

Nonlinear Optical Thin Film Device from a Chiral Octopolar Phenylacetylene Liquid Crystal

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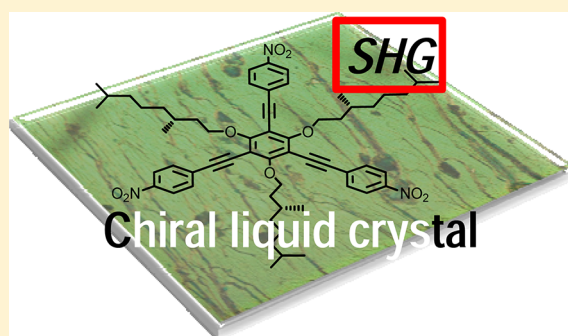
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S Supporting Information

ABSTRACT: A set of chiral discotic phenylacetylenes have been synthesized by 3-fold Sonogashira coupling between different ethynylbenzenes and triiodobenzenes. The resultant bulk materials are fully characterized by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction. The octopolar nature of the target compounds is studied by UV–vis absorption spectroscopy and hyper-Raleigh scattering in solution. Optimization of the donor–acceptor substitution yields both high hyperpolarizability values and appreciable mesomorphic properties. A simple thin film device for second harmonic generation has been prepared from the nitro-substituted liquid crystalline derivative.



1. INTRODUCTION

Organic materials for second-order nonlinear optics (NLO) and photonics remain in the focus of interest in material science.¹ Absence of centrosymmetry is a fundamental requirement for second-order NLO effects to occur. During the past decade a great deal of effort has been invested in the design of chromophores that favor the non-centrosymmetric alignment on the macroscopic scale.² Supramolecular engineering of organic and organometallic systems with non-dipolar symmetry has shown outstanding results in nonlinear optics.^{3,4} The spontaneous induction of polar order in the crystalline and liquid crystalline phase has been recently observed in NLO materials based on octopolar chromophores.^{5,6} The preparation of bulk materials by self-assembly of molecular units into ordered liquid crystal (LC) phases is an extremely useful concept that has been utilized to prepare organic thin film devices earlier on.⁷ The molecular shape and dimensionality of organic octopoles favors their controlled self-assembly and thus allows for the preparation of NLO-active thin film devices.⁸ The general scheme for the design of discotic liquid crystals is guided by the following considerations: a polarizable aromatic nucleus surrounded by apolar lipophilic alkyl chains leads to nanometric phase segregation. Solvophobic and π -stacking interactions are responsible for both two-dimensional mobility of the mesogenic molecules at the same time as 3D macroscopic orientational order in the bulk material. Densely functionalized low molecular weight systems such as benzene- or triazine-based mesogens typically present low aspect ratios, which favors their self-assembly into columnar stacks.⁹ The

right choice of the terminal end groups allows for controlling the intramolecular charge-transfer character of the π -systems, their polarizability, and thus the supramolecular order in the bulk.¹⁰ As a further structural element, chirality as imparted by homochiral substituents on the molecular scaffold should be efficiently transferred to the macroscopic level and thus contributes to the microstructuring of the final bulk material. The use of inherently chiral mesogens results in the formation of chiral discotic nematic LC phases as recently reviewed.¹¹ Instead of relying on the spontaneous induction of polar order in chiral domains,¹² the introduction of chirality in the supramolecular material leads predictably to non-centrosymmetric order in the bulk.¹³ This idea has been applied recently by Cui and co-workers in the construction of NLO-active metal–organic frameworks based on chiral building blocks with octopolar symmetry.¹⁴

2. RESULTS AND DISCUSSION

2.1. Synthesis. In this work we present a set of C_3 -symmetric alkynylbenzenes with different substituents at the terminal phenyl rings and with an electron-rich central benzene core carrying electron-donor alkoxy chains. In order to achieve high molecular susceptibilities, i.e., β -values, the molecular design follows the same deliberations that lead to the desired LC properties. The electronic nature of the central benzene core is complemented by the peripheral *p*-phenylethynyl

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Scheme 1. Synthesis of Chiral Octopolar Trisalkynylbenzenes 1–4

