Synthesis and Characterization of Fluorescent, Low-Symmetry Triphenylene Discotic Liquid Crystals: Tailoring of Mesomorphic and Optical Properties

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A series of monofunctionalized triphenylene-based discotic liquid crystals were synthesized starting from 2-hydroxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene. These compounds are unique in that they possess a single electron-withdrawing group (and consequently a large dipole moment) connected directly to the polyaromatic core. All of the new liquid crystals show a significantly broader range of mesogenicity relative to the parent compound 2,3,6,7,-10,11-hexakis(pentyloxy)triphenylene. Moreover, some of the new mesogens exhibit a more ordered mesophase relative to the hexagonal columnar phase (D_h) at lower temperatures. Monofunctionalization of the triphenylene core has a dramatic effect on the photophysical properties of the mesogens such as the color and efficiency of fluorescence.

Introduction

Discotic liquid crystals (LCs) are anisotropic fluids comprised of supermolecular assemblies of disk-shaped molecules.[1] Discotic LC molecules (mesogens) typically contain a flat, rigid "core" radially substituted with flexible aliphatic chains or "tails". Discotic mesophases possess varying degrees of long-range order typically associated with crystalline solids, while at the same time retaining the fluidity and processability of liquids allowing for the formation of highly oriented thin films. Due to their photoconductivity and high charge carrier mobilities, triphenylene-based columnar discotic LCs show great potential as molecular organic materials for optoelectronic devices.[2,3] Although device applications involving rod-shaped nematic and smectic LCs are numerous, the design of optoelectronic devices based on discotic LCs is a newly emerging field. Photoconductive discotics could potentially be exploited for applications such as xerography and have already been used in photovoltaic cells[4] and optical data storage.[5,6]

All optoelectronic LC device configurations place specific requirements on the physical properties of the LC material in use. In general, there are three main physical parameters to control: (1) stability of the mesophase, (2) supermolecular order of the mesophase, and (3) photophysical and electronic properties of the LC material. In light of these considerations, we herein describe our efforts to synthesize new functionalized triphenylene discotic LCs for optoelectronic investigations.

Besides the obvious need for chemical stability, the supermolecular structure of the desired mesophase must be thermodynamically stable over a broad temperature range above and below room temperature. In calamitic LCs, broadening of the mesophase range is often accomplished by mixing of different components (not necessarily mesogenic) to achieve eutectic mixtures with depressed melting points. This concept has been applied to phthalocyanine-based discotics containing branched hydrocarbon tails obtained from the reduction of farnesol.[7] Since both of the two stereogenic centers in each tail were created in a stereorandom reaction, the final octasubstituted phthalocyanine discotic is a complex mixture of many diasterieomers. Although this mixture is mesogenic at room temperature, the clearing point has also been greatly reduced, thus indicating a shift of mesogenic range to lower temperatures rather than a true overall enhancement.

When investigating structure−property relationships in new optoelectronic applications of LCs, the simplicity of single-component materials is generally preferred. Thus, new strategies have been developed for broadening the mesogenic range of single-component smectic LC materials that allow flexibility in choice of core substituents.[8,9] Such efforts are now underway for discotic mesogens. One promising route to broadening the mesogenic range of discotics is the incorporation of β-oxygen atoms in the tails of alkoxy[10] and alkanoyloxy[11,12] substituted derivatives. Although this strategy

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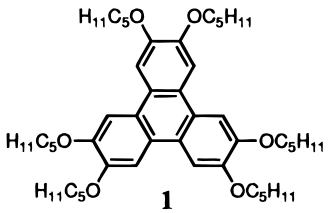
can result in a significant widening of the mesogenic temperature range, it has only been applied to high-symmetry discotic cores having oxo substituents and is not effective in all tail lengths. Moreover, the mechanism by which β-oxygen substitution enhances mesogenicity is not known.

Collard and Lillya have also shown that branching in the aliphatic tails of hexasubstituted benzenes and cyclohexanes substantially broadens the mesogenic range by introducing disorder and thus suppressing crystallization.[13] Additionally, Spiess and co-workers have shown that monoesterification of pentakis(pentyloxy)triphenylenes significantly broadens the discotic mesophase and produces room-temperature LCs with low-temperature glass transitions.[14] Using dielectric spectroscopy, they showed that the glass transition in these materials corresponds to a freezing of rotation of molecules within the columns. They have attributed both suppression of crystallization and increased clearing points to steric interactions between the ester carbonyl groups protruding from the plane of neighboring disk-shaped molecules. However, we believe that energetically favorable dipole−dipole interactions between molecules within the columns may account for the decreased stacking distance and increased mesophase stability in these triphenylene monoesters.

All of the above approaches to enhancing mesophase stability in discotics have focused on modification of the aliphatic tails. Clearly there is a strong relationship between molecular structure and mesophase stability. However, to our knowledge no one has investigated the effects of systematic core modification on the mesogenic properties of discotics. Thus, we have initiated a synthetic program[15] that will allow us to carefully probe the effects of core substitution and molecular symmetry on mesogenic range and supermolecular order in triphenylene discotic LCs.

