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Discotic liquid crystalline materials for potential nonlinear optical applications: synthesis and liquid crystalline behavior of 1,3,5-triphenyl-2,4,6-triazine derivatives containing achiral and chiral alkyl chains at the periphery ☆

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Abstract—As a novel approach to nonlinear optical materials, new octupolar discotic liquid crystalline materials 1,3,5-triphenyl-2,4,6-triazine derivatives containing achiral alkyl chains (**5a**) and chiral alkyl chains (**5b**) at the periphery were synthesized. The former exhibits an ordered hexagonal columnar mesophase, whereas the latter displays a rectangular columnar mesophase. The negative exciton splitting observed in the CD spectrum of a thin film of **5b** suggests that it has a left-handed helical structure within the column.

In conjunction with developing nonlinear optical (NLO) materials for optoelectronics and photonics, there has been growing interest in the second order nonlinear optical properties of octupolar molecules in recent years.[1] Octupolar NLO molecules have several advantages over traditional dipolar NLO molecules. First, dipolar molecules have the strong tendency to adopt centrosymmetric packing in the solid states nullifying bulk nonlinearity whereas octupolar molecules lacking permanent dipole moments have better chances to adopt noncentrosymmetric packing. Second, the β value of a dipolar molecule increases to a maximum value and then decreases as the bond-length alternation increases, whereas that of an octupolar molecule increases steadily as the extent of the charge transfer increases,[2] which provides a firm basis for designing NLO molecules with large β values. For the last decade, therefore, considerable research efforts have been focused on the design and synthesis of octupolar molecules with large β values, and a number of organic and metal-organic octupolar molecules whose β values match those of the best-known dipolar NLO chromophores have been reported.[3] The biggest challenge is however the macroscopic organization of such octupolar molecules in a noncentrosymmetric environment leading to large bulk second order NLO properties. Building noncentrosymmetric octupolar networks in crystalline solids using weak intermolecular interactions,[4] and orientation of octupolar chromophores in polymers or sol–gel matrices using all optical poling[5] have been attempted with only a moderate success. Our long interests in NLO materials[6] and liquid crystalline materials[7] led us to take a novel approach to this problem, which involves the synthesis of a discotic liquid crystalline material comprising a flat, octupolar chromophore as a core and long, chiral alkyl tails at the periphery, which lead to a helical columnar structure.[8] We anticipated that such octupolar discotic liquid crystalline materials with noncentrosymmetric structures may have large bulk second order NLO properties because Langmuir–Blodgett films composed

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Keywords: Nonlinear optical materials; Discotic liquid crystals; Left-handed helix.

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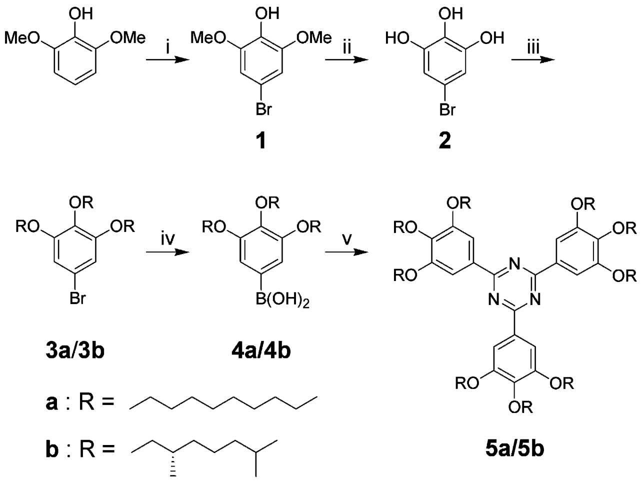
of a supramolecular array of a chiral helicene had been reported to show highly enhanced NLO properties.[9] We chose the octupolar molecule 1,3,5-triphenyl-2,4,6-triazine as a discotic mesogen because the NLO properties of its derivatives have been well studied.[10] Here we report the synthesis of a novel discotic liquid crystalline material derived from 1,3,5-triphenyl-2,4,6-triazine that displays a rectangular columnar phase in which the molecules are stacked along the columns with a left-handed helical structure.[11]