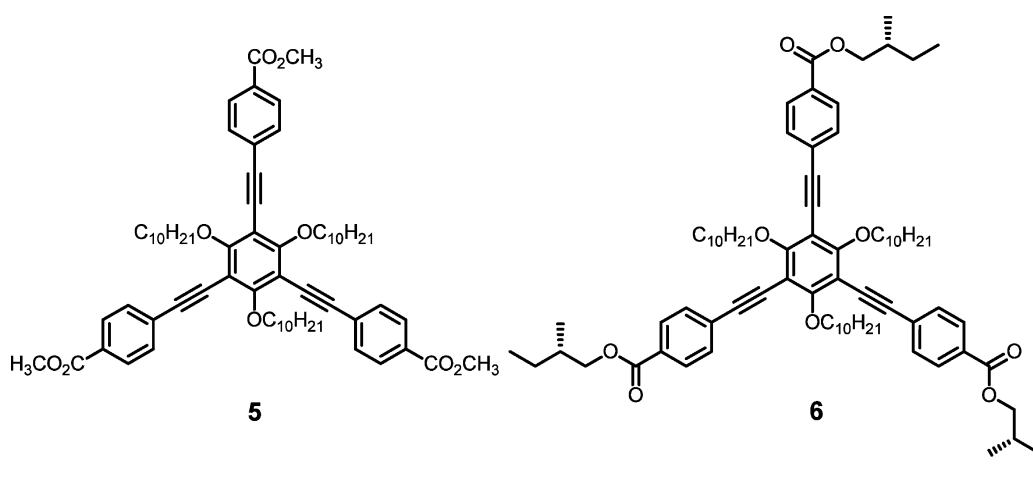
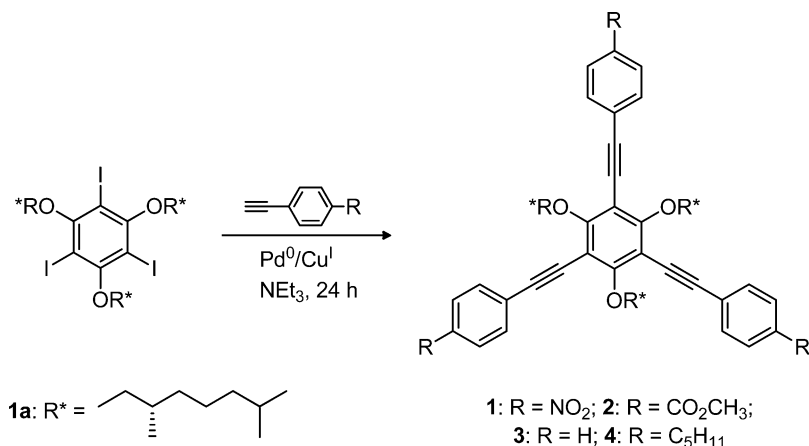


Figure 1. Discotics 5 and 6.

fragments of variable electronic nature. The polarizability of the π -extended disk-shaped molecules depends on the balance of the donor–acceptor character of the lateral and central aryl moieties.¹⁵ Therefore, the NLO and mesomorphic properties of the organic material is affected likewise. The synthesis of the chiral discotics 1–4 follows a similar procedure as described previously for achiral LC analogues.¹⁶ The functionalization of 1,3,5-trifluoro-2,4,6-triodobenzene with chiral dimethyloctanoate is followed by a 3-fold Sonogashira coupling of the triioderivative with the corresponding *p*-phenylacetylenes to give the chiral discotic target compounds 1–4 (scheme 1). The obtained final yields are moderate yet very reasonable for a 3-fold coupling step.

In this work we also include a series of different ester end-capped octopoles and study their mesomorphic properties. Here, the nature and position of the homochiral substituents is varied to examine the influence of the structural changes in the molecular building blocks on the macroscopic properties of the resulting materials. The preparation of the chiral discotics 5 and 6 follows the same synthetic procedure as applied for 1–4 (Figure 1 and Supporting Information).

2.2. LC Properties. The importance of the polarizability of the π -system of discotic mesogens for the liquid crystallinity has been stressed on various occasions.^{16,17} While aggregation of the non-mesogenic 3 can be induced in suitable solvents,¹⁸ 1 and 5 display LC properties. Although solid 2 does not form a

LC phase, it is a promising candidate as active material in thin film devices. Octopole 1 forms a mesophase that has been characterized using polarized light optical microscopy (POM) and differential scanning calorimetry (DSC). POM reveals an “oily streaks” texture, characteristic of a chiral nematic discotic phase between 66 and 99 °C. As common for chiral nematic LCs,¹¹ no conclusive data have been obtained from XRD measurements. In the ester-terminated discotics 2, 5 and 6, only the achiral reference 5 displays LC properties forming a columnar hexagonal mesophase between 60 and 96 °C with a lattice constant of $a = 21.9$ Å and a stacking distance h of 4.1 Å as determined by X-ray diffraction in the mesophase (75 °C). POM of 5 displays a characteristic mosaic texture (Table 1, Figure 2).