The degree of molecular positional order in a discotic columnar phase can have a significant effect on the efficiency of photoconductivity in these systems. For example, a charge carrier mobility of 10^{-5} m^2 V^{-1} s^{-1} was measured in the highly ordered helical phase of hexahexylthiotriphenylene.[16] Charge migration in this unique phase is 2 orders of magnitude faster than in the D_h phase of hexakis(pentyloxy)triphenylene (**1**, Chart 1). Thus, we have a great interest in obtaining triphenylene discotics possessing higher order discotic phases. We are currently developing a simple model that addresses the degree of order in columnar mesophases. We propose that biasing of the rotation of individual discotic molecules within the columns will lead to fewer degrees of rotational freedom within the column and result in higher overall order in the mesophase. In principle, hindrance to rotation could be achieved by unfavorable steric interactions and/or dipole−dipole interactions. However, too much steric crowding may threaten the stability of the mesophase. Moreover, given the disordered liquidlike state of the aliphatic tails, structural modification of the central rigid core seemed to be a reasonable approach to influence molecular rotation.

Chart 1



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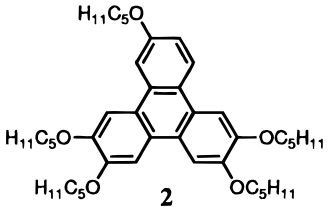

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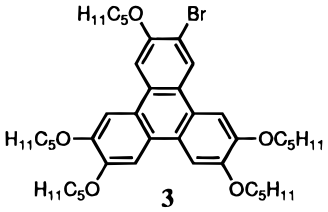

3

Another key reason for core modification is that in LCs the optical and electronic properties are dominated by the structure of the aromatic core. Clearly, if one is to tailor the optical and/or electronic properties of a discotic system, one must have flexibility in modifying the core without sacrificing mesogenicity. In addition to being photoconductors, triphenylene discotic LCs form Schottky barriers when in contact with several types of metal and semiconductor electrodes, making them attractive candidates for organic diode device applications such as photovoltaics.[17] Schottky barriers are analogous to p/n junctions in semiconductors. However, these organic/inorganic interfaces are still poorly understood and are very sensitive to the electronic nature of the organic material. Thus, to better study this surface interaction, we required a synthetic methodology with which to selectively modify the electronic nature of the triphenylene core.

One particular property we wished to enhance in triphenylene discotics is fluorescence. Markovitsi and co-workers have utilized fluorescence decay measurements to study energy migration in triphenylene discotics.[18] Unfortunately, the fluorescence quantum yield of **1** is rather low (0.068) due primarily to the fact that the $S_0 \rightarrow S_1$ transition is symmetry forbidden. In an effort to enhance fluorescence we have synthesized a number of new monofunctionalized triphenylene discotics bearing conjugative electron-withdrawing substituents attached directly to the triphenylene core. Our strategy for improving fluorescence is 2-fold. First, by extending the conjugation of the polyaromatic core of the LC, the maximum absorption (λ_{max}) should be red-

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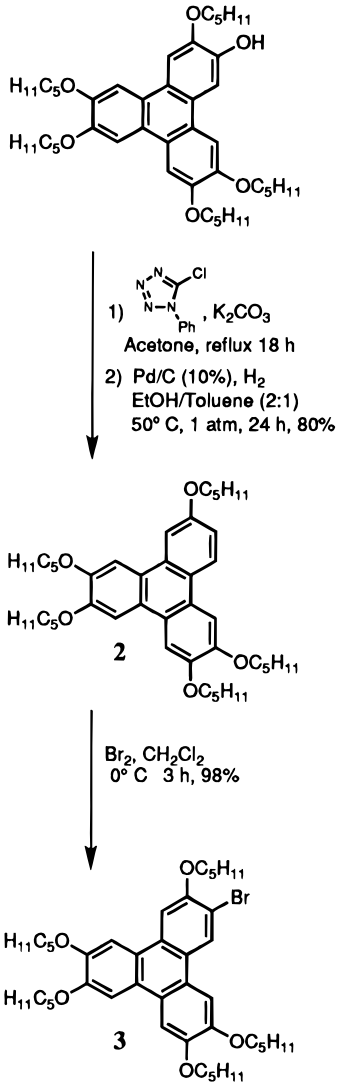
Scheme 1. Synthesis of Pentakis(pentyloxy)triphenylene

