essentially of enantiotropic phase transition as seen in **C14TEsAz** reported previously [2].

In the microscopic observations of optical texture, the phase transition at 206°C was found to be the isotropization and 202°C for the crystal melting, thus for the phase notified that the large degree of super cooling (ca. 50°C) is observed for the melting / crystallization even at the cooling rate 1°C min$^{-1}$, indicating a difficulty of crystallization probably due to the conformational variation of triphenylene and six alkoxyazobenzene moieties in a dynamic molecular aggregation. The high-temperature mesophase was identified to be smectic A phase by polarizing microscopic observation of optical textures where one can see the formation of "bâtonnets" on cooling from the isotropic phase followed by a spontaneous change to homeotropic dark area (indicating an optically uniaxial phase with a layered structure) and also followed by fan-shaped texture formation in the non-homeotropic alignment domains (Fig. 3). Further cooling leads to the texture change which indicate that SmC phase is formed. Schlieren texture comes up for the homeotropic domains of SmA phase and the fan-shaped texture was modified to be broken. These are typical for SmC phase formation. At ca. 189°C, the texture was gradually deformed to be a mosaic one.

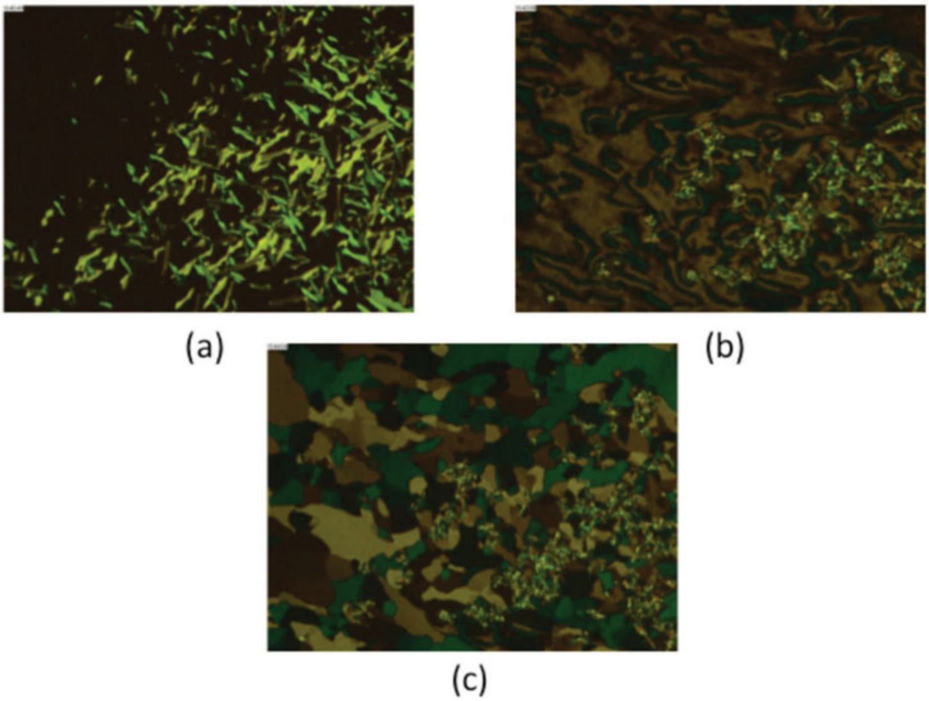
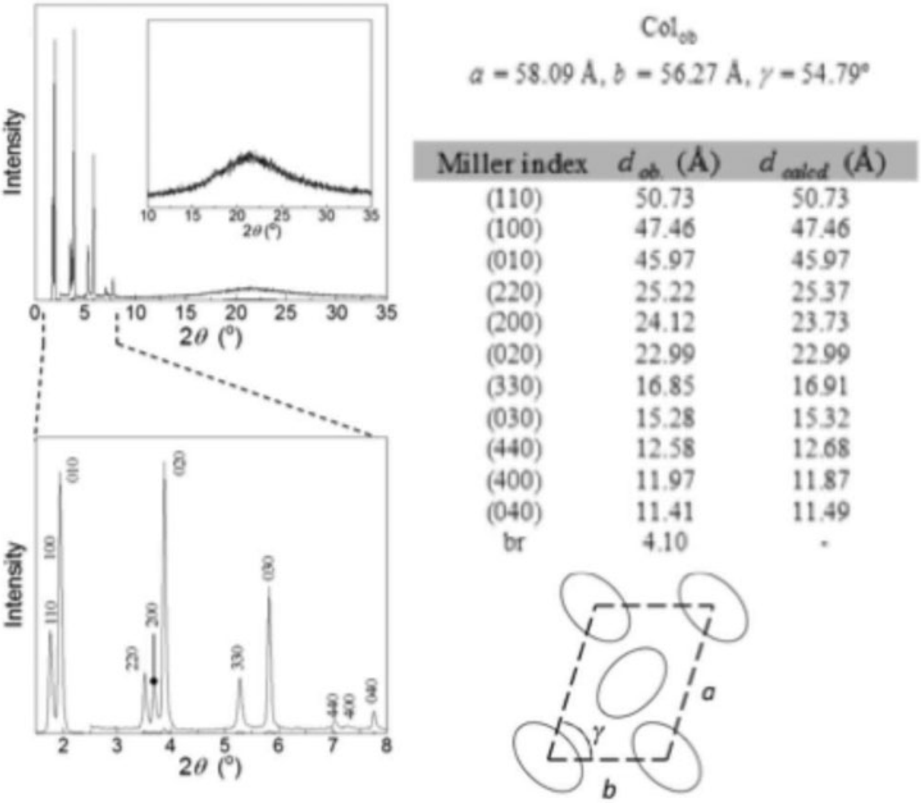