The supramolecular arrangement of the octopolar mesogens of 5 in the LC phase is clearly centrosymmetric, which makes

Table 1. LC Phase Properties of 1 and 5

	Phase ^a T [°C] ($\Delta H/kJ mol^{-1}$)
1	Cr $\xrightleftharpoons{66(16.1)}$ N _D * $\xrightleftharpoons{99(0.8)}$ I
5	Cr $\xrightleftharpoons{60(26.2)}$ Col _h $\xrightleftharpoons{96(3.2)}$ I

^aCr, crystalline; I, isotropic liquid; N_D*, chiral discotic nematic; Col_h, hexagonal columnar; 2nd heating scan.

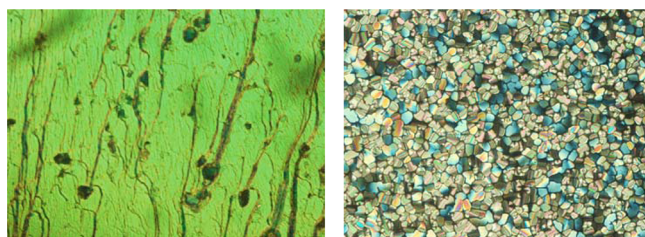


Figure 2. POM image of **1** at 82 °C and **5** at 65 °C.

this material of no use for second-order nonlinear optics,² and **6** is an isotropic liquid at room temperature. Therefore **5** and **6** have not been the object of further spectroscopic studies.

Circular Dichroism. In order to evaluate the supramolecular order of **1** in the chiral discotic nematic mesophase, both vibrational and electronic circular dichroism (CD) spectra are recorded at different temperatures. In the absence of any supramolecular order, the isotropic liquid (>100 °C) gives no CD response. In the mesophase, a nonabsorptive CD signal centered at 480 nm is measured between 65 and 95 °C. An intense CD band appears that rapidly saturates the instrument's detection system (90–70 °C, first cooling scan). Upon cooling of the LC phase below its transition temperature, crystalline **1** displays a CD signal of increased intensity due to further increasing the order in the crystalline bulk (<65 °C). The signals obtained in the heating scans are less intense than those measured in the corresponding cooling scans due to a poor organization of the material.¹⁹ The signature and spectral position of the reflection band permits an estimation of a helical pitch of around 320 nm for a left-handed helix at the mesophase temperature (ESI).²⁰

Vibrational circular dichroism (VCD) is a powerful tool to study the supramolecular chirality that is employed additionally.²¹ While **1** is VCD silent in its isotropic liquid state as expected, basically all molecular features show characteristic vibrational transitions in the LC state (Figure 3). The CH-stretching vibrations of the peripheral phenyl units are only weakly reflected in the VCD spectrum between 2975 and 2940 cm⁻¹. In contrast, the most intense feature is a bisignate signal