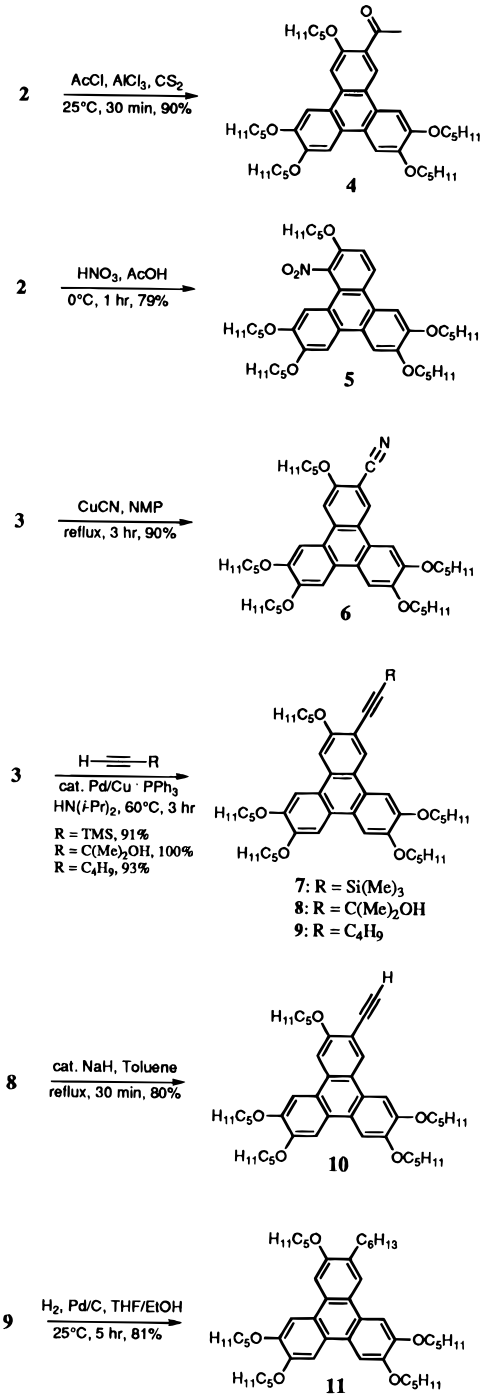


shifted and the fluorescence emission efficiency greatly enhanced.[19] Second, the C_1 symmetry of the monofunctionalized core should make the $S_0 \rightarrow S_1$ transition allowed. Moreover, we can use this extension of the core to introduce both sterically bulky groups as well as large dipole moments in hopes of influencing both stability and order of the mesophase.

Results and Discussion

Synthesis of Monosubstituted Triphenylene Discotics. Previously, we have reported the synthesis of pentapentyloxytriphenylene (compound **2**) and its subsequent bromination[15] to give the broadly mesogenic monobromotriphenylene (**3**, Scheme 1). Both **2** and **3** have proven to be valuable precursors for attachment of electron-withdrawing groups directly to the core of triphenylene discotic LCs. This is noteworthy since both the classical trimerization of substituted benzenes,[20,21] as well as the so called "biphenyl route"[22−25] to functionalized triphenylenes require electron-rich starting materials. Thus, the fluorescent discotic triphenylenes presented here can not be synthesized by previously existing methods. Scheme 2 summarizes the synthesis of these new derivatives.

Scheme 2. Synthesis of Monofunctionalized Triphenylene Discotic LCs



Friedel−Crafts acylation of **2** with acetyl chloride and aluminum trichloride proceeds in high yield with acy-

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Table 1. Phase Behavior of Monofunctionalized Triphenylene Discotic LCs

compound	phase sequence (°C)[a]	increase in mesogenic range relative to **1** (°C)
1	Cr 69 D_h 122 I	
2	mp 86, no LC phases	
3	g −40 D_x 14 D_h 163 I	+150
4	Cr_1 58 Cr_2 76 D_h 169 I	+40
5	mp 83, no LC phases	
6	Cr 51 D_x 85 D_h 226 I	+122
7	g −50 D_h 184 I	+181
8	Cr 58 D_h 180 I	+69[b]
9	Cr 44 D_h 155 I	+61
10	g? < −30 D_h 146 I	+73[c]
11	mp 81, no LC phases	

[a] g, glass; Cr, crystal; D_h, hexagonal discotic; D_x, unidentified discotic; I, isotropic liquid. [b] Crystallization does not occur from the melt, and a glass transition is observed at −47 °C. [c] A definitive melting point has not been observed.

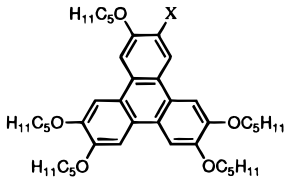
lation occurring in the 2-position. Somewhat surprisingly, classical nitration of **2** with nitric acid in acetic acid occurs preferentially in the sterically hindered 4-position as unambiguously indicated in the ^{1}H NMR. This result contradicts claims that steric crowding strongly disfavors substitution in the 1- and 4-positions relative to the 2- and 3-positions.[26] Evidently, electronic effects dominate in the nitration of alkoxytriphenylenes. Efforts are underway to explore alternate nitration procedures in hopes of nitrating the 2-position of compound **2**.

Copper-mediated carbon−carbon bond formation with compound **3** is extremely efficient. Reaction of **3** with copper cyanide gives the cyanotriphenylene **6** in excellent yield. Palladium/copper-catalyzed alkynylation[27] of **3** can be accomplished in excellent-to-quantitative yields with a variety of substituted alkynes as demonstrated with compounds **7**−**9**. In addition, triphenylenes **7** and **8** can be deprotected to yield free phenylacetylenes for further elaboration or potential polymerization. For example, treatment of **8** with catalytic base gives alkyne **10** in good yield. Although not shown here, **7** can be desilylated with fluoride ion to give **10** in good yield as well. Finally, **9** was hydrogenated with catalytic palladium to yield the alkyl/alkoxytriphenylene derivative **11**.

Phase Behavior of Monofunctionalized Triphenylene Discotics. Every new mesogenic triphenylene derivative shows a depression in the melting point and a substantial broadening of the LC temperature range relative to the parent compound **1**. The phase behavior of these new discotic mesogens is summarized in Table 1, and the calorimetric data are shown in Table 2. It should be noted that the assignment of a D_h phase was determined by polarized optical microscopy. Focal conic textures[28] very similar to that of compound **1** were observed for all of the new mesogenic derivatives just below the clearing point.

