

Supramolecular Liquid Crystals Containing Hydrogen Bond between Carboxylic Acid and Pyridyl Moieties and Their Mesomorphism

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Introduction

In general, supramolecular columnar liquid crystals consist of mesogenic unit which can aggregate into discs that will make up the columns. These columns associate to form a two-dimensional network leading to various types of columnar arrangements including hexagonal, rectangular, and oblique arrays [1]. Recently, these thermotropic columnar liquid crystals have been studied because of their possible application to one-dimensional electronic conductor [2], photoconductors [3], organic photovoltaic [4], and organic light emitting diodes [5].

Previously, we reported hydrogen-bonded complexes which show the thermotropic columnar behavior using stilbazoles and phloroglucinol [6]. The objective of this study is to design complexes that show the thermotropic columnar behavior using strong hydrogen bonding between two different molecules. (Figure 1) Cyclohexane-1,3,5-tricarboxylic acid was used as the core molecule for hydrogen donor and 3,4,5-trimethoxybenzoate-trans-stilbazoles with $n = 10$ (n is the number of carbon in the alkyl chain) as the peripheral units for hydrogen acceptor.

Experimental

Trans-4-Hydroxy-4'-stilbazole was synthesized by the modified procedure of Chiang and Hartung [7]. Trialkoxybenzene carboxylic acid was synthesized by the modified methods of Percec [8]. Trimethoxybenzoate-trans-stilbazoles were synthesized by esterification using oxalic chloride. All products were characterized by ^1H NMR. Hydrogen-bonded complex was obtained by dissolving phloroglucinol and 3,4,5-Trimethoxybenzoate-trans-stilbazoles (1/3 mol / mol) in anhydrous THF and subsequent evaporating THF.

Results and discussion

Figure 2 shows FT-IR spectrum of (a) cyclohexane-1,3,5-tricarboxylic acid and (b) 3,4,5-trimethoxybenzoate-trans-stilbazoles, and (c) prepared complex. O-H stretching band of cyclohexane-1,3,5-tricarboxylic acid was observed at 2673 cm^{-1} and 2564 cm^{-1} . But, prepared complex showed different stretching of O-H band at 2564 cm^{-1} and 2528 cm^{-1} . Vibration frequency of O-H stretching band was shifted to lower region after formation of complex, which is the result of the intermolecular hydrogen bonding between the core unit and the peripheral unit. Also, we can observe disappearance of C=O stretching band at 1936 cm^{-1} , and it also support successful formation of hydrogen bonding between carboxylic acid and pyridyl moieties [9].

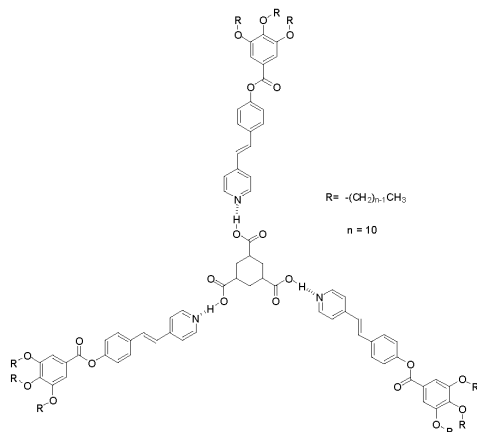


Figure 1. Structure of prepared complex.

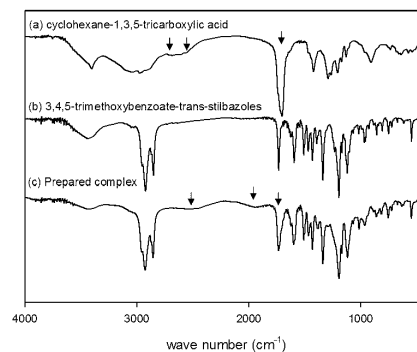


Figure 2. FT-IR of (a) core, (b) peripheral, and (c) complex

The DSC results for prepared complex showed isotropic to mesophase transition around $41\text{ }^\circ\text{C}$ upon cooling and heating. Polarized optical microscopy experiments confirmed the result of DSC with the observed fine texture.

Figure 3 shows X-ray diffraction pattern of prepared complex at room temperature. We observed three peaks at 47.2 \AA , 27.2 \AA , and 23.6 \AA . These are characteristic of the hexagonal columnar (Col_h) phase with a d-spacing ratio of 1, $(1/3)^{1/2}$ and $(1/4)^{1/2}$ corresponding to Miller indices (100), (110) and (200), respectively [10, 11]. A broad halo was also observed at 4.2 \AA in the wide-angle region, which is ascribed to the alkyl chains.

Conclusions

We prepared supramolecular columnar liquid crystals using hydrogen bonding between carboxylic acid and pyridine moieties. The prepared complex showed a hexagonal columnar disordered structure (Col_h) upon cooling from $41\text{ }^\circ\text{C}$ to room temperature.

References

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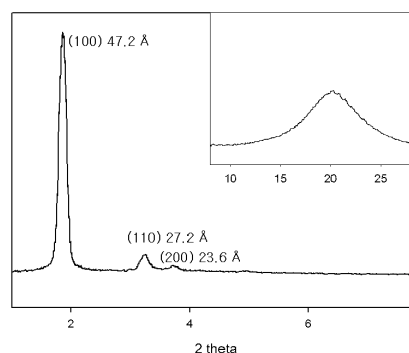


Figure 3. X-ray diffraction pattern of prepared complex