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Discotic Liquid Crystals: Synthesis and Characterization of Radial Polyalkynylbenzene Derivatives

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New radial polyalkynylbenzene derivatives, which consist of 4-phenylacetylene unit connected with a central phenyl or phenoxy or tolyl linking moiety, are presented. The mesomorphic properties of these compounds in their pure form and as donor–accepter (D–A) complexes with 2,4,7-trinitrofluoren-9-one (TNF) were investigated with polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) studies. The hexaalkynylbenzene derivatives in a pure form had a columnar mesophase texture, and pentaalkynylphenyl and pentaalkynyltoluene derivatives remained in a highly viscous liquid state even at room temperature, whereas D–A complexes showed a the columnar hexagonal ($\mathrm{Col_h}$) mesophase. The unexpected mesophase behavior of these radial polyalkynylbenzene derivatives comes from the molecular architecture arising from the branched aliphatic chain.

The six-fold Sonogashira coupling reaction of some terminal phenyl acetylene with a hexabromobenzene is known to form a new class of discotic liquid crystals (DLCs).[1] The penta- and hexaalkynylbenzene derivatives regularly show nematic mesophase that is not very common for DLCs. The synthesis of symmetrical and unsymmetrical polyalkynylbenzene derivatives has been reported. Due to the absence of long aliphatic chains, a mesophase was not found. Later, first liquid crystalline polyalkynylbenzene derivative has been reported by Kohne and Praefcke.[1b] Several penta- and hexaalkynylbenzene derivatives with aliphatic and branched aliphatic chains have been reported. They all show stable discotic nematic mesophase above and below room temperature.[2–4] A few penta- and hexakis(biphenylethynyl)benzene and naphthalene derivatives exhibiting discotic nematic and columnar mesophases at higher temperature have been reported.[5,6]

DLCs have many promising applications. In recent times. they have been found to form negative retardation film which enhances their viewing angle behavior that is an important part of twisted nematic liquid crystal display (TNLCD).[7] In the columnar mesophase, remarkable high charge carrier mobility ($0.71\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) has been reported, which is comparable to the amorphous silicon ($1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$).[8] It offers potential applications as an organic charge-transport material in different types of electronic devices, such as one-dimensional conductors, photovoltaic solar cells, field effect transistors, etc. The advantages of columnar mesophase of DLCs over inorganic material are easy alignment by external forces, such as shear and electrical field, their ability of self-healing, etc.[9–12]

DLCs consist of peripheral branched aliphatic chains connected with a central unit via different functional groups and often decrease the melting and clearing temperatures of the mesogens, but the phase behavior is often not affected.[13–15] The segregation of the peripheral aliphatic chains from the rigid aromatic cores is the main deriving force for their self-assembly.

Various intermolecular interactions are very effective for forming the mesophase morphology. In addition to the intermolecular forces, such as hydrogen bonding, dipole–dipole interactions, and charge-transfer interactions, and steric and ion-dipole interactions can import the phase formation and self-organization mechanisms at several length scales.[16] Investigation of charge-transfer interactions in binary mixtures of donor and acceptor has proven to be an effective tool to manipulate or induce liquid crystalline properties and already has been incorporated into self-assembled systems.[17] D–A complexes of disk-shaped molecules or discotic liquid crystals with TNF as an electron-acceptor moiety have been extensively studied to achieve the unexpected mesophase.[18] D–A complexes based on triphenylene or pentaalkynylbenzene derivatives displaying novel types of mesomorphic behavior have been reported.[18b] A variety of D–A complexes, such as composite form or a twin, in which donor moiety is connected with a acceptor moiety via a flexible spacer, has been prepared in different methods and their thermal behavior has been reported. The aim of this work was to study the effect of the branched aliphatic chain (specially the second carbon atom substituted) on the mesophase morphology of polyalkynylbenzene super-disk-based discotic liquid crystals. The particular focus was to synthesize these molecules, to prepare D–A complexes with TNF and to study the thermal properties.

Experimental

The synthesis of the new polyalkynylbenzene derivatives **5** was carried out in four steps starting from 4-bromophenyl (**1**) to 4-ethynylphenyl (**4**), followed by coupling with hexabromobenzene, or 1,2,3,4,5-pentabromo-6-(2-ethylhexyloxy)benzene or pentabromotoluene to achieve the target molecules. Hexabromobenzene