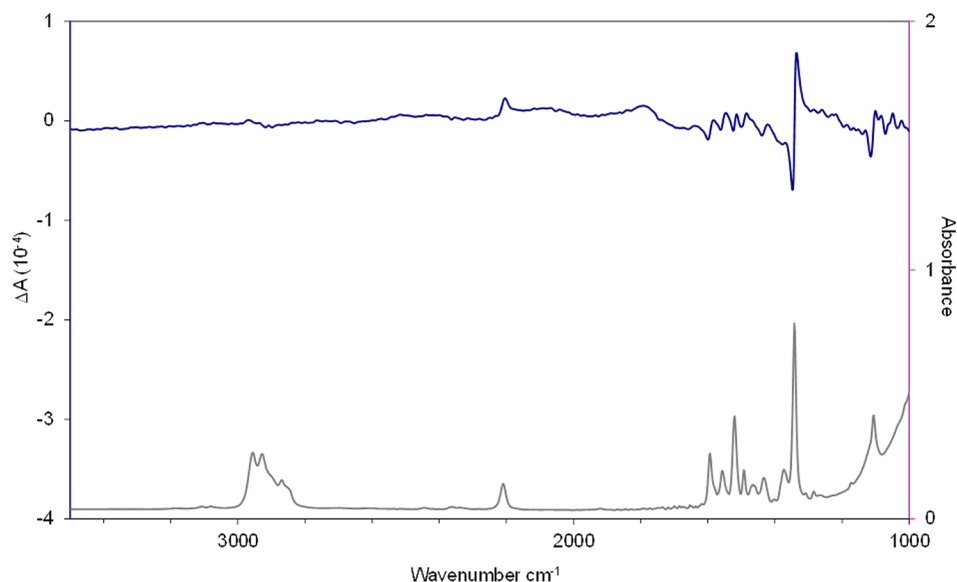


Figure 3. VCD (black) and IR (gray) spectrum of liquid crystalline **1** at 70 °C.

centered around 1350 cm⁻¹ corresponding to a complex vibration with contributions (stretching and bending) from the central and peripheral benzene moieties that directly participate in the intramolecular self-organization. Various negative bands in the 1610–1400 cm⁻¹ region, together with the characteristic C≡C stretching vibration at 2212 cm⁻¹, show that the molecular chirality is efficiently transcribed in the LC material.

2.3. Optical and Nonlinear Optical Spectroscopy. UV–vis absorption spectroscopy in dichloromethane solution clearly reveals an increase of the charge-transfer character upon increasing the electron-withdrawing nature of the terminal phenyl substituent. Compounds **1** and **2** show a pronounced octopolar character reflected by broad, structureless absorption bands that are consecutively red-shifted with respect to **3** (Figure 4).

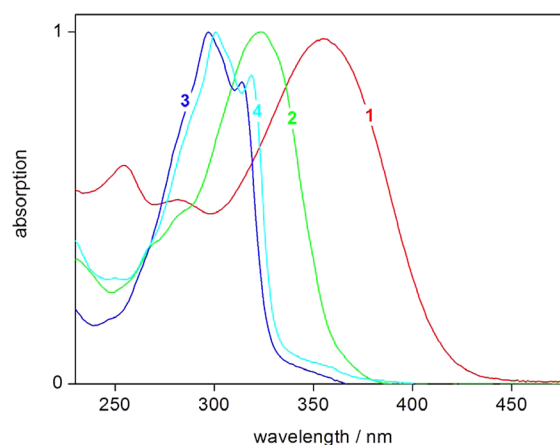


Figure 4. Normalized UV–vis absorption spectra of **1–4** in CH₂Cl₂.

Hyper-Rayleigh scattering (HRS) measurements in solution confirm these findings. In absence of peripheral acceptor groups (**3**), and particularly for the pentyl-substituted **4**, low β -values are measured, whereas compounds **1** and **2**, substituted with nitro or methylester acceptor groups, respectively, display high second-order hyperpolarizabilities β (Table 2).²² Except

Table 2. Spectroscopic Properties of 1–4 Measured in CH₂Cl₂ Solution

	$\lambda_{\text{max}}(\text{abs})$ [nm]	$\log \epsilon$	$\tau_{\text{fl}}^{\text{a}}$ [ns]	$\beta_{\text{xxx},800}$ [10 ⁻³⁰ esu]	$\beta_{\text{xxx},0}$ [10 ⁻³⁰ esu]	σ_{p}
1	355	4.798		360 ± 30	60 ± 6	0.78
2	323	4.981	3.0 ± 0.2	220 ± 30	65 ± 10	0.45
3	296	4.925	3.2 ± 0.7	50 ± 20	20 ± 10	0.00
4	301	5.073	2.5 ± 0.3	70 ± 20	26 ± 10	-0.15

^aFluorescent lifetime (τ) derived from the HRS demodulation fitting;²⁶ nitro-derivative **1** is virtually nonfluorescent.

for the nitro derivative **1**, the determination of the HRS polarization ratios is hampered by strong (multi)photon fluorescence of **2**–**4**.²³ Given the molecular structure, however, the octopolar character of the target compounds is beyond doubt. Table 2 correlates in a conclusive manner the experimental findings (absorption maxima $\lambda_{\text{max}}(\text{abs})$, extinction coefficients ϵ , β -values) attributed to the octopolar character with the predicted behavior based on the substituent constants σ_{p} for the *p*-phenyl substituents.²⁴ The supposed discrepancy between the electronegativity of the nitro and the methylester functions and the stated hyperpolarizabilities (β_0) is the result of a rough estimation based on a simple two-level model, which nevertheless is within the accepted error margin. A more complete and quantitative analysis of the absolute values of the hyperpolarizabilities requires more elaborated dispersion models.²⁵

