

# Low-Temperature Discotic Nematic Superstructures

**A** new concept of replacing one sidearm of the discotic hexakis(4-hexyloxyphenylethynyl)benzene with a trisalkoxy-sidearm, 1-ethynyl-2,3,4-tris-hexyloxybenzene, for pursuing room-temperature discotic nematic materials was proposed and stepwise developed to accomplish effective improvements of discotic nematic properties, lowering transition temperatures, manipulations of discotic nematic ranges, and preserving the discotic nematic superstructure while avoiding column formation. By powder X-ray diffraction studies, detailed intermolecular correlations within the discotic nematic superstructure were obtained.

Disc-like molecules exhibiting a nematic mesophase have drawn much attention recently as materials in compensating films or as potential materials in the liquid crystal layer for improving viewing angle characteristics of liquid crystal displays. Compared to a mass number of calamitic nematogens, there are only a few disc-like molecules reported to show the discotic nematic ( $N_D$ ) phase. Often, disc-like molecules are prone to form columnar (Col) mesophases due to strong inter-disc interactions, e.g.  $\pi$ - $\pi$  interactions, from the planar core structures. For multiynyl compounds, however, the rotational freedom provided by the ethynyl linkers thwarts efficient stacking of the discs, and hence reduces the inter-disc attractions to prevent column formation. Unfortunately,  $N_D$  phases are usually accompanied with narrow mesophase ranges and high transition temperatures, especially high melting points. For practical applications, room-temperature  $N_D$  materials with reasonable ranges are to be achieved.

To obtain desired molecular superstructures, especially the discotic nematic packing motif, delicate balance of complex intermolecular interactions is necessary. Increasing intermolecular attractions on the periphery rather than the whole disc should lead to a wider range of the  $N_D$  superstructure while the column formation can be avoided. Lateral substitutions have been utilized in calamitic mesogens to favour the formation of the nematic phase, to depress lamellar structures, and more importantly, to significantly lower the transition temperatures. However, only a few examples have been reported for discotic systems with lateral substitutions. In this context, an effective way to achieve low-temperature and stable  $N_D$  materials are presented by installing one laterally substituted sidearm onto a hexaynylbenzene core. The aforementioned restricted rotation of the laterally substituted sidearm should enhance  $\pi$ - $\pi$  interactions

