

行政院國家科學委員會專題研究計畫 成果報告

不對稱聯伸三苯類及多炔苯環類液晶材料之合成及性質研究(2/2)

計畫類別：個別型計畫

計畫編號：NSC91-2113-M-032-009-

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執行單位：淡江大學化學系

計畫主持人：徐秀福

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報告類型：完整報告

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中 華 民 國 93 年 2 月 25 日

新型態盤狀液晶之設計，開發合成，物性及應用研究

計畫類別： 個別型計畫 整合型計畫

計畫編號：NSC 91 - 2113 - M - 032 - 009 -

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計畫主持人：徐秀福

共同主持人：

計畫參與人員：

成果報告類型(依經費核定清單規定繳交)： 精簡報告 完整報告

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執行單位：淡江大學化學系

中 華 民 國 九 十 二 年 二 月 二 十 五
日

行政院國家科學委員會專題研究計畫成果報告

不對稱聯伸三苯類及多炔苯環類液晶材料之合成及性質研究(2/2)

Synthesis and Liquid Crystal Property Study of Unsymmetrical Triphenylene, Multialkynylbenzene, and Related Compounds (2/2)

計畫編號：91-2113-M-032-009-

執行期限：91年8月1日至92年12月31日

主持人：徐秀福 執行機構及單位名稱：淡江大學化學系

I. 中文摘要

本計畫合成出之不對稱三伸聯苯化合物皆不具液晶性質。而另一類多炔化合物則具有液晶特性，其中包括三炔三苯及多炔吡吩化合物。本報告包含以上三大類化合物之熱性質之探討。

關鍵詞：筒狀液晶相、向列型液晶相、層列液晶相

Abstract

Unsymmetrical triphenylene derivatives have been synthesized. However, no mesogenic behaviors can be observed. On the other hand, liquid crystal materials derived from multiynyl compounds were achieved. These includes triynyltriphenylbenzenes and multiynylthiophenes. The thermal behaviors of the above mentioned three types of compounds are summarized in this report.

Keywords: Liquid Crystal, Multiynyl compounds, Triphenylene

II. Background and Objectives

Triphenylene has been the most investigated class of discotic liquid crystals. However, few reports are devoted to the study of the unsymmetrical triphenylenes. In the first part of this report, these unsymmetrical derivatives were prepared via facile synthetic routes.

Materials with columnar mesophases have been of interests due to their potential application as one-dimensional conductors.¹ However, compared with nematic and smectic liquid crystals, fewer structural skeletons have been found to exhibit columnar phases. Cyclotrimerization of three 1,2-diphenylethynyl units with one alkoxy chain on the para-ends of each phenyl ring afforded the hexaphenylbenzene system which exhibited a columnar mesophase.² When the central benzene and each outer alkoxyphenyl group were separated by a ethynyl linker as in the hexaynylbenzene derivatives, instead of showing the columnar phase, the less observed discotic nematic (N_D) phase was detected.³

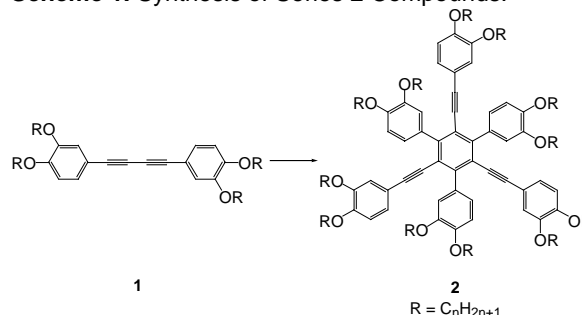
Both systems have identical peripheral moieties as for most discotic materials. Usually, symmetry breaking of discotic materials was achieved by variations on the outer long chains.⁴ However, there are a few examples utilizing inositol,⁵ triazine,⁶ and sugar⁷ to introduce asymmetry onto the cores. No reports were found to explore the potential mesogenic materials of a hybrid system incorporating phenyl and phenylethynyl peripheral groups onto the central benzene to break the core symmetry. In the second part of this report, cyclotrimerization followed by easy purification, that is recrystallization, has yielded thermodynamically stable columnar liquid crystals, series compounds **2**, with a new core of the hybrid system, 1,3,5-triphenylethynyl-2,4,6-triphenylbenzene.

Also included in the second part of this report are the synthesis and properties of **3**, unsymmetrical analogs of **2**, and multiynylthiophenes.