2.4. Second Harmonic Generation (SHG) Measurements. For the preparation of a simple NLO device, a quartz LC cell was filled with neat **1** in its isotropic liquid state. Upon repetitive heating (above 100 °C) and subsequent cooling, a homogeneous film of 1.5 μm thickness is obtained. The sample is irradiated at 1064 nm (10 Hz, 5 ns pulses) using a Nd:YAG laser at a 45° angle. The SHG signal at 532 nm is detected in a reflective mode. In order to avoid a dielectric breakdown by continuous laser irradiation and a potential alteration of the geometry of the optics during the heating process, discrete data points were measured in steps of 5 °C, allowing the signal at each data point to stabilize (5 min). The SHG signal produced by the cell itself (<2 times the background noise) is negligible. Figure 5 shows the NLO response of the thin film device. Starting at 110 °C, the intensity of the SHG signal increase becomes evident below roughly 90 °C, when the isotropic

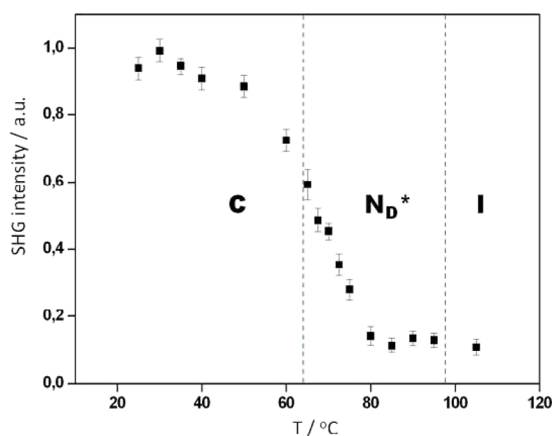


Figure 5. Plot of the SHG signal against temperature upon cooling of **1** from 110 °C.

liquid (SHG silent) of **1** enters the chiral nematic discotic (N_{D}^*) phase. The LC phase is demarcated by the dashed gray lines. We attribute the delayed signal onset to the time required by the bulk material to adopt the necessary non-centrosymmetric order. Upon further cooling, the intensity of the signal increases due to continuous ordering of the LC phase. The supramolecular order is maintained below 66 °C when the sample has crystallized, reaching its maximum value around 35 °C. This behavior of the LC phase is in agreement with the chiral memory effect observed in polymeric and LC materials.²⁷

4. CONCLUSIONS

The optimization of the donor–acceptor substitution in the octopolar discotics is beneficial for both the NLO and the LC properties of the target compounds. The ambiguous electronic nature of **3** and **4**, an isotropic liquid at room temperature, is the result of the neutral or electron-donor properties of the terminal *p*-phenyl substituents (H or C₃H₁₁, respectively). The acceptor-substituted octopoles **1** (NO₂) and **2** (CO₂CH₃) display high β -values in solution confirming a pronounced octopolar character. The high polarizability of the π -extended aromatic system of **1** is essential for LC behavior as well. The mesogens form chiral discotic nematic liquid crystals and thus act as the active layer in a simple, efficient NLO device as probed by second-harmonic generation experiments. The crucial non-centrosymmetric order in the bulk is guaranteed by efficient chirality transfer from the molecular to the supramolecular level as evidenced by circular dichroism measurements in the LC bulk. As for the LC properties, it becomes evident that supposedly small structural changes in the mesogens provoke dramatic differences in the bulk properties of the resulting material. Upon comparing the benzoic acid ester terminated discotics, a change from the linear alkoxy chains to homochiral alkoxy substituents at the central or peripheral benzene rings alters drastically the behavior of the resultant bulk material. We attribute these differences to the difficulties in the packing of the molecular units with sterically more demanding side chains (**2** vs **5**). The importance of the right proportion of rigid and flexible units within the mesogen is apparent when comparing liquid **6** with solid **2** or mesomorphic **5**.

In summary, the careful design of small organic molecules in combination with liquid crystal engineering can give access to advanced functional materials. However, this work also reveals the difficulties of this bottom-up approach where the subtle interplay of numerous structural and electronic parameters needs to be adjusted to coincide in a favorable way to obtain the final material.