Not surprisingly, the 4-nitro derivative **5** is not mesogenic. Like pentakis(pentyloxy)triphenylene (**2**), the vacant site on the core probably allows too much unfilled space to achieve a true disklike molecular shape. However, compound **5** may prove to be a useful precursor for the creation of monosubstituted triphenylene discotics nitrated in the bay region of the core. The monoalkyltriphenylene **11** is likewise nonmesogenic. This is reasonable considering the conformational preference of alkyl chains attached to phenyl rings to reside perpendicular to the plane of the ring and thus out of the plane of the molecular disk. This loss of mesogenicity underscores the significant influence of molecular conformation on the delicate balance between crystallization and mesophase formation.

Table 2. Calorimetric Data of Monofunctionalized Triphenylene Discotic LCs



compound	X	transition	T (°C)	ΔH (kJ/mol)	ΔS (J,K mol)
1	OC_5H_{11}	Cr → D_h	69	32.6	95.3
		D_h → I	122	8.53	21.6
2	H	Cr → I	86		
3	Br	g → D_x	-47		
		D_x → D_h	14	4.19	14.6
		D_h → I	163	8.83	20.2
4		Cr → D_h	76	33.2	95.1
		D_h → I	169	8.57	19.4
6	−C≡N	Cr → D_x	51	22.8	70.4
		D_x → D_h	85	4.93	13.8
		D_h → I	226	9.60	19.2
7		g → D_h	-50		
		D_h → I	184	11.8	25.8
8		Cr → D_h	58	23.3	70.4
		D_h → I	180	13.6	30.0
9		Cr → D_h	44	30.6	96.5
		D_h → I	157	8.02	18.6

Two of the new derivatives, **7** and **10**, show no sign of crystallization, and these materials possess low-temperature glass transitions. While certainly not fluid at room temperature, these plasticlike materials are clearly deformable under physical stress. Although the hydroxyalkynyl derivative **8** melts at 58 °C when recrystallized from solution, the material does not crystallize from the neat discotic phase and shows a glass transition at −47 °C. Certainly the steric bulk of the trimethylsilyl group of **7** and the 2-hydroxypropyl group of **8** could act to inhibit crystallization in a manner similar to the monoesters of Spiess et. al. Examination of the entropies of clearing show that both **7** and **8** form a significantly more ordered D_h phase than **1** relative to the isotropic state ($\Delta S_{D_h-I} = 25.8$ and 30.0 for **7** and **8**, respectively, and $\Delta S_{D_h-I} = 21.6$ for **1**; all values in J K^{-1} mol^{-1}). Like the monoester triphenylene discotics, **8** contains a polar group that can reside orthogonal to the plane of the molecule; moreover, one cannot rule out the chance of intermolecular hydrogen

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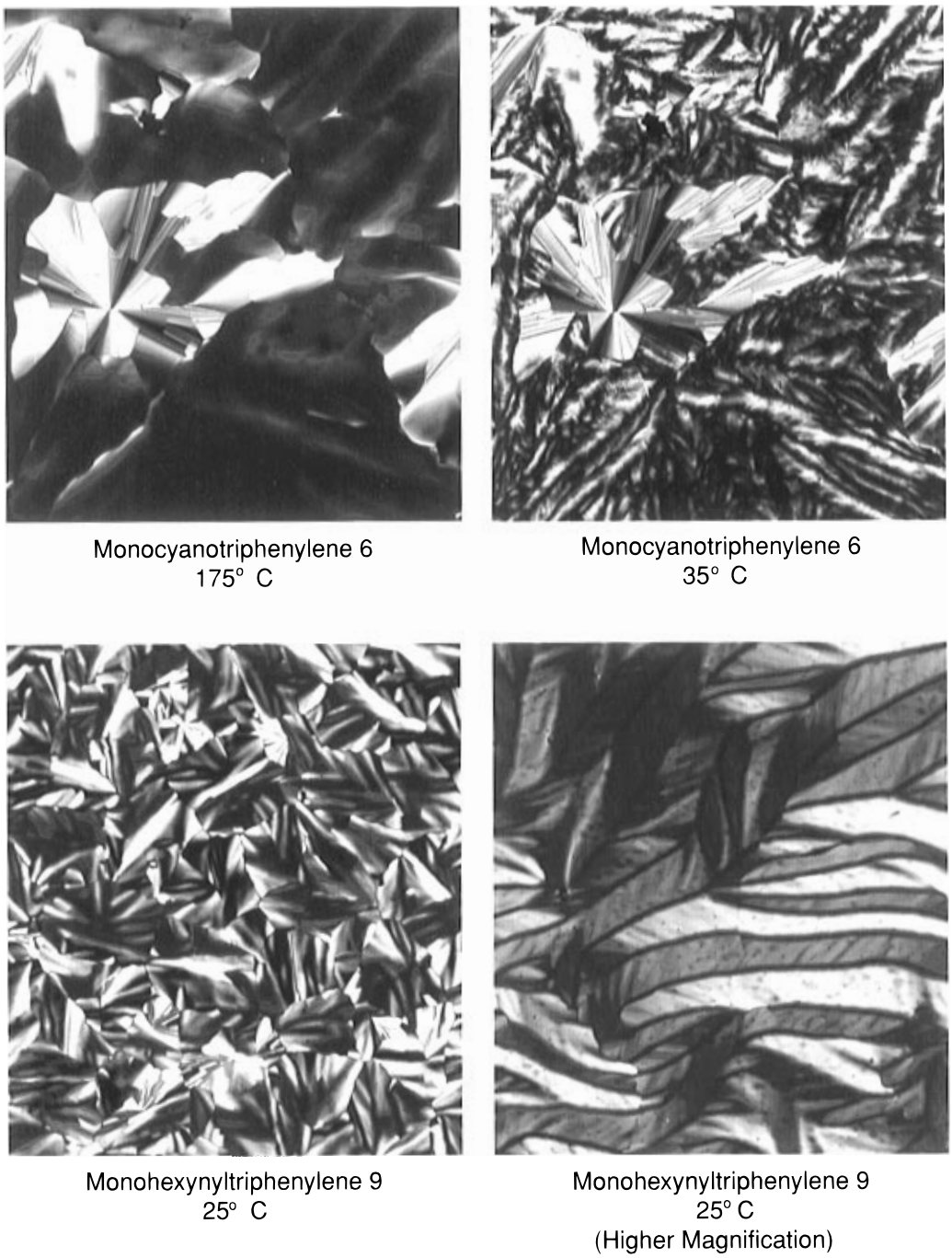