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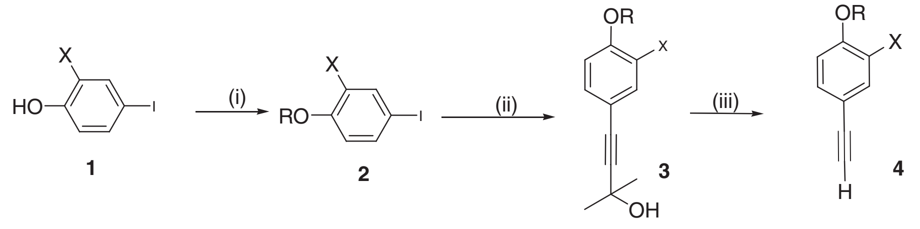
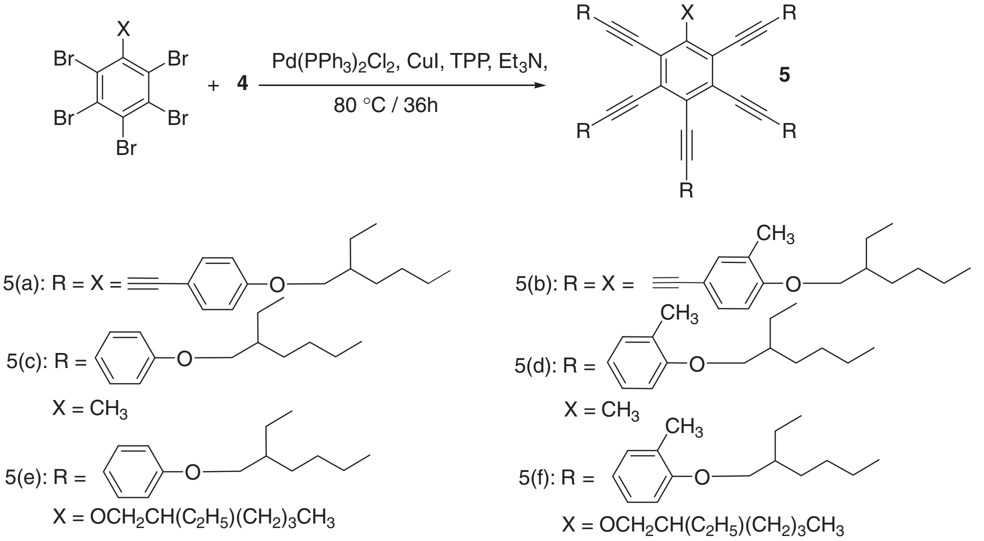


(a): R = $CH_2CH(C_2H_5)(CH_2)_3CH_3$, X = H
(b): R = $CH_2CH(C_2H_5)(CH_2)_3CH_3$, X = CH_3

Reagents and reaction conditions:
(i) $BrCH_2CH(C_2H_5)(CH_2)_3CH_3$, $CsCO_3$, MEK, 60 °C /20h
(ii) 2-methyl-3-butyne-2-ol, $Pd(PPh_3)_2Cl_2$, CuI, TPP, Et_3N, 80 °C /18h
(iii) KOH , PhMe, 110 °C / 2h

Scheme 1. The synthesis of phenylacetylenes.



Scheme 2. Synthesis of radial polyalkynylbenzene derivatives by Sonogashira coupling.

and pentabromotoluene were purchased from Aldrich (10-713-1) and Acros organic (344080250), respectively. 1,2,3,4,5-Pentabromo-6-(2-ethylhexyloxy)benzene was prepared by alkylation of pentabromophenol with 2-ethylhexyl bromide. The two key phenylacetylenes were prepared by using reported methods.[19] All of the derivatives of **5** had 2-ethylhexyl as a branched aliphatic chain. The TNF was prepared as reported earlier.[20] The preparation of the phenylacetylenes is as shown in Scheme 1.

All of the target molecules reporting here were synthesized by using a multifold Sonogashira cross-coupling reaction as shown in Scheme 2.

Results and Discussion

All of the derivatives showed an unexpected columnar mesophase. The hexaalkynylbenzene derivatives were solid at room temperature, whereas pentaalkynylbenzene and tolyl derivatives remained in a highly viscous liquid state.

Compound **5a** was yellow crystalline solid at room temperature and melted into a columnar mesophase at 78.3 °C (ΔH 47.8 J g^{-1}). On further heating, the mesophase clears to an isotropic liquid state at 231 °C (ΔH 4.1 J g^{-1}). Identical mesophase texture was observed on cooling at 189.2 °C (ΔH −2.8 J g^{-1}) (see Fig. 1a), and it crystallized at 63.7 °C (ΔH −4.3 J g^{-1}). Derivative **5b** was crystalline yellow solid, which melted into a columnar mesophase at 64.3 °C (ΔH 34.2 J g^{-1}), and converted into isotropic liquid phase at 199.9 °C (ΔH 2.9 J g^{-1}). On cooling, the columnar mesophase appeared at 188.7 °C (ΔH −1.7 J g^{-1}) with dendritic growth (see Fig. 1b). The texture remained unaltered even after several hours at ambient temperature.