III. Results and Discussions

Series **2** compounds were synthesized according to scheme 1. Coupling two units of the acetylene containing compounds with copper acetate in refluxing MeOH/pyridine (1:1) led to the formation of the butadiynyl series **1** compounds in good yields. Catalyzing with $\text{Co}_2(\text{CO})_8$, cyclotrimerization of three units of 1,4-bis(3,4-dialkoxyphenyl)butadiyne led to

Scheme 1. Synthesis of Series **2** Compounds.



many inseparable closely spaced spots on analytical thin layer chromatography for most of the cases. Attempts on separation with column chromatography were not successful. Fortunately, recrystallization with *n*-hexane gave pure **2** in reasonable yields of 20-26% which are more than three times of the

reported yield of the chainless analog from cyclotrimerization of 1,4-diphenylbutadiyne catalyzed by $\text{CoCp}(\text{CO})_2$.⁸

The mesogenic behaviors of **2a-2d** were studied by polarized optical microscopy (POM). When cooled slowly from isotropic melts, all compounds showed liquid crystal behavior evidenced by large domains of dendritic homeotropic texture, which is typical for columnar mesophases. The easiness of homeotropic texture formation can be ascribed to the favored packing into columns by the big but not flat core. However, typical columnar focal conic textures can be observed when the cover glass was removed. Under such circumstance, glass-surface interaction was absent from the top of the sample to generate birefringent texture from gradually tilted columns caused by surface tension.

The thermal properties of **2** were investigated by differential scanning calorimetry (DSC) and the results were summarized in Table 1. The mesophases of series **2** compounds were confirmed by X-ray diffraction (XRD).

Table 1. Phase behaviors of series **2** compounds.

Compound	Phase Transitions ^a	
2 (n = 4)	$\text{K1} \xrightarrow{85.8 (4.97)} \text{K2} \xrightarrow{96.9 (12.50)} \text{K3} \xrightarrow{109.1 (4.34)} \text{Col}_{\text{hd}} \xrightarrow{126.5 (4.59)} \text{I}$	
		$\text{K2} \xrightarrow{97.6 (3.85)} \text{I}$
2 (n = 6)	$\text{K1} \xrightarrow{68.8 (12.12)} \text{K2} \xrightarrow{84.9 (11.18)} \text{Col}_{\text{hd}} \xrightarrow{132.2 (5.08)} \text{I}$	
		$\text{K2} \xrightarrow{53.1 (-21.60)} \text{I}$
2 (n = 10)	$\text{K} \xrightarrow{69.9 (26.31)} \text{Col}_{\text{hd}} \xrightarrow{129.8 (4.16)} \text{I}$	
		$\text{K} \xrightarrow{56.2 (-17.24)} \text{I}$
2 (n = 14)	$\text{K} \xrightarrow{78.5 (70.53)} \text{Col}_{\text{hd}} \xrightarrow{115.8 (6.68)} \text{I}$	
		$\text{K} \xrightarrow{61.9 (-77.78)} \text{I}$

^a The transition temperatures (°C) and enthalpies (in parentheses/kJ mol⁻¹) were determined by DSC at 10 °C/min. K, K1, and K2, crystalline phases; N, nematic mesophase; I, isotropic liquid. n denotes the length of the alkoxy chains.

The optical properties of compounds **2a-2d** were investigated by means of UV-vis and fluorescence spectrometry. The absorption and emission spectra of **2** in dichloromethane are shown in Figure 1. For compound with n = 10, the absorption and emission spectra in its crystalline phase, in its columnar phase, and in its isotropic liquid are shown in Figure 2. In solution, they all showed an intense chain-length independent absorption maximum at 338 nm. No change can be detected when the solvent was changed to the less polar cyclohexane. The photoluminescence spectra are independent of the excitation wavelength and a broad emission peak at 428 nm appears for all compounds in solution. The quantum yields are chain length dependent and range between 36% when n = 4 and 44% when n = 14.⁹ A Stokes shift of 90 nm may imply significant conformational change upon excitation. A small red-shift of 87 cm⁻¹ found for the absorption spectra of **2** in its columnar phase at 100 °C with respect to that in dichloromethane solution indicates the molecular organization has little effect on the absorption maximum. This is intriguing since a large blue-shift of 2000 cm⁻¹ has been observed for the columnar