## Beamline

17A1 X-ray Powder Diffraction

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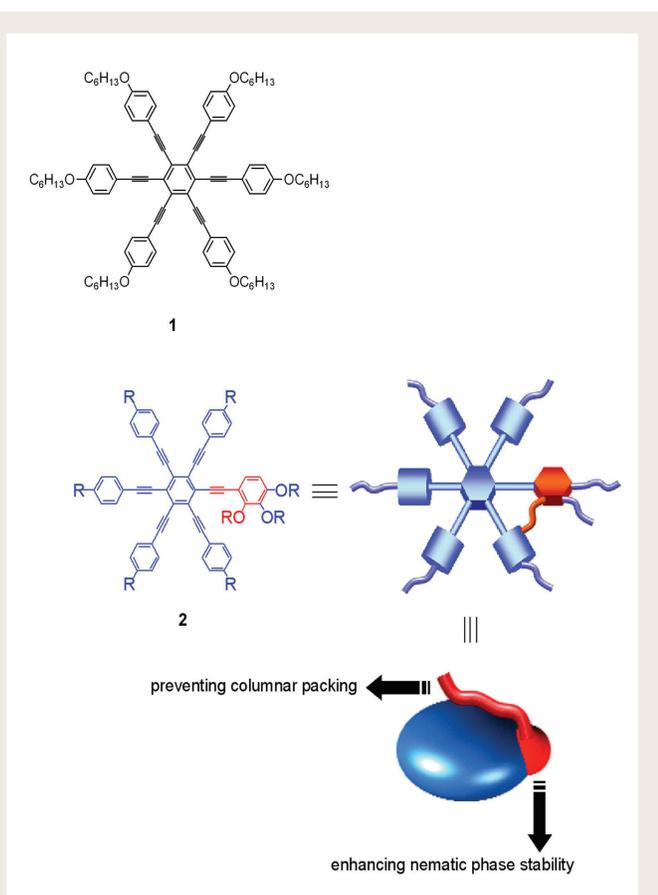
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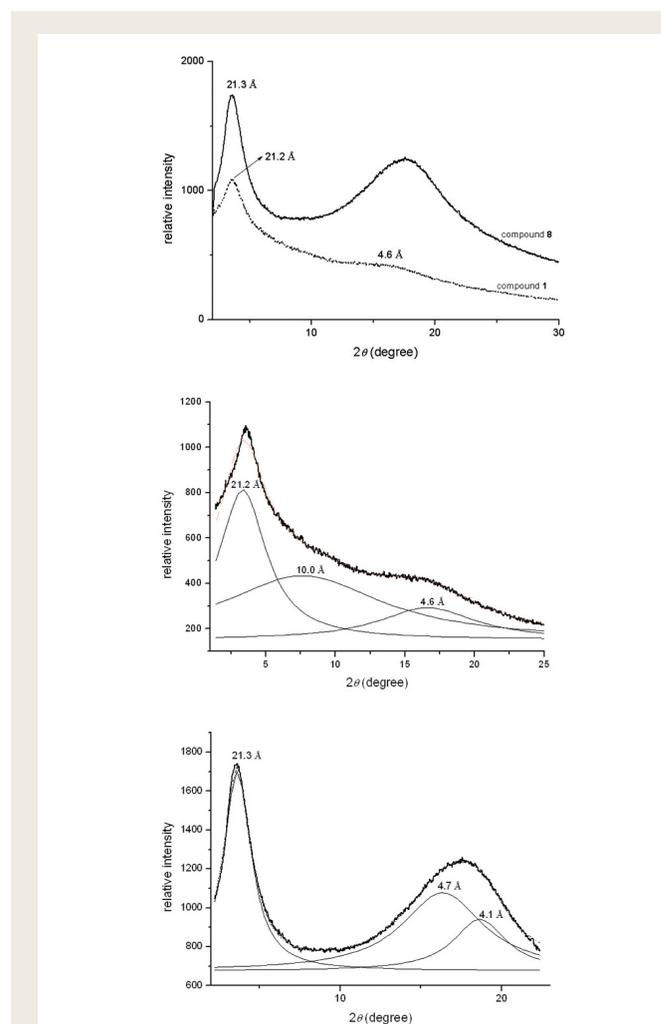
on the periphery of the disc to stabilize the existing  $N_D$  phase. On the other hand, the protrusion of the introduced lateral substitution off the disc plane should avoid column formation by preventing face-to-face packing motifs. Furthermore, lateral substitution in the peripheral phenyl rings *ortho* to the ethynyl group should lead to significantly lowered transition temperatures.

A series of discotic hexaynylbenzene compounds with a laterally substituted sidearm were synthesized (Figure 1). A discotic nematic mesophase was observed for these discotic compounds by polarized optical microscopy and differential scanning calorimetry. The identity of the nematic phase of these compounds was detailed by powder X-ray investigations. Diffractograms of the mesophases of compounds **1** and **2** are shown in Fig. 2 The diffraction pattern of the discotic nematic phase of **1** shows one distinct reflection in the small angle regime, one very broad halo in the mid-angle range, and one halo in the wide angle area. The halo in the mid-angle range was confirmed by fitting with Lorentzian profiles. The calculated d-spacing of 21.2 Å for the reflection in the small angle region approximates the diameter of the discotic unit, 19.30 Å. The spacing of the wide angle halo is calculated to be 4.6 Å which is attributed to the liquid-like correlation of the molten chains.



**Fig. 1:** Structures of compounds **1** and **2** with a laterally substituted sidearm to prevent columnar packing and enhance discotic nematic phase stability.