**Figure 3.** Optical textures of mesophases for **C12TEsAz** coming up on cooling from Iso phase. (a) "bâtonnets" formation in the early stage of SmA domain growth at 204.6°C, (b) the following Schlieren texture formation in the homeotropic domains of SmA phase at 205.0°C and (c) mosaic texture of the columnar mesophase at 190.0°C.



Col$_{ob}$

$a = 58.09$ Å, $b = 56.27$ Å, $\gamma = 54.79°$

| Miller index | $d_{ob.}$ (Å) | $d_{calcd}$ (Å) |
|---|---|---|
| (110) | 50.73 | 50.73 |
| (100) | 47.46 | 47.46 |
| (010) | 45.97 | 45.97 |
| (220) | 25.22 | 25.37 |
| (200) | 24.12 | 23.73 |
| (020) | 22.99 | 22.99 |
| (330) | 16.85 | 16.91 |
| (030) | 15.28 | 15.32 |
| (440) | 12.58 | 12.68 |
| (400) | 11.97 | 11.87 |
| (040) | 11.41 | 11.49 |
| br | 4.10 | - |

**Figure 4.** XRD patterns of columnar mesophase in **C12TEsAz** at 180°C and the analysis by indexing all reflections.

No dark image was observed for this phase under crossed polarizing condition, indicating it is not of optically uniaxial phase such as hexagonal and tetragonal columnar phases.

XRD patterns at 180°C are shown in Fig. 4 as an evidence for the assignment to be of Col*ob* mesophase of which 2D lattice of columnar arrangement is of oblique-shaped ($a = 58.1$ Å, $b = 56.3$ Å, $\gamma = 54.8°$, Z = 2). The lattice size determined is reasonable, considering that the molecular diameter with a fully extended chains is estimated to be ca. 60 Å. Therefore, these results consequently clarify that **C12TEsAz** has bimesomorphy of calamitic smectic and discotic columnar mesophases in an enantiotropic manner as **C14TEsAz** does and the phase sequence is similar except for the additional SmC phase and the modified lattice shape of columnar arrangement (rectangular to oblique).

On the same procedure in the identification of mesophase, another shorter chain homologue, **C11TEsAz**, is found to exhibit the same phase sequence as that of **C12TEsAz**. Also the longer homologues, **C13-C16TEsAz** were found to show the same type of bimesomorphism as that of **C14TEsAz** with only two mesophases, SmA and Colr phases.