Figure 1. Optical textures of monofunctionalized triphenylene discotic LCs.

bonding, although the relatively low enthalpy of melting ($\Delta H_{Cr-D_h} = 23.3$ kJ mol^{-1}) seems to indicate otherwise. Unlike the monoesters of Spiess, **7** possesses a dipole moment in the plane of the core, and thus it is possible that intermolecular dipole−dipole interactions may play a role in the increased order and higher clearing point of the D_h phase.

We were pleased to find that like the monobromotriphenylene (**3**), the monocyano derivative **6** exhibits a more ordered phase below the D_h phase. Both of these derivatives have a strong dipole moment in the plane of the core. However, their entropies of clearing are essentially the same as **1**, indicating a similar degree of order in the D_h phase. Perhaps dipole−dipole interactions are decreasing intracolumnar rotational freedom and promoting a higher degree of order, but only at lower temperatures. Finally, we should note that the monoethynyl derivative **10** decomposes in the scanning calorimeter and reproducible transition enthalpies were not obtainable. Transition temperatures for this compound were determined with optical microscopy; however, this sample became progressively darker yellow with exposure to heat under the microscope.

Optical Textures. As stated above, the optical textures of the monofunctionalized triphenylene discotics are very similar to the parent compound **1** at high temperatures. However, significant changes occur with decreasing temperature. Figure 1 shows the optical textures of **6** and **9**. Notice the evolution of birefringence with decreasing temperature within the dark homeotropically aligned domains of **6**; this cyano derivative shows a more ordered phase at lower temperature by DSC. However, this gradual appearance of a herringbone like texture in the homeotropic regions at

Table 3. Spectral Properties of Monofunctionalized Triphenylene Discotic LCs

compound	$\lambda_{absorption}$ (nm)[a]	$\epsilon^b/10^4$	$\lambda_{emission}$ (nm)[c]
1	279	9.91	387
2	277	8.85	387
3	279	9.65	387
4	286	7.45	487
5	280	7.75	353
6	284	9.66	428
7	284	9.68	411
8	284	11.14	417
9	279	8.68	416
10	283	8.85	415
11	278	9.53	388

[a] 10^{-5} M in CH_3Cl. [b] Extinction coefficient (L mol^{-1} cm^{-1}). [c] 10^{-6} M in CH_3Cl, irradiated at λ_{max}.

lower temperature is seen in all these new derivatives, for example, alkynyl derivative **9**.

Clearly, these are not typical textures for a D_h phase. The gradual appearance of birefringence in the homeotropic regions is reminiscent of an A phase (untilted) to C phase (tilted) transition seen in smectics; thus, these new derivatives may be undergoing a gradual second-order transition to a tilted phase with decreasing temperature. X-ray analysis is currently underway to elucidate the supermolecular structure of these materials.

Spectral Properties of Monofunctionalized Triphenylenes. The spectral properties of the new derivatives are summarized in Table 3. As expected, a general red-shift of the λ_{max} (relative to **1**) is seen in all the monofunctionalized triphenylenes. Several compounds have absorption spectra tailing into the visible and are yellow in color. The largest shift of λ_{max} of 7 nm is exhibited by the monoacetyl derivative **4**. An even greater red-shift is seen in the fluorescence spectra of the new compounds. Emission spectra were recorded for 10^{-6} M chloroform solutions. Triphenylene derivatives are known to aggregate in solution above a concentration of 10^{-3} M;[29,30] thus excimer formation should not be a factor in these measurements. It should also be noted that the fluorescence of discotic materials is influenced by microenvironment. Even though previous work has shown that thin films of bulk 2,3,6,7,10,-11-hexakis(hexyloxy)triphenylene do not form eximers in the LC state,[31] the solution values shown here may differ from those obtained with thin films of these new liquid-crystalline materials.[32] Regardless, solution measurements allow us to examine the effect of core substitution on fluorescence. Compound **4** emits at 487 nm and shows the largest red-shift in emission of 100 nm relative to **1**. Comparison of **9** and **11** clearly shows the effect of extended conjugation of the LC core on the wavelength of emission. Interestingly, although the λ_{max} is essentially the same for the two (279 and 278 nm), the emission of the monoalkynyltriphenylene **9** is red-shifted 28 nm relative to the monoalkyl derivative. In fact, the spectral properties of **11** are nearly identical with those of the parent compound **1**.

