Novel Columnar Liquid Crystals with Nonidentical Peripheral Groups: 1,3,5-Triphenylethynyl-2,4,6-triphenylbenzene

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Received November 19, 2002
Revised Manuscript Received April 4, 2003

Materials with columnar mesophases have been of interest 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 alkoxylphenyl 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 sugar[7] 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. This may be due to a potentially tedious synthetic procedure involving sequential multiple phenyl−phenyl coupling and multiple phenyl−ethynyl coupling. Also, complicated purification may be encountered in both coupling steps. However, the hybrid system will have in-between sterics of the hexaphenylbenzene and hexaynylbenzene systems. Releasing the steric crowdedness around the central benzene of the hexaphenylbenzene core by inserting three ethynyl linkers should lead to a more planar core with better conjugation.

As mentioned, cyclotrimerization has been applied to prepare liquid crystal materials from diphenylethyne derivatives to yield columnar liquid crystals with identical peripheral moieties, but it has not been extended to trimerize the butadiyne analogue to afford the targeted hybrid system. However, in the latter case, two isomeric core structures of the trimer are possible. Moreover, it was shown that cyclization of butadiynyl derivatives usually yielded complex reaction mixtures that not only afforded low yields of the desired symmetrical trimer but also complicated the purification process.[8,9] In this context, cyclotrimerization followed by easy purification, that is recrystallization, has yielded thermodynamically stable columnar liquid crystals, compounds **3a**−**3d**, with a new core of the hybrid system, 1,3,5-triphenylethynyl-2,4,6-triphenylbenzene.

Compounds of **3a**−**3d** were synthesized according to Scheme 1. Coupling two units of the acetylene-containing compounds **1a**−**1d** with copper acetate in refluxing MeOH/pyridine (1:1) led to the formation of the butadiynyl compounds **2a**−**2d** in good yields. Catalyzed with $Co_2(CO)_8$, cyclotrimerization of three units of 1,4-bis-(3,4-dialkoxyphenyl)butadiyne led to many inseparable closely spaced spots on analytical thin-layer chromatography for most of the cases. Attempts on separation with column chromatography were not successful for all compounds except the shortest alkyl chain analogue **3a**. Fortunately, recrystallization with *n*-hexane gave pure **3b**−**3d** in reasonable yields of 20−26%, which is more than 3 times the reported yield of the chainless analogue from cyclotrimerization of 1,4-diphenylbutadiyne catalyzed by $CoCp(CO)_2$.[8]

The core structure was identified by its ^1H and ^{13}C NMR spectra. In addition to the targeted structure of **3**, structure of **4** is also possible from cyclotrimerization of 1,4-diphenylbutadiyne. In solution, rotation of the peripheral phenyl and phenylethyne arms simplifies the core symmetry to be D_{3h} for **3** and C_s for **4**. For the aromatic protons, 6 inequivalent protons for **3** and 18 for **4** can be expected. In the ^1H NMR spectra of series **3** compounds, six aromatic signals, four doublets, and two singlets were found. These aromatic signals correspond well with structure **3**, having two nonequivalent phenyl rings. Another diagnostic area in the ^1H NMR spectra are the signals from the methylene units adjacent to the oxygen atoms. For **3**, there are 4 unique such methylene groups and there are 12 for **4**. Four sets

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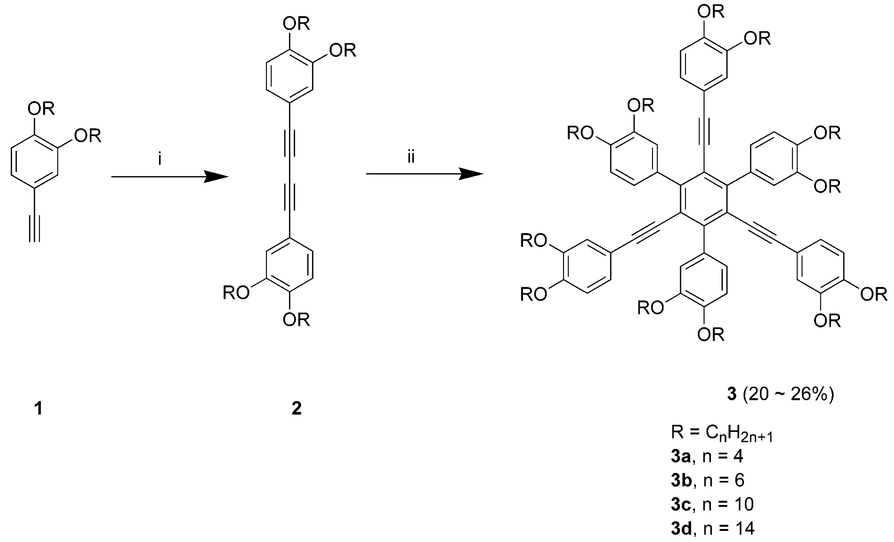
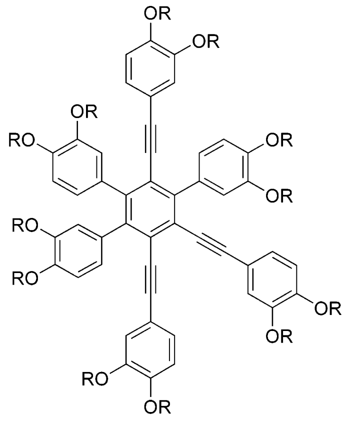
Scheme 1. Synthetic Scheme for Compounds of 3a−3d[a]