mesophase of triphenylene esters¹⁰ and a small red-shift of 169 cm⁻¹ was reported for the less ordered discotic nematic phase of phenylethynylbenzenes.¹¹ The fluorescence spectra of **2** in its columnar mesophase at 100 °C is blue-shifted (275 cm⁻¹) with respect to that in dichloromethane solution. Upon cooling to crystalline phase, the spectrum is further blue-shifted and more structured. In addition to the spectral shift, the intensity as well as the area of the peak decreased dramatically from solid phase to liquid crystal phase. In the columnar phase, the emission intensity decreased with increasing temperature. Upon further heating into the isotropic phase, a large but not as pronounced increase of the intensity was found. These intensity and area changes in different states were also observed for a hexacatenar mesogen showing columnar liquid crystal phase and were ascribed to the different extent of forming self-quenching aggregates in different states.¹²

Figure 1. Absorption and fluorescence spectra of **2** in dichloromethane. Extinction unit: 10⁴ dm³ mol⁻¹ cm⁻¹.

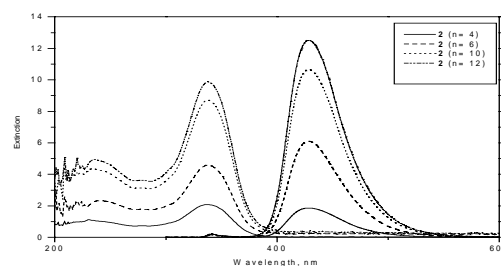
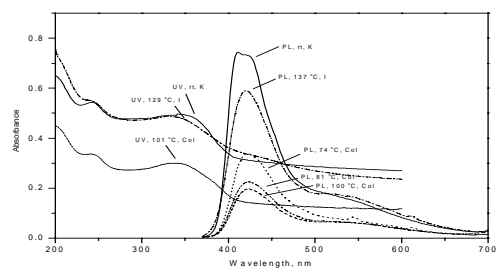
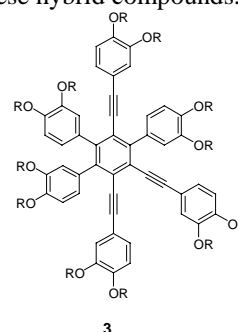


Figure 2. Absorption and fluorescence spectra of **2** (n = 10) in its crystal, columnar, and isotropic phases.



We have also prepared series **3** compounds, the unsymmetrical version of **2**. It is noticed that lowering the symmetry does improve the stability of mesophases for these hybrid compounds.



3

In the second part of this report, liquid crystals derived from multiynylthiophenes were achieved and

their mesogenic behaviors are listed in Table 2.

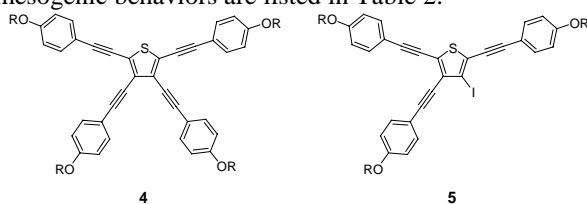


Table 2. Phase Behavior of Series 5 Compounds.^a

Compound	Behavior
5, n = 8	K $\xrightleftharpoons[63.3 (-39.56)]{93.4 (59.10)}$ N $\xrightleftharpoons[70.1 (-0.04)]{}$ I
5, n = 10	K1 $\xrightleftharpoons[40.0 (-52.08)]{72.2 (58.33)}$ K2 $\xrightleftharpoons[72.4 (-0.73)]{75.6 (17.08)}$ I N $\xrightleftharpoons[72.4 (-0.73)]{}$ I
5, n = 12	K1 $\xrightleftharpoons[61.6 (-74.74)]{88.8 (61.72)}$ K2 $\xrightleftharpoons[69.6 (-0.44)]{93.2 (57.59)}$ I N $\xrightleftharpoons[69.6 (-0.44)]{}$ I

^aThe transition temperatures (°C) and enthalpies (in parentheses/kJ mol⁻¹) were determined by DSC at 10 °C/min. K, K1, and K2, crystalline phases; N, nematic mesophase; I, isotropic liquid. n denotes the length of the alkoxy chains.

These thienyl compounds does not show better liquid crystallinity than their phenyl analogues. However, the novel rigid Y-shape core of series 5 compounds opens up a new direction for liquid crystal material reaserch.

IV. Self-Evaluation

In this project, we have achieved the preparation and property study of unsymmetrical triphenylenes, triynyltriphenylbenzenes, and multiynylthiophenes. The acetylene-containing compounds showed promising potential for further investigation.

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