Only the 4-nitro derivative **5** shows a blue-shift of fluorescence emitting at 353 nm, 34 nm to the blue relative to **1**. Also, one would normally expect a large red-shift of the absorption λ_{max} of an aromatic upon nitration which is not seen with **5**. Examination of space-filling models suggests that the nitro group in the 4-position of compound **5** is most likely orthogonal to the triphenylene plane due to unfavorable steric interactions with ortho substituents. Thus, the nitro group is effectively twisted out of conjugation with the aromatic ring and does not extend the π-system of the triphenylene core. Also, the fluorescence of this nitro derivative was noticeably lower than the others. As nitration of aromatics is known to reduce fluorescence,[16] this is not particularly surprising. All of the other new monofunctionalized derivatives were qualitatively much more fluorescent than the parent compound **1**. While an absolute determination of fluorescence quantum yields is beyond the scope of this study, preliminary results indicate a 3-fold increase in quantum yield for the monocyano derivative **6** relative to **1**.[33]

In conclusion, we have shown that monosubstitution of triphenylene discotic LCs directly on the aromatic core with polar functionalities has dramatic effects on both the mesogenic and optical properties of these materials. Remarkably, enhancement of fluorescence has been concomitant with increased mesophase stability and order. Extremely broad discotic mesophases have been obtained with several exhibiting highly ordered plasticlike mesophases at room temperature. We have proposed that steric and/or dipole−dipole interactions may be limiting intracolumnar rotational freedom leading to a higher degree of positional order in the mesophase. This proposition is supported by the appearance of new more ordered columnar phases below the D_h phase in compounds with large dipole moments along the core. We feel these new fluorescent discotics are prime candidates for optoelectronic device applications and studies of photoconductivity and fluorescence migration are now underway.

Experimental Section

Proton NMR spectra were recorded on a Bruker AC200 spectrometer, and chemical shifts are referenced to chloroform (δ = 7.24 ppm). Elemental analysis was performed by the Microanalysis Laboratories of the University of Mainz. Enthalpies of transition were determined using a Perkin-Elmer DSC 7 differential scanning calorimeter at a scan rate of 10 °C/min. Transition temperatures were confirmed and optical textures observed using a Leitz Ortholux II polarizing microscope equipped with a Mettler FP 5 temperature-controlled hot stage. Florescence spectra were recorded on a SPEX Fluorolog 2 spectrofluorometer. Solutions were made using Merck Uvasol grade chloroform and were rigorously purged with dry argon prior to measurement. UV spectra were recorded on a Perkin-Elmer Lamda 5 spectrophotometer. Synthetic reagents were used as supplied by commercial vendors. Solvents were reagent grade and dried by storage over molecular sieves. All compounds were recrystallized from ether/methanol prior to thermal analysis.

3,6,7,10,11-Pentakis(pentyloxy)triphenylene (2). 2-Hydroxy-3,6,7,10,11-pentakis(pentyloxy)triphenylene (750 mg, 1.09 mmol), 5-chloro-1-phenyl-1*H*-tetrazole (295 mg, 1.63 mmol), and potassium carbonate (276 mg, 2.0 mmol) were combined in 40 mL of dry acetone. The mixture was stirred at reflux for 18 h after which the solvent was removed under vacuum. The crude product was redissolved in dichloromethane and washed with three equal portions of water

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followed by one portion of saturated aqueous NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and removed under vacuum.

The crude tetrazolic ether was dissolved in 60 mL of 2:1/ethanol:toluene, and 10% palladium on activated carbon (232 mg, 0.22 mmol) was added. The solution was purged with hydrogen for 5 min and then brought to reflux under a positive pressure of hydrogen. The reaction was stirred at reflux for 24 h. The catalyst was removed by filtration, and the solvent removed under vacuum. The crude product was chromatographed through silica with 95:5/hexanes:ethyl acetate to give 578 mg (80%) of a beige solid: mp 86 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 6.9 Hz, 15H), 1.53 (m, 20H), 1.93 (m, 10H), 4.21 (m, 10H), 7.21 (dd, J = 2.4, 9.17 Hz, 1H), 7.80 (s, 2H), 7.84 (d, J = 2.4 Hz, 1H), 7.90 (s, 2H), 8.36 (d, J = 9.2 Hz, 1H); MS (EI$^+$) m/z 658.4 (M^+). Anal. Calcd for $C_{43}H_{62}O_5$: C, 78.38; H, 9.48. Found: C, 78.38; H, 9.61.