The thermal stability of the mesophase was rather low. By heating the materials above 190 °C for few minutes, extended domains formed and the mesophase texture became surrounded by brown domains, which are indicative of material decomposition. Compound **5b** is relatively more stable than compound **5a**. The transition temperatures of the derivatives **5** are summarized in Table 1. According to the results of microscopic observations (Fig. 1), DSC data and literature, the mesophase was easily determined to be columnar mesophase. Finally, the mesophase was confirmed by X-ray analysis.

On cooling, the mesophase transition temperature was lower in the comparison to the heating transition, which could be due to the supramolecular assembly or the partial decomposition. Pure samples of phenoxy and tolyl derivatives **5c**–**5f** were highly viscous liquid at room temperature. POM study showed no birefringence on a plain glass plate, and no transition peak

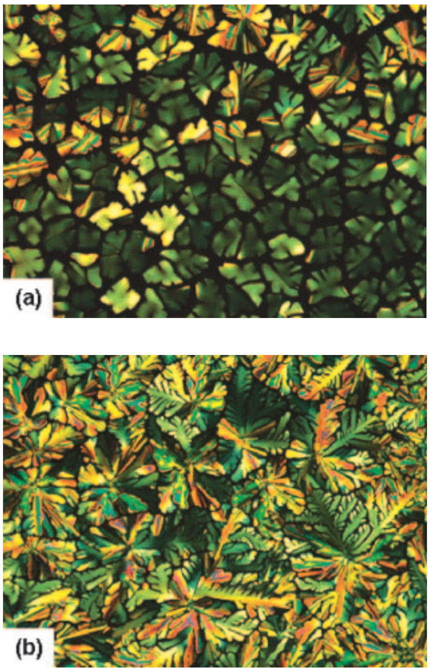


Fig. 1. Columnar mesophase textures observed by POM cooling from isotropic liquid: (a) **5a** at 156 °C (b) **5b** at 142 °C.

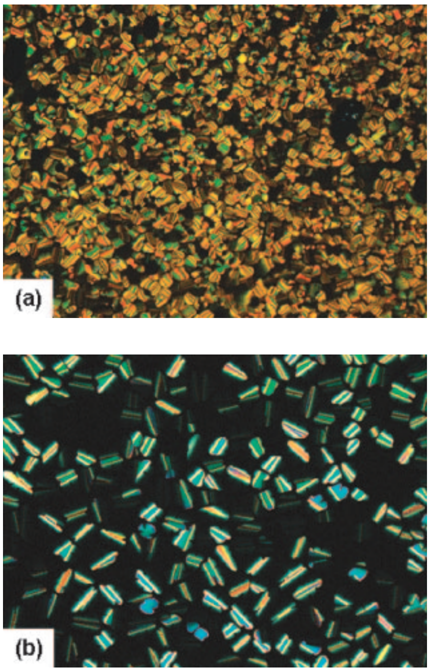


Fig. 2. Columnar hexagonal mesophase textures observed by POM: (a) **5e**/TNF at 43 °C, (b) **5f**/TNF at 83 °C. Both the images are taken on cooling from the isotropic liquid.

Table 1. Thermal Properties and X-ray Results of **5a**–**5f** and Their D–A Complexes with TNF

Compd[a]	Thermal behavior[b]	X-ray results/Å
		lattice parameter/stacking distance
5a	Cr 78.3 (47.8) Col 231 (4.1) I 189 (−2.8) Col 63.7 (−4.3) Cr	
5b	Cr 64.3 (34.2) Col 199.9 (2.9) I 188.7 (−1.7) Col[d]	
5c/TNF[c]	75–81 I 70 M	
5d/TNF[c]	81–92 I 83 $\mathrm{Col_h}$[d]	22.24/3.43
5e/TNF[c]	58–62 I 57 $\mathrm{Col_h}$[d]	19.34/3.46
5f/TNF[c]	110–160 I 150 $\mathrm{Col_h}$[d]	20.67/3.45

a) Molar ratio of TNF to is 1.0. b) Cr = crystal, Col = columnar, $\mathrm{Col_h}$ = columnar hexagonal, M = unidentified mesophase, I = isotropic. Phase-transition temperatures (°C) and the enthalpies ($\mathrm{J\,g^{-1}}$) in parentheses. c) Transition was observed by POM. d) No crystallization observed at ambient temperature.

was observed even in the DSC scans. The D–A complexes of tolyl derivative **5c** showed an unidentified mesophase at 70 °C on cooling, and it was assigned to be an M mesophase, whereas derivative **5d** showed a columnar hexagonal phase. The D–A complexes of phenoxy derivatives **5e**–**5f** shows the focal conic texture of the columnar hexagonal phase as shown in Fig. 2. The transition temperatures are summarized in Table 1. On cooling, the columnar phase that appeared, remained unchanged till room temperature. The mesophase texture remained unaltered even after several days. The D–A complexes of the tolyl derivatives show a broad isotropic transition. The results of these D–A complexes are in the initial stage of characterization, and some of them are still not fully understood. Detailed investigations on these compounds are necessary to determine their intricate order and to understand their induced phase behaviour.

