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Star-shaped discotic nematic liquid crystal containing 1,3,5-triethynylbenzene and oxadiazole-based rigid arms

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Abstract—A novel three-armed discotic liquid crystal based on 1,3,5-triethynylbenzene as a core and 2,5-diphenyloxadiazole as rigid arms has been synthesized, which is the first star-shaped molecule exhibiting a discotic nematic phase.

Discotic liquid crystals (LCs) have been a research subject of great interest from theoretical and practical viewpoints since their discovery.[1] LC assembly of disk-like molecules is influenced not only by the mesogenic shape anisotropy, but also by the inter-core interaction along the disk normal. Because the conventional discogenic cores are usually very flat structures consisting of π-electron-rich aromatic rings[2] with strong inter-core interaction, the columnar phase is normally predominant over nematic phase for discotic LCs. Actually, there are only a limited number of reported examples for discotic nematic phase including derivatives of triphenylene,[3,4] naphthalene,[5] hexa- and penta-alkynyl benzene.[2] Due to the higher viscosity and multidomain scattering of columnar phase, nematic phase is often preferred for the electrooptic application of discotic LCs. Considering that the reduced inter-core interaction is necessary for the nematic phase, discotic LCs with smaller core seem to be an appropriate candidate for this purpose. Recently, three-armed, planar star molecules composed of small polar core have been reported to exhibit discotic LC phases.[6] These nonconventional discotic LCs, however, tended to form columnar phase rather than discotic nematic phase due to the polar inter-core interaction along the disk normal. In this contribution, we present the first report on discotic nematic phase in a C_{3h}-symmetric star molecule with unusual shape of a small core and three extended rigid arms.

Scheme 1 shows the structure and synthetic routes of a discotic LC studied in this work, which are characterized by 1,3,5-triethynylbenzene unit linked with 2,5-diphenyloxadiazoles. The synthesis followed the general methodology of oxadiazole preparation and palladium-catalyzed ethynylation. 4-Hydroxy ethylbenzoate was alkylated with 1-bromohexane, followed by the hydrolysis of ester and conversion into the corresponding acyl chloride (**1**), which were subsequently reacted with 5-fold hydrazine monohydrate to give phenyl hydrazide (**2**). The obtained compound **2** was reacted with 4-bromobenzoyl chloride, followed by dehydration in $POCl_3$ to form oxadiazole ring (**3**). 1,3,5-Triethynylbenzene (**4**) prepared by literature procedure[7] was reacted with compound **3** through palladium-catalyzed coupling and we could get the desired star-shaped molecule containing oxadiazole moiety in the middle of its arms in good yield (54%). Final product **5** was isolated using column chromatography on silica gel and successive reprecipitation in *n*-hexane was performed for high purity. Compounds **5** showed good solubility in common organic solvent. The key compounds **3** and **5** were carefully identified by ^{1}H NMR and MALDI-TOF mass spectroscopy.[8]

The thermal behavior of **5** was checked by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). As summarized in Table 1, **5** showed crystal to LC phase transition at 189°C and LC to isotropic phase transition at 200°C in the heating trace. In the subsequent cooling cycle, however, isotropic to LC phase transition with very small enthalpy change (–0.1 J g^{-1}) was only observed with no further changes down to room tem-

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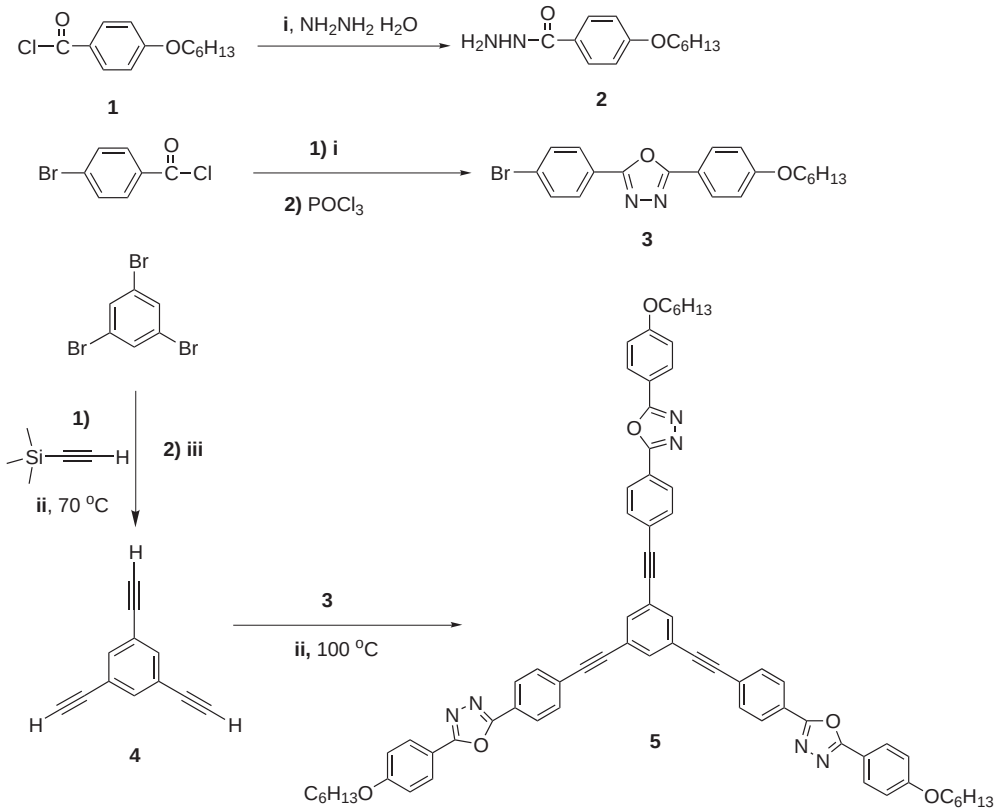