The 1,3,5-triphenyl-2,4,6-triazine derivative **5a** having achiral alkyl chains at the periphery was synthesized in five steps (Scheme 1). 3,4,5-Trihydroxy-1-bromobenzene **2** was prepared in two steps from commercially available 2,6-dimethoxyphenol: bromination[12] followed by deprotection of the methyl groups gave **2** in 64% yield. Alkylation of **2** with bromoalkane in DMF in the presence of potassium carbonate and a catalytic amount of potassium iodide produced **3a** in 81% yield. Lithiation of **3a** with *tert*-butyl lithium at −78 °C followed by treating with trimethyl borate and 3 N HCl gave aryl boronic acid **4a**.[13] Finally, the Suzuki-coupling reaction of **4a** and cyanuric chloride in toluene using Pd(PPh$_3$)$_4$ as the catalyst yielded **5a** in 52% yield.[14,15]

The synthesis of 1,3,5-triphenyl-2,4,6-triazine derivative **5b** having chiral alkyl chains at the periphery was carried out similarly. Hydrogenation of (*S*)(−)-β-citronellol with 10% Pd/C in dry ethyl acetate followed by bromination gave (3*S*)-1-bromo-3,7-dimethyloctane,[16] which was then reacted with **2** to yield **3b** in 79% yield. The conversion of **3b** to its boronic acid derivative **4b** was achieved by lithiation with *tert*-butyl lithium followed by treating with trimethyl borate. The Suzuki-coupling reaction of **4b** with cyanuric chloride gave **5b** in 33% yield.[17]



Scheme 1. Reagents and conditions: (i) NaH, NBS, CHCl$_3$, −45 °C; (ii) BBr$_3$, MC, rt; (iii) RBr, K$_2$CO$_3$, KI, DMF, reflux; (iv) *t*-BuLi, B(OMe)$_3$, THF, −78 °C; (v) C$_3$N$_3$Cl$_3$, Na$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene, reflux.

Both **5a** and **5b** show enantiotropic liquid crystalline behavior as revealed by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Their phase behavior is summarized in Table 1. Compound **5a** exhibits a mesophase from 36 to 145 °C on heating and from 145 to 26 °C on cooling, whereas **5b** shows a mesophase from −15 to 56 °C on heating and below 41 °C on cooling. For the latter, the transition from mesophase to crystalline phase on cooling was not observed down to −20 °C. Compared to **5a**, **5b** exhibits not only much lower phase transition temperatures but also much smaller enthalpy changes associated with the phase transitions, which is probably due to the loose packing of the branched alkyl chains in the latter. The POM image of **5a** in mesophase reveals a pseudo-focal conic texture (Fig. 1a), which is characteristic of hexagonal columnar phases, whereas that of **5b** shows a dendritic texture, which is often observed in rectangular columnar phase (Fig. 1b).[18]

To obtain more information on the structures of **5a** and **5b** in mesophase X-ray diffraction (XRD) studies were carried out using synchrotron radiation. The X-ray pattern of the mesophase of **5a** taken at 80 °C displays a strong peak and a weak peak in the small-angle region with reciprocal Bragg spacings in a ratio of $1{:}\sqrt{3}$. These peaks were assigned to the (100) and (110) reflections of a hexagonal arrangement with a lattice constant $a = 28.0$ Å. The lattice parameter decreases with increasing temperature as usual. On the other hand, the X-ray pattern of **5b** taken at room temperature shows three peaks at 23.1, 20.7, and 11.6 Å, which were assigned to the (200), (110), and (020) reflections, respectively, of a rectangular columnar structure with lattice parameters of $a = 46.4$ Å and $b = 23.1$ Å[8b] (Table 2).