2-Bromo-3,6,7,10,11-pentakis(pentyloxy)triphenylene (3). 3,6,7,10,11-Pentakis(pentyloxy)triphenylene (100 mg, 0.152 mmol) was dissolved in 5 mL dichloromethane and cooled to 0 °C. Bromine (27 mg, 0.167 mmol) dissolved in 2 mL of dichloromethane, was added dropwise over a period of 30 min. The reaction was stirred another 2 h at 0 °C. The reaction mixture was diluted with dichloromethane and washed with three equal portions of 5% aqueous sodium thiosulfate. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude product was chromatographed through silica with 60:40 hexanes:dichloromethane to give 109 mg of a white solid (98%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, J = 6.4 Hz, 15H), 1.51 (m, 20H), 1.95 (m, 10H), 4.22 (m, 10H), 7.74 (s, 1H), 7.76 (s, 3H), 7.81 (s, 1H), 8.54 (s, 1H); MS (FD+) m/z 736.3 (M+). Anal. Calcd for $C_{43}H_{61}BrO_5$: C, 70.00; H, 8.33. Found: C, 69.95; H, 8.31.

2-Acetyl-3,6,7,10,11-pentakis(pentyloxy)triphenylene (4). 3,6,7,10,11-Pentakis(pentyloxy)triphenylene (**2**, 66 mg, 0.10 mmol) was dissolved in 2 mL of carbon disulfide and cooled to 0 °C. Aluminum trichloride (20 mg, 0.15 mmol) and acetyl chloride (12 mg, 0.15 mmol) were added, and the reaction was stirred at room temperature for 30 min. The reaction was then poured into cold 2 N HCl and the suspension was extracted with three 10 mL portions of ether. The combined ether layers were dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude product was recrystallized from ether/methanol to give 64 mg of a light yellow solid (90%): mp 76 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 7.0 Hz, 15H), 1.50 (m, 20H), 1.95 (m, 10H), 2.77 (s, 3H), 4.25 (m, 10H), 7.79 (s, 3H), 7.87 (s, 1H), 7.96 (s, 1H), 8.86 (s, 1H); MS (EI$^+$) m/z 700.5 (M^+). Anal. Calcd for $C_{45}H_{64}O_6$: C, 77.10; H, 9.20. Found: C, 77.21; H, 9.18.

4-Nitro-3,6,7,10,11-pentakis(pentyloxy)triphenylene (5). 3,6,7,10,11-Pentakis(pentyloxy)triphenylene (**2**, 50 mg, 0.076 mmol) was dissolved in 3 mL of acetic acid and 2 mL of dichloromethane. The solution was cooled to 0 °C, and 5 drops of concentrated nitric acid was added in one portion at 0 °C. The reaction was stirred at 0 °C for 1 h. The reaction mixture was then poured into 25 mL of saturated aqueous sodium bicarbonate. The aqueous suspension was extracted with three 20 mL portions of ether. The combined ether layers were dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude product was chromatographed through silica with 95:5 hexanes:ethyl acetate to give 42 mg of a yellow solid (79%): mp 83 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 6.8 Hz, 15H), 1.48 (m, 20H), 1.92 (m, 10H), 4.07 (t, J = 6.6 Hz, 2H), 4.21 (m, 8H), 7.25 (d, J = 9.2 Hz, 1H), 7.55 (s, 1H), 7.73 (s, 1H), 7.77 (s, 1H), 7.81 (s, 1H), 8.46 (d, J = 9.4 Hz, 1H); MS (EI+) m/z 703.4 (M^+). Anal. Calcd for $C_{43}H_{61}NO_7$: C, 73.37; H, 8.73; N, 1.99. Found: C, 73.42; H, 8.76; N, 2.04.

2-Cyano-3,6,7,10,11-pentakis(pentyloxy)triphenylene (6). 2-Bromo-3,6,7,10,11-pentakis(pentyloxy)triphenylene (**3**, 100 mg, 0.136 mmol) and copper cyanide (18 mg, 0.20 mmol) were combined in 1.5 mL of *N*-methylpyrolidone and stirred at reflux for 3 h. The reaction was then cooled to room temperature and poured onto ice. The resulting aqueous suspension was extracted with three equal portions of dichloromethane, and the organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude product was chromatographed through silica gel with 40:60 hexanes:dichloromethane to give 90 mg of a white solid (95%): mp 51 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 5.9 Hz, 15H), 1.56 (m, 20H), 1.94 (m, 10H), 4.22 (m, 10H), 7.77 (s, 4H), 7.82 (s, 1H), 8.64 (s, 1H); MS (EI$^+$) m/z 683.4 (M^+). Anal. Calcd for $C_{44}H_{61}NO_5$: C, 77.27; H, 8.99; N, 2.05. Found: C, 77.26; H, 8.89; N, 2.06.