Scheme 1. Reagents and conditions; (i) THF, triethylamine, 0°C; (ii) triethylamine, CuI, $PdCl_2(PPh_3)_2$, PPh_3; (iii) K_2CO_3, methanol, room temperature.

perature. In this LC state, Schlieren texture, typical of nematic phase, was observed between the crossed polarizer as shown in Fig. 1. The X-ray diffractogram of **5** taken at 140°C showed two diffuse haloes corresponding to spacing of 44–35 Å and 6.3–5.0 Å, attributable to the lateral and vertical disk-to-disk distances of discotic nematic phase, respectively. To our best knowledge, this is the first observation of a discotic nematic phase in three-armed small-core discotic LCs. The driving force for the nematic phase can be found in the peculiar molecular shape of **5**, that is, fairly long rigid arms comparable to the calamitic mesogen in C_{3h} symmetry. Since these linearly elongated arms are attached to a small nonpolar core, i.e. triethynylbenzene, large free space favorable to arm-to-arm interaction between neighboring molecules exists. In addition to the appropriate arm-to-arm interaction, the negligible core-to-core interaction between small nonpolar cores seems to be an important factor for the formation of discotic nematic assembly rather than columnar stacking in **5**.

Table 1. Phase transitions of star-shaped discotic liquid crystal containing 1,3,5-triethynylbenzene unit linked with 2,3-diphenyloxadiazoles[a]

Compound	T/°C (ΔH/J g^{-1})	
	Heating	Cooling
5	1st heating, K_1 125 (−2.7), K_2 189, N_D 200 I[b] 2nd heating, FN 127 (−10.8) K 190, N_D 200 I[b]	I 149 (−0.1), N_D 110 FN[c]

K, crystalline phase; N_D, discotic nematic mesophase; I, isotropic liquid; FN, frozen nematic state.

[a] Transition temperatures and enthalpies were determined by DSC (scan rate, 10°Cmin^{-1}).

[b] Enthalpy change could not be determined due to the peak overlap.

[c] Transition observed only by POM.

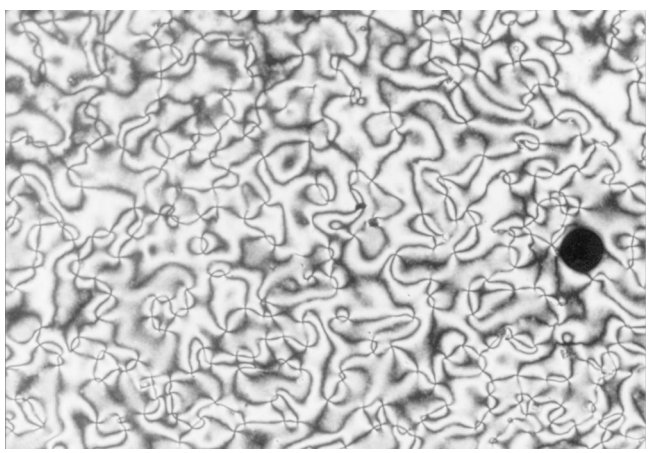

Figure 1. Polarized optical microscopic image of discotic mesogen (Table 1).

Actually, it should be noted that the lateral disk-to-disk distance in the nematic phase (44–35 Å) is much smaller than the fully extended disk diameter (46 Å) calculated by molecular mechanics. This result suggests that the hexyloxy groups attached to the end of rigid arms would be interdigitated to some extent. Another interesting point is that below 110°C fluidity of nematic phase disappeared with a subtle change of optical texture. Because the room temperature XRD pattern is identical to that taken at 140°C, it can be mentioned that the nematic phase was frozen due to the high viscosity before crystallization. This meta-stable frozen nematic state is transformed to the thermodynamically stable crystalline phase by reheating as summarized in Table 1.

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8. Compound **3**: yield 56%, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.03 (d, 2H), 8.01 (d, 2H), 7.01 (d, 2H), 7.67 (d, 2H), 4.04 (t, 2H); Compound **4**: yield 54%, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.15 (d, 6H), 8.08 (d, 6H), 7.75 (s, 3H), 7.69 (d, 6H), 7.04 (d, 6H), 4.05 (t, 6H); MALDI-TOF (reflector, positive) m/z 1112.