The reflection in the mid-angle range corresponds to a distance of 10.0 Å. A similar signal was also reported for its analog with heptyl chains, however, its origin is not clear. For compound **2**, two distinct reflections in the small and wide angle ranges are recognized. The mid-angle reflection of **1** is not identifiable for compound **8** with Lorentzian fitting profiles. The small angle reflection of **2** corresponding to 21.3 Å is similar to that of **1**. The maximum of the halo in the wide angle range of **2** is apparently shifted to the large angle direction with respect to that of **1**. However, the single maximum Lorentzian fitting of this signal reveals its unsymmetrical shape with a shoulder at its wider angle side. It can be analyzed to show splitting into two maxima with a better Lorentzian fitting ( $R^2 = 0.9951$ ). Calculated d-spacings of the two best fitted peaks are 4.7 and 4.1 Å, corresponding to the chain correlation and the interdisc correlation for somewhat aggregated discs respectively. The fact that the reflection at 4.1 Å is detected for compound **2** but is unattainable for compound **1** indicates that the



**Fig. 2:** Top: Powder X-ray diffraction patterns of compound **1** at 200°C upon heating and compound **2** at 100°C upon cooling. Middle: Lorentzian fittings of the diffractogram of compound **1** at 200°C upon heating. Bottom: Lorentzian fittings of the diffractogram of compound **2** at 100°C upon cooling

structural modification of attaching two lateral chains on to a peripheral phenyl ring has probably induced a moderate aggregation of the hexaynylbenzene discs.

The degree of order within the mesophase, the correlation length, was calculated using Scherrer's equation  $l = 0.89\lambda/(w_{1/2}\cos\theta)$ . Here,  $\lambda$  is the wavelength of the incident X-ray beam,  $w_{1/2}$  is the full-width at half-maximum of the reflection, and  $\theta$  is the maximum of the reflection. Both  $w_{1/2}$  and  $\theta$  can be obtained by Lorentzian fitting of the diffraction pattern. For compound **1**, the correlation lengths for the reflections at 21.2 and 4.6 Å are calculated to be 17 and 8 Å respectively. For compound **2**, the correlation lengths for reflections of 21.3, 4.7, and 4.1 Å are of 33, 11, and 17 Å respectively. For both compounds, the correlation lengths of the small and wide angle regimes are comparable with those reported for the discotic nematic mesophase and are significantly smaller than those of the columnar nematic mesophase. However, it is clear that the correlation lengths of reflections at 21.3 and 4.7 Å for **2** are significantly larger than those of corresponding signals of **1**. The almost doubled correlation length of the small angle signal of **2** indicates higher degree of order along the direction perpendicular to the disc normal. For the halo at ~4.6 Å, although the added chains are laterally attached in compound **2**, the side-chain correlation of **2** is higher than that of **1**. Absent for compound **1**, the signal at 4.1 Å of **2** may point to the attraction along the direction parallel to the disc normal within the aggregated ensembles. The correlation length of 17 Å is approximately four disc thicknesses if the discs are stacked to avoid the lateral side chains and roughly three disc thicknesses if disc thickness is estimated including the lateral side chains. Herein, aggregation of discs may imply attractions along the direction parallel to the disc normal. In sum, relative to compound **1**, structural modification of attaching two lateral chains onto one peripheral phenyl ring as in compound **2** has induced not only higher correlation of the chains but also higher degree of order both parallel and perpendicular to the disc normal.

In conclusion, a new concept of replacing one sidearm of the discotic hexakis(4-hexyloxyphenyl)ethynyl)benzene with a trisalkoxy-sidearm, 1-ethynyl-2,3,4-trishexyloxybenzene, was proposed and stepwise developed to accomplish effective improvements of discotic nematic properties, i.e. lowering transition temperatures, manipulations of  $N_D$  ranges, and preserving the discotic nematic superstructure while avoiding column formation. The intermolecular correlations within the discotic nematic superstructures were investigated by powder X-ray diffraction studies. Employing the new concept to other  $N_D$  systems is under investigation. ■

### Experimental Station

X-ray powder diffraction end station

### Publications

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- L.-L. Lai, C.-H. Lee, L.-Y. Wang, K.-L. Cheng, and H.-F. Hsu, *J. Org. Chem.*, **73**, 485 (2008).

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