[a] (i) $Cu(OAc)_2$, MeOH/pyridine(1/1), reflux; (ii) $Co_2(CO)_8$, 1,4-dioxane, reflux.



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of triplets at 3.8−4.1 ppm with equal integration were detected in the ^{1}H NMR spectra of **3**. Again, the result fits the core structure **3**. The core structure was further verified by ^{13}C NMR spectrometry. In the aromatic region, 14 peaks, 2 for the central benzene and 12 for the two inequivalent outer phenyl rings, are expected for **3**. Exactly 14 aromatic signals were located. The three ethynyl units resonate as two peaks at ca. 87.4 and 97.3 ppm, showing a single environment as expected for the D_{3h} form.

The mesogenic behaviors of **3a**−**3d** 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 **3a**−**3d** were investigated by differential scanning calorimetry (DSC) and the results were summarized in Table 1. All **3**-series compounds showed an enantiotropic mesophase. The smallest liquid crystal range of 17 °C from heating trace was found for the butyloxy analogue, **3a**. However, it was more than tripled to 60 °C for the octyloxyl analogue **3b**. Further lengthening of the side chains shrinks the range and the C14 analogue still holds a 37 °C columnar phase range. The relatively smaller enthalpy of the I−Col transition to that of the Col−K transition in these compounds suggests a disordered arrangement within columns. Not much supercool, <4 °C, was observed for **3** with such a large core.

The closest analogous liquid crystal materials found are hexa(4-phenylbenzene and hexa(phenylethynyl)-benzene derivatives. However, in both cases, there are only six total alkoxy chains with one on the para position of each peripheral phenyl ring. The hexa(4-hexyloxyphenyl)benzene compound exhibited a columnar mesophase from 64 to 102 °C by heating.[2] On the other hand, a discotic nematic phase from 109 to 193 °C upon heating was found for hexa(4-hexyloxyphenyl-ethnyl)benzene.[3] Series **3** compounds showed only a columnar mesophase and no discotic nematic phase was observed. This is not too surprising since the attractions among cores are still relatively strong for **3b** when compared with hexa(4-hexyloxyphenyl)benzene. However, higher transition temperatures and a slightly larger columnar mesophase range of 47 °C, from 85 to 132 °C upon heating, were observed for **3b**. These differences may result from steric crowding release and core symmetry lowering by replacing three phenyl peripheral groups with three phenylethynyl groups. The greater dispersive forces in **3b** with higher side chain density may also contribute.

The mesophases of **3a**−**3d** were also investigated by X-ray diffraction (XRD). As an example, the diffractogram of **3c** at 98 °C is shown in Figure 1. All compounds exhibited the same diffraction pattern corresponding to the disordered hexagonal columnar mesophase at temperatures within the respective mesophase temperature range. In the small angle region, only one sharp signal was observed, which indicates the macroscopic order of

Table 1. Phase Behavior of Compounds 3a−3d[a]