The effect of the chiral alkyl tails attached to the core on the structure of **5b** in the mesophase was investigated by CD spectroscopy. First of all, the UV spectra of thin films of **5a** and **5b** are essentially identical with a broad absorption at 318 nm (Fig. 2), which confirms that the alkyl tails do not affect the absorption of the triazine core in **5a** and **5b**. Most importantly, the CD spectrum of a thin film of **5a** is featureless whereas that of **5b** exhibits strong circular dichroism (Fig. 2) with a negative exciton splitting centered around 318 nm, which

Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) of **5a** and **5b**[a]

Compound	Heating	Cooling
5a	K 35.6 (15.6) Col$_{hd}$ 145.3 (1.66) I	I 144.7 (1.05) Col$_{hd}$ 25.7 (15.7) K
5b	K −15.2 (2.45) *Col$_r$ 55.8 (0.40) I	I 41.5 (0.56) *Col$_r$

[a] K = crystalline phase; Col$_{hd}$ = hexagonal columnar mesophase; I = isotropic phase.

*Col$_r$ = chiral rectangular columnar mesophase.

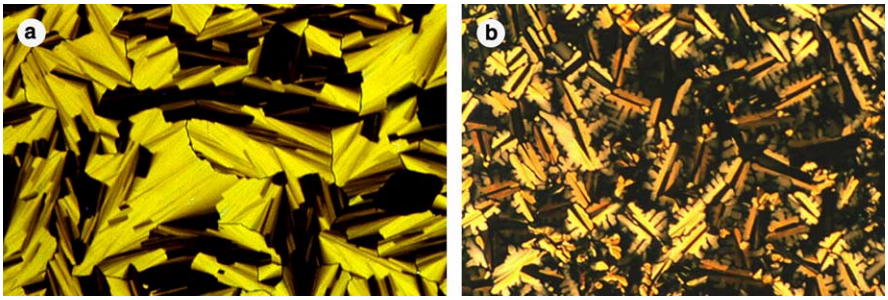


Figure 1. Polarized optical micrograph (×160) of (a) **5a** at 88 °C and (b) **5b** at rt.

Table 2. X-ray diffraction data for **5a** and **5b** (lattice constants, measured and calculated lattice spacings, and proposed indexing)

Compound	*T* (°C)	Lattice constants (Å)	q^{a} (nm^{-1})	d_{obs}^{b} (Å)	d_{cal} (Å)	*hkl*
5a	80	$a = 28.0$	2.59	24.2	24.3	100
			4.53	13.9	13.9	110
5b	rt	$a = 46.4$	2.72	23.1	23.1	200
		$b = 23.1$	3.03	20.7	20.7	110
			5.44	11.6	11.6	020

[a] $q = 4\pi \sin\theta/\lambda$, $\lambda = 1.54019$ Å.
[b] $d = 2\pi/q$.

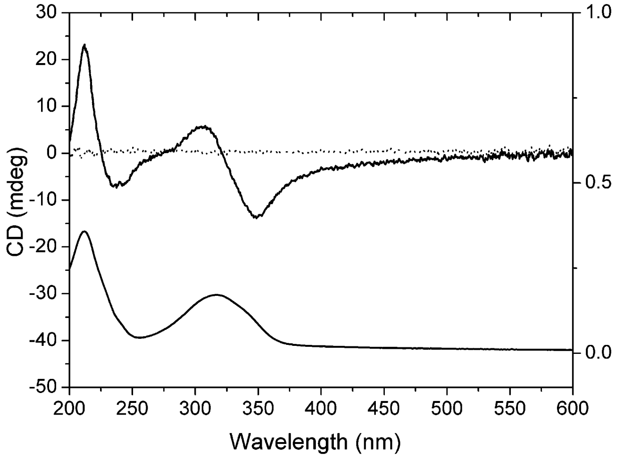


Figure 2. CD (top, scale at left) and UV–vis absorption spectra (bottom, scale at right) of thin films of **5a** (dot) and **5b** (solid) deposited on a quartz substrate by spin coating.