5. EXPERIMENTAL SECTION

1,3,5-Triiodo-2,4,6-tri[(S)-3,7-dimethyloctyloxy]benzene (1a). To 1,3,5-triiodo-2,4,6-triiodobenzene (510 mg, 1.0 mmol) and sodium(S)-3,7-dimethyloctanoate (5.0 mmol, prepared *in situ* by adding alkanol, 6.0 mmol, dropwise onto neat NaH) is added *N,N*-dimethylimidazolidinone (1 mL), and the mixture is stirred at rt overnight. The reaction mixture is purified by column chromatography (80:1 hex–Et₂O) to leave pure **1a** as colorless, waxy solid. Yield: 350 mg, 49%. ¹H NMR (300 MHz, CDCl₃) δ 4.00 (t, *J* = 6.2 Hz, 6 H), 2.02–1.94 (m, 3 H), 1.80–1.70 (m, 6H), 1.61–1.48 (m, 3H), 1.42–1.28 (m, 9H), 1.21–1.14 (m, 9H), 1.00 (d, *J* = 6.3 Hz, 9H), 0.88 (d, *J* = 6.7 Hz, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 166.5, 163.8, 132.5, 131.2, 128.1, 107.7, 96.5, 89.5, 73.3, 52.2, 39.2, 37.5, 37.4, 29.7, 27.9, 24.7, 22.6, 19.6. MALDI-HRMS: calcd for C₃₆H₆₃I₃O₃ + Na⁺ 947.1803, found 947.1802.

General Procedure for the Synthesis of 1, 2, and 4. 1,3,5-Triiodo-2,4,6-trialkoxybenzene **1a** (0.5 mmol) was stirred together with Pd(PPh₃)₂Cl₂ (0.075 mmol, 53 mg) and CuI (0.075 mmol, 14 mg) in degassed triethylamine (5 mL) for 30 min at room temperature before the respective phenylethynyl compound (2.5 mmol) was added. The mixture was heated at 70 °C for 24 h. The solvent was removed, and the remaining solid was suspended in water (50 mL) and extracted with ethylacetate (3 × 25 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo to give the crude product, which was purified by column chromatography (20:1 hex–EtOAc).

1,3,5-Tris[(S)-3,7-dimethyloctyloxy]-2,4,6-tris(4-nitrophenyl)ethynyl]benzene (1). Yellow, waxy solid; 13% yield (102 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.26 (d_{AB}, J = 8.9 Hz, 6 H), 7.65 (d_{AB}, J = 8.9 Hz, 6 H), 4.51–4.37 (m, 6 H), 2.07–1.96 (m, 3 H), 1.88–1.66 (m, 6 H), 1.55–1.42 (m, 3 H), 1.40–1.04 (m, 18 H), 0.93 (d, J = 6.5 Hz, 9 H), 0.81 (d, J = 6.6 Hz, 18 H); ¹³C NMR (125 MHz, CDCl₃) δ 164.4, 147.2, 131.9, 130.1, 123.8, 107.1, 95.6, 86.7, 73.6, 39.2, 37.5, 37.4, 29.8, 27.9, 24.7, 22.6, 22.5, 19.6. FAB-MS *m/z* 982 (M⁺). Anal. Calcd for C₆₀H₇₅N₃O₉·H₂O: C, 72.04; H, 7.76; N, 4.20. Found: C, 72.36; H, 7.34; N, 4.40.

1,3,5-Tris[(S)-3,7-dimethyloctyloxy]-2,4,6-tris(4-methylacetylphenyl)ethynyl]benzene (2). Waxy, colorless solid; 14% yield (71 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d_{AB}, J = 8.2 Hz, 6 H), 7.57 (d_{AB}, J = 8.9 Hz, 6 H), 4.48–4.35 (m, 6 H), 3.94 (s, 9 H), 2.03–1.92 (m, 3 H), 1.85–1.61 (m, 6 H), 1.51–1.38 (m, 3 H), 1.32–1.04 (m, 18 H), 0.92 (d, J = 6.5 Hz, 9 H), 0.81 (d, J = 6.5 Hz, 18 H); ¹³C NMR (125 MHz, CDCl₃) δ 166.5, 163.8, 132.5, 131.2, 128.1, 107.7, 96.5, 84.6, 73.3, 52.2, 39.2, 37.5, 37.4, 29.7, 27.9, 24.7, 22.6, 22.5, 19.6. MALDI-MS *m/z* 1021 (M⁺). Anal. Calcd for C₆₆H₈₄O₉·H₂O: C, 76.27; H, 8.34. Found: C, 76.29; H, 7.97.