Compound	Behavior
3a, *n* = 4	$\mathrm{K1} \xrightarrow{85.7\ (15.70)} \mathrm{K2} \xrightarrow{96.6\ (46.72)} \mathrm{K3} \xrightarrow{108.8\ (15.64)} \mathrm{Col_h} \xrightleftharpoons[123.9\ (-16.99)]{126.3\ (16.40)} \mathrm{I}$ $\mathrm{K1} \xleftarrow{98.5\ (-14.32)} \mathrm{Col_h}$
3b, *n* = 6	$\mathrm{K1} \xrightarrow{68.8\ (35.15)} \mathrm{K2} \xrightarrow{84.9\ (32.42)} \mathrm{Col_h} \xrightleftharpoons[130.4\ (-14.76)]{132.2\ (14.73)} \mathrm{I}$ $\mathrm{K1} \xleftarrow{53.1\ (-62.64)} \mathrm{Col_h}$
3c, *n* = 10	$\mathrm{K} \xrightleftharpoons[57.5\ (-83.14)]{70.2\ (98.73)} \mathrm{Col_h} \xrightleftharpoons[128.1\ (-13.75)]{129.4\ (13.69)} \mathrm{I}$
3d, *n* =14	$\mathrm{K} \xrightleftharpoons[61.9\ (-248.90)]{78.5\ (225.70)} \mathrm{Col_h} \xrightleftharpoons[114.7\ (-20.67)]{115.8\ (21.38)} \mathrm{I}$

[a] The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 5 °C /min. K, K1, K2, and K3, crystalline phases; Col$_h$, hexagonal columnar mesophase; I, isotropic liquid. *n* denotes the length of the alkoxy chains.

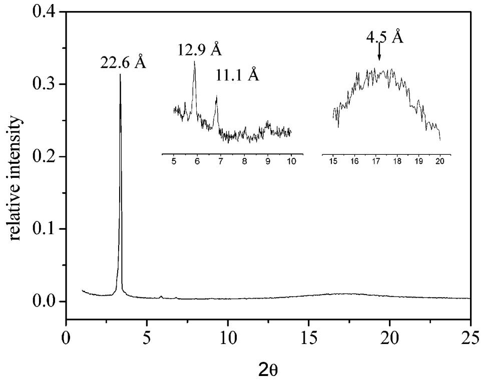

Figure 1. X-ray diffractogram of **3c** at 98 °C.

the mesophase to be hexagonally arranged. The lattice constants of 22.79, 26.13, 31.34, and 35.61 Å for **3a**, **3b**, **3c**, and **3d** are smaller than the calculated molecule diameters of circumscribed/inscribed circles, 29.5/24.4, 34.5/29.4, 44.6/39.5, and 54.7/49.6 Å, respectively.[10] This suggests interdigitation of the side chains between columns and a trend of increasing chain penetration is found with increasing chain length. In the wide-angle region, the broad halo peaked at ca. 4.5 Å could be from molten aliphatic chains, from the intermolecular distance within a column, or more likely from a combination of both.

The optical properties of compounds **3a**−**3d** were investigated by means of UV−vis and fluorescence spectrometry. The absorption and emission spectra of **3a**−**3d** in dichloromethane are shown in Figure 2. For compound **3c**, the absorption and emission spectra in its crystalline phase, in its columnar phase, and in its isotropic liquid are shown in Figure 3. In solution, they all showed an intense chain-length-independent absorption maximum at 338 nm and molar extinction coefficients range between 2.1 × 10^4 dm^3 mol^{-1} cm^{-1} for **3a** and 9.9 × 10^4 dm^3 mol^{-1} cm^{-1} for **3d**. 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% for **3a** and 44% for **3d**.[11] 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 **3c** 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 esters[12] and a small red shift of 169 cm^{-1} was reported for the less ordered discotic nematic phase of phenylethynylbenzenes.[13] The fluorescence spectra of **3c** 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.[14]

In conclusion, utilization of the cyclotrimerization of 1,4-diphenylbutadiyne derivatives reaction by $Co_2(CO)_8$ catalyst, a new mesogenic core with nonidentical peripheral moieties has been developed. The easiness of purification has enabled the investigation of the liquid

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(10) The molecular geometry was optimized using the MM2 method by molecular software, Chem3D (Cambridge Software Corporation).

(11) Quantum yields were calculated using 9,10-diphenylanthracene as the reference.