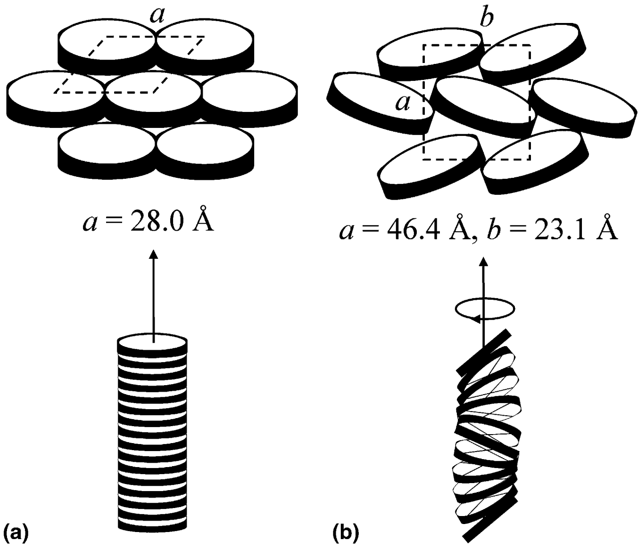


Figure 3. Schematic representations of (a) the hexagonal columnar mesophase of **5a** and (b) the rectangular columnar mesophase with a left-handed helix of **5b**. The illustrations are idealized; the discs may be laterally shifted toward each other and may not have the same distance.

suggests that the discotic molecules are stacked along the column, while tilted with respect to the column axis, to form a left-handed helix within the column (Fig. 3b).[19] No circular dichroism observed with a solution of **5b**, and the decreasing circular dichroism of a film of **5b** with increasing temperature support that the optical activity of **5b** is not derived from the stereogenic center of the chiral alkyl tails, but from the helical arrangement of the molecules induced by the chiral alkyl tails.[20]

In summary, as part of a novel approach to organizing octupolar molecules in a noncentrosymmetric environment, we designed and synthesized a new octupolar discotic liquid crystalline material, 1,3,5-triphenyl-2,4,6-triazine derivative (**5b**) containing chiral alkyl chains at the periphery, which displays a rectangular columnar mesophase. Furthermore, the negative exciton splitting observed in the CD spectrum of a thin film of **5b** suggests that it has a left-handed helical structure within the column. The noncentrosymmetric arrangement of **5b** in the liquid crystalline film should result in nonzero bulk second order NLO properties, which are currently being investigated. With the expected NLO properties as well as the liquid crystalline behavior at room temperature **5b** may find useful applications in optoelectronics and photonics.

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15. Compound **5a**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.98 (s, 6H), 4.07–4.18 (m, 18H), 1.77–1.93 (m, 18H), 1.50–1.54 (m, 18H), 1.28 (m, 108H), 0.88 (m, 27H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 171.1, 153.4, 142.6, 131.2, 107.7, 73.8, 69.4, 32.2, 30.6, 29.9, 29.8, 29.7, 29.6, 26.4, 26.3, 22.9, 14.3; MS (FAB): *m/z* [M+H$^+$] 1715.0. Anal. Calcd for $C_{111}H_{195}O_9N_3$: C, 77.70; H, 11.46; N, 2.45. Found: C, 77.89; H, 11.25; N, 2.48.
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17. Compound **5b**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.99 (s, 6H), 4.04–4.25 (m, 18H), 1.92–1.96 (m, 9H), 1.60–1.86 (m, 9H), 1.50–1.63 (m, 18H), 1.29–1.35 (m, 27H), 1.15–1.24 (m, 27H), 0.93–0.99 (m, 27H), 0.85–0.88 (m, 54H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.22, 153.42, 142.57, 131.23, 107.61, 72.10, 67.58, 39.61, 39.52, 37.76, 37.62, 36.68, 30.14, 29.93, 28.23, 25.02, 24.96, 22.92, 22.82, 19.83; MS (FAB): *m/z* [M+H$^+$] 1715.8. Anal. Calcd for $C_{111}H_{195}O_9N_3$: C, 77.70; H, 11.46; N, 2.45. Found: C, 77.28; H, 11.48; N, 2.45.
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