The synthesis and characterization of compound **3** is reported in a previous paper,¹⁸ although the data is erroneously assigned to the tris[(R)-3-methyloctyl]oxy]benzene derivative.

1,3,5-Tris[4-(n-pentylphenyl)ethynyl]-2,4,6-tris[(S)-3,7-dimethyloctyloxy]benzene (4). Orange viscous liquid, 24% yield (129 mg). ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d_{AB}, J = 8.1 Hz, 6 H), 7.19 (d_{AB}, J = 8.1 Hz, 6 H), 4.48–4.34 (m, 6 H), 2.65 (t, J = 7.7 Hz, 6 H), 2.06–1.95 (m, 3 H), 1.89–1.79 (m, 3 H), 1.75–1.59 (m, 9 H), 1.53–1.44 (m, 3 H), 1.38–1.08 (m, 30 H), 0.96–0.91 (m, 18 H), 0.85 (d, J = 6.5 Hz, 18 H); ¹³C NMR (125 MHz, CDCl₃) δ 162.7, 143.4, 131.3, 128.5, 120.9, 108.5, 97.2, 81.1, 73.0, 39.3, 37.6, 37.5, 35.9, 31.5, 31.0, 29.8, 28.0, 24.7, 22.7, 22.6(3), 22.5(7), 19.7, 14.1; MALDI-MS *m/z* 1058 (M⁺). Anal. Calcd for C₇₅H₁₀₈O₃: C, 85.17; H, 10.29. Found: C, 85.26; H, 10.21.

The ester end-capped discotics **5** and **6** are prepared in the same way by utilizing the respective ethynylbenzenes.

From 1,3,5-triiodo-2,4,6-tridecyloxybenzene,⁶ pure **5** is obtained from the remaining oil as pale colorless solid after column chromatography (10:1 hex–EtOAc) and final recrystallization from EtOH in 29% yield (148 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 8.2 Hz, 6 H), 7.57 (d, J = 8.2 Hz, 6 H), 4.37 (t, J = 6.4 Hz, 6 H), 3.94 (s, 9 H), 1.89 (q, J = 6.3 Hz, 6 H), 1.61–1.51 (m, 6 H), 1.33–1.21 (m, 36 H), 0.87 (t, J = 6.7 Hz, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 163.7, 131.1, 129.6, 128.2, 107.7, 96.5, 84.5, 75.0, 52.2, 31.9, 31.2, 30.6, 29.6(2), 29.5(7), 29.3, 26.3, 22.7, 14.1; MALDI-MS *m/z* 1021 (M⁺). Anal. Calcd for C₆₆H₈₄O₉·1/2H₂O: C, 76.93; H, 8.31. Found: C, 77.03; H, 8.34.

From 1,3,5-triiodo-2,4,6-tridecyloxybenzene and 1-[(S)-2-methylbutyloxy]-4-ethynylbenzene,²⁸ pure **6** is obtained as yellow oil after column chromatography (50:1 hex–Et₂O) in 12% yield (73 mg). ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 8.2 Hz, 6 H), 7.58 (d, J = 8.2 Hz, 6 H), 4.38 (t, J = 6.2 Hz, 6 H), 4.11–4.27 (m, 9 H), 1.93–1.82 (m, 9 H), 1.62–1.48 (m, 12 H), 1.33–1.18 (m, 12 H), 1.03 (d, J = 6.7 Hz, 9 H), 0.97 (t, J = 7.4 Hz, 9 H), 0.86 (t, J = 6.4 Hz, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 166.0, 163.7, 131.1, 130.0, 129.5, 128.0, 107.7, 96.5, 84.4, 75.0, 69.7, 65.8, 34.3, 31.8, 30.6, 29.6, 29.5, 29.3, 26.3, 26.2, 22.6, 16.5, 15.2, 14.1, 11.3; MALDI-HRMS: calcd for C₇₈H₁₀₈O₉ + Na 1211.7886, found 1211.7884.

■ ASSOCIATED CONTENT

📄 Supporting Information

General methods, ¹H and ¹³C NMR spectra of all new compounds, and temperature-dependent CD spectroscopy of thin films of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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