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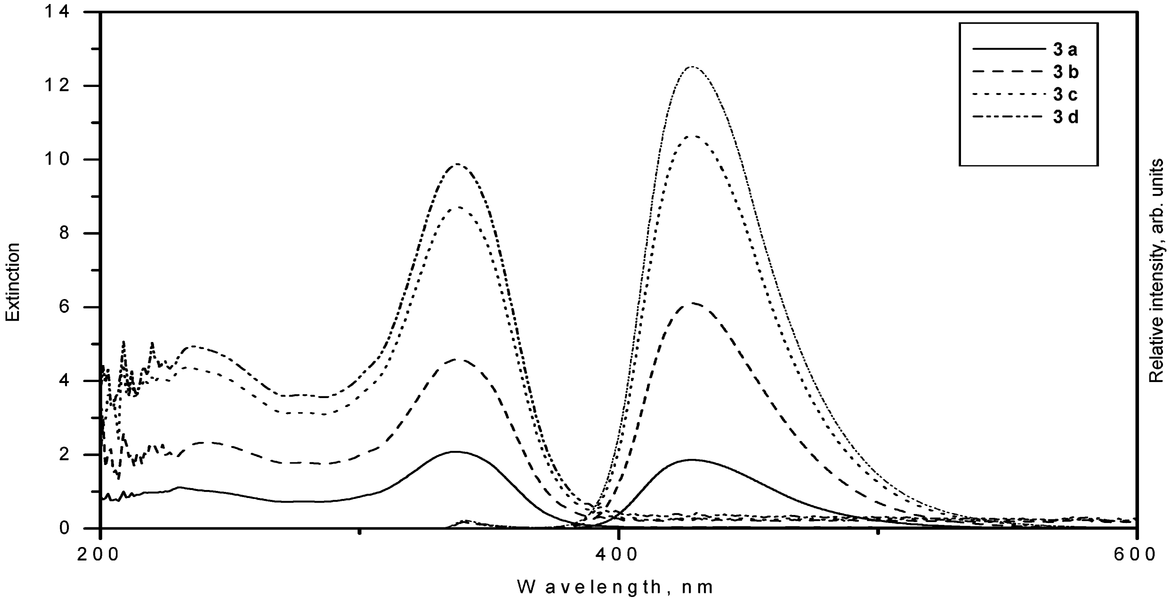

Figure 2. Absorption and fluorescence spectra of **3a**~**3d** in dichloromethane. Extinction unit: 10^4 dm^3 mol^{-1} cm^{-1}.

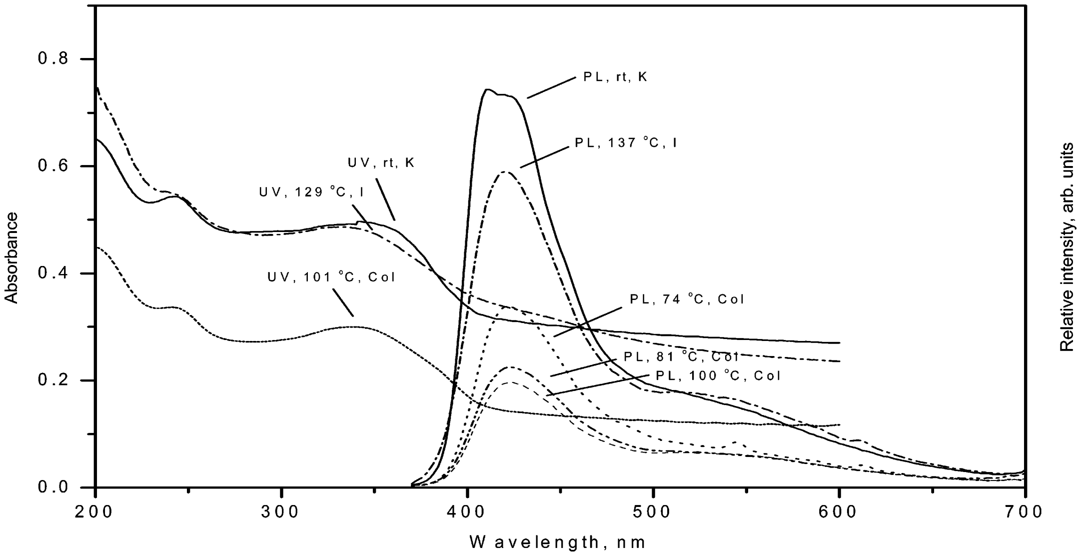

Figure 3. Absorption and fluorescence spectra of **3c** in its crystal, columnar, and isotropic phases.

crystal behavior of these compounds. As a hybrid of the multiaryl- and multiynyl-benzene, series **3** compounds exhibited a hexagonal columnar mesophase indicated by POM and XRD investigations. The spectroscopic studies of these compounds in different states revealed that molecular organization has little influence on the absorption maximum but caused a more pronounced spectral shift in emission spectra. In future work, application of the synthetic protocol onto other diarylbutadiyne systems will be explored and the mesogenic behavior as well as the spectroscopic properties of the subsequent products will be addressed.

Acknowledgment. This work was supported by a grant from the National Science Council of Taiwan (NSC 90-2113-M-032-010). Variable temperature XRD measurements were taken at the Synchrotron Radiation Research Center in Taiwan.

Supporting Information Available: Synthesis and spectroscopic data of **2a**–**2d** and **3a**–**3d** and ^{1}H and ^{13}C NMR spectra of **3a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM021727K