XRD experiments were carried out on derivatives **5b** and on D–A complexes of **5c**, **5e**, and **5f**. Figure 3a shows a representative 2D diffraction pattern and 1D intensity vs. 2θ profile for the D–A complex of **5f**. A Sharp reflection in the low-angle region corresponds to the disc diameter (or inter-columnar distance, 20.67 Å).[21] In the wide-angle region two diffuse reflections were observed. The broad one corresponds to the liquid like order of the aliphatic chains, whereas the relatively sharper one observed at high 2θ values, which is well separated from the broad one, is due to the stacking of the aromatic cores in the columnar fashion (see Fig. 3b). The core–core distance is 3.45 Å. The fixed intra-columnar distance indicates the formation of an alternately stacked structure. Similar features of the D–A complexes of **5c** and **5e** (see Supporting Information) were observed. XRD results of pure compound **5b** showed a sharp reflection in low-angle region that indicate a 2D columnar lattice, whereas the wide-angle ring is very broad (see Supporting Information). We do not know the reason for this, but speculate that it could be due to the decomposition of the sample upon heating it to the isotropic phase. Thus, the X-ray results clearly indicate a columnar order of the aromatic cores, suggesting a columnar mesophase.

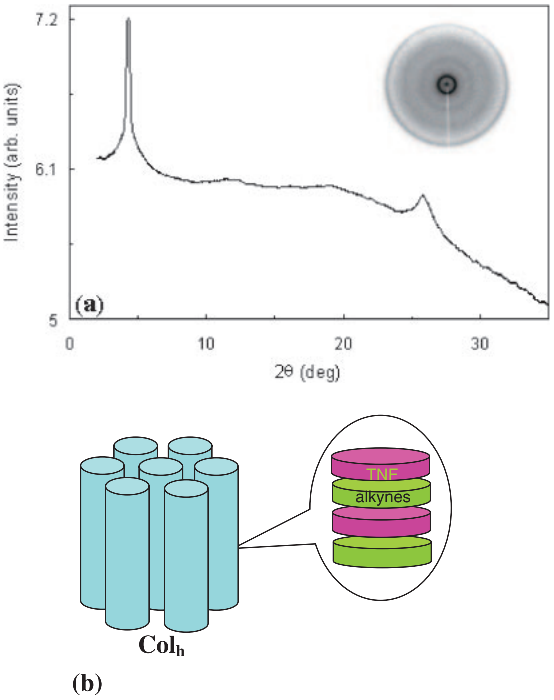


Fig. 3. (a) Image plate and intensity vs. 2θ profile of Col$_h$ phase of the complex of **5f** and TNF at 25 °C. (b) Illustrated of the molecular arrangements in the hexagonal columnar phase induced by D–A interactions.

The structure–property relationship of these derivatives is interesting in respect of mesomorphism. The non liquid-crystalline behavior of pentaalkyne derivatives having the first carbon atom substituted by chiral aliphatic chain attached ((*R*)- or (*S*)-1-methylheptyl group) to an oxygen heteroatom has been reported.[22] Whereas the hexa- and pentaalkyne having a third and seventh (3,7-dimethyloctane) carbon atom substituted by chiral or achiral chains showed a nematic mesophase.[3b,22] In each instance, the branch carbon atom substituted at first or third or fourth position away from the phenyl ring has been reported so far. The nematic mesophase behavior of (*S*)-2-methylbutane-substituted pentaalkyne has also been reported.[22] Compounds **5a** and **5b** showed a columnar mesophase above room temperature. Tolyl derivatives **5c** and **5d**, were less viscous liquid in pure state, whereas the D–A complexes showed Col$_h$ and M phase respectively. Phenoxy derivatives **5e** and **5f** were highly viscous liquid in pure state, and the D–A complexes showed a Col$_h$ mesophase at room temperature having a fixed molecular stacking distance.

Conclusion

In conclusion, we synthesized a series of novel radial polyalkynylbenzene derivatives exhibiting a hexagonal columnar mesophase. These new branched aliphatic chain substituted polyalkynylbenzene derivatives have higher melting and clearing temperatures. The aliphatic chain was substituted near or towards the phenyl ring. Thus, these results show that the second carbon atom substituted by branched aliphatic chain can change the molecular anisotropy and thermal properties. Further investigations of branching-effects with different heteroatoms and lateral substitution are in progress, and the mesomorphism will be revealed in due course. This approach to organic materials or "soft-materials," such as discotic liquid crystals, makes the induction of columnar hexagonal phase via D–A interactions of interest for technical applications.

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Supporting Information

Synthesis procedure, characterization of the compounds and XRD patterns of D–A complexes. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj.

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