The preliminary results of phase transition sequence for these homologues are summarized in Table 1. It is noteworthy to notice that all homologues with n ≥ 11 exhibit an enantiotropic sequence of phase transitions involving calamitic smectic and discotic columnar mesophases, whilst **C10TEsAz** shows only an monotropic Colh mesophase on

**Table 1.** Phase transition parameters of **1-C11∼1-C16**

| | Thermal transitions (°C) and corresponding enthalpy changes (kJ/mol) | |
|---|---|---|
| Compound | Heating | Cooling |
| **1-C11** | Cryst 198 (50.4) Col$_{ob}$ 202 (0.8) SmC 203 (0.5) SmA 204 (12.0) Iso | Iso 204 (12.8) SmA 202 (0.9) SmC 182 (0.6) Col$_{ob}$ 159 (55.4) Cryst |
| **1-C12** | Cryst 202 (52.4) Col$_{ob}$ 204 (0.9) SmC 205 (0.4) SmA 206 (13.9) Iso | Iso 205 (14.7) SmA 204 (1.0) SmC 189 (0.5) Col$_{ob}$ 152 (59.5) Cryst |
| **1-C13** | Cryst 132 (4.2) Col$_r$ 205 (12.3) SmA 206 (16.2) Iso | Iso 205 (10.1) SmA 202 (14.1) Col$_r$ 127 (6.8) Cryst |
| **1-C14** | Cryst 174 (10.2) Col$_r$ 205 (10.1) SmA 206 (8.0) Iso | Iso 202 (8.2) SmA 197 (12.3) Col$_r$ 126 (5.3) Cryst |
| **1-C15** | Amorphous 173 (13.5) Col$_r$ 201 (10.3) SmA 204 (6.7) Iso | Iso 203 (6.8) SmA 196 (11.2) Col$_r$ 114 (8.9) Amorphous |
| **1-C16** | Col$_r$* 84 (9.7) Col$_r$ 202 (10.5) SmA 203 (5.6) Iso | Iso 201 (5.2) SmA 196 (9.9) Col$_r$ 82 (9.3) Col$_r$* |

Cryst, crystalline; Col$_{ob}$, oblique columnar; SmC, smectic C; SmA, smectic A; Iso, isotropic liquid; Col$_r$, rectangular columnar with symmetry P2/a; Col$_r$*, rectangular columnar with symmetry P2$_1$/a; Amorphous, amorphous solid.

slow cooling of iso phase which is replaced with SmA phase on rapid cooling as a transient state. Small difference corresponding to only one methylene group results in a drastic change of mesomorphism. In the shorter chain homologues (C10-C14), the crystal phase is significantly stabilized. In addition, Colh phase in C10 homologue [5] is changed to Colob one. This is a phase change induced by inclination of molecular plane against the columnar axis to modify the lattice shape from hexagonal to oblique to raise up the thermal stability of columnar mesophase. The alkyl chain volume seems to affect the molecular packing in the columnar mesophase. For the chain length, however, the thermal stability of SmA phase is influenced in a moderate way to give the maximum at the C13 chain homologue, while the melting points are sensitive to it. Further studies are under progress.

## Conclusion

The homologous series of an alkoxyazobenzene-triphenylene system (**CnTEsAz**) were synthesized to study their mesomorphism. The series of experimental results clarify these homologues to be mesomorphic showing bimesomorphy of calamitic smectoic and discotic columnar mesophases in an enantioropic way. Therefore, **CnTEsAz** is a good candidature for a large anisotropy change of refractive index which could be provided by reversible change of rod to disc in molecular shape in an enantiotropic way. Considering the recent studies of photo-induced phase transitions on mesophase have shown an interesting evolution where one can see the more complicated mesophase order could be controlled [6], the details of mesomorphism and phase transition behavior of **CnTEsAz** under UV-irradiation which causes the *trans-ci*s isomerization of azobenzene moieties to deform the mesomorphic orders should be important for further discussion toward novel optical materials.

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