2-(Trimethylsilyl)ethynyl-3,6,7,10,11-pentakis(pentyloxy)triphenylene (7). 2-Bromo-3,6,7,10,11-pentakis(pentyloxy)triphenylene (**3**, 160 mg, 0.217 mmol), was dissolved in 10 mL of dry diisopropylamine, and the solution was purged with nitrogen for 2 min. (Trimethylsilyl)acetylene (0.15 mL, 1.08 mmol) was added followed by 20 mg of a mixed catalyst containing palladium dichloride, copper diacetate, and triphenylphosphine.[34] The reaction was heated to 60 °C and stirred for 8 h. The mixture was cooled to room temperature and filtered through a bed of Celite. The solvent was removed under vacuum and the crude product was chromatographed through silica gel with 60:40 CH_2Cl_2:hexanes to give 150 mg of a light yellow gummy solid (91%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.32 (s, 9H), 0.96 (t, J = 6.8 Hz, 15H), 1.54 (m, 20H), 1.94 (m, 10H), 4.21 (m, 10H), 7.73 (s, 1H), 7.79 (s, 2H), 7.84 (s, 1H), 7.88 (s, 1H), 8.51 (s, 1H); MS (EI$^+$) m/z 754.6 (M^+). Anal. Calcd for $C_{48}H_{70}SiO_5$: C, 76.34; H, 9.34. Found: C, 76.28; H, 9.36.

2-(2-Hydroxy-2-methylbutynyl)-3,6,7,10,11-pentakis(pentyloxy)triphenylene (8). 2-Bromo-3,6,7,10,11-pentakis(pentyloxy)triphenylene (150 mg, 0.203 mmol) and 2-methyl-3-butyn-2-ol (85 mg, 1.02 mmol) were dissolved in 10 mL of dry diisopropylamine, and the solution was purged with nitrogen for 2 min. A mixed catalyst containing palladium dichloride, copper diacetate, and triphenylphosphine (20 mg) was added. The reaction was heated to 60 °C and stirred for 8 h. The mixture was cooled to room temperature and filtered through a bed of Celite. The solvent was removed under vacuum and the crude product was chromatographed through silica gel with 80:20 hexanes:ethyl acetate to give 150 mg of a white solid (100%): mp 58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 7.0 Hz, 15H), 1.5 (m, 20H), 1.70 (s, 6H), 1.93 (m, 10H), 2.13 (s, 1H), 4.22 (m, 10H), 7.72 (s, 1H), 7.78 (s, 2H), 7.83 (s, 1H), 7.85 (s, 1H), 8.43 (s, 1H); MS (EI$^+$) m/z 740.5 (M^+); Anal. Calcd for $C_{48}H_{68}O_6$: C, 77.80; H, 9.25. Found: C, 77.86; H, 9.24.

2-(2-Butylethynyl)-3,6,7,10,11-pentakis(pentyloxy)triphenylene (9). 2-Bromo-3,6,7,10,11-pentakis(pentyloxy)triphenylene (150 mg, 0.23 mmol) and 1-hexyne (0.23 mL, 2.03 mmol) were combined in 15 mL of dry diisopropylamine, and the solution was purged with nitrogen for 1 min. A mixed catalyst of palladium dichloride, copper diacetate, and triphenylphosphine (20 mg) was added. The reaction was brought to reflux under an atmosphere of nitrogen and stirred at reflux for 5 h. The reaction mixture was filtered through Celite, and the solvent was removed under vacuum. The crude product was chromatographed through silica with 95:5 hexanes:ethyl acetate to give 140 mg of a light yellow solid (93%): mp 16 °C (D_h); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (t, J = 6.5 Hz, 18H), 1.50 (m, 24H), 1.95 (m, 10H), 2.56 (t, J = 6.8 Hz, 2H), 4.22 (t, J = 6.5 Hz, 10H), 7.74 (s, 1H), 7.80 (s, 2H), 7.85 (s, 1H), 7.87 (s, 1H), 8.45 (s, 1H); MS (EI$^+$) m/z 738.6 (M^+). Anal. Calcd for $C_{49}H_{70}O_5$: C, 79.63; H, 9.55. Found: C, 79.59; H, 9.51.

2-Ethynyl-3,6,7,10,11-pentakis(pentyloxy)triphenylene (10). 2-(2-hydroxy-2-methylbutynyl)-3,6,7,10,11-pentapentyloxytriphenylene (**8**, 100 mg, 0.135 mmol) was dissolved in 40 mL of toluene, and sodium hydride (5 mg, 0.21 mmol) was added in one portion at room temperature. The reaction mixture was equipped for a short-path distillation and brought to a boil. Approximately half of the solvent was distilled off, and the reaction mixture was then cooled to room temperature.

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The remaining solvent was removed under vacuum. The crude product was chromatographed through silica gel with 90:10 hexanes:ethyl acetate to give 70 mg of a light yellow liquid crystal (80%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 7.0 Hz, 15H), 1.50 (m, 20H), 1.95 (m, 10H), 3.40 (s, 1H), 4.22 (m, 10H), 7.74 (s, 1H), 7.78 (s, 2H), 7.84 (s, 2H), 8.54 (s, 1H); MS (EI^+) m/z 682.6 (M^+). Anal. Calcd for $C_{45}H_{62}O_5$: C, 79.14; H, 9.15. Found: C, 78.97; H, 9.21.

2-Hexyl-3,6,7,10,11-pentakis(pentyloxy)triphenylene (11). 2-(2-butylethynyl)-3,6,7,10,11-pentapentyloxytriphenylene (**9**, 100 mg, 0.135 mmol) was dissolved in 20 mL of 1:1/THF:ethanol. 10% Palladium on activated carbon (14 mg, 0.013 mmol) was added, and the suspension was stirred under hydrogen for 12 h at room temperature. The mixture was filtered through Celite, and the solvent removed under vacuum. The crude product was chromatographed through silica gel with 60:40 CH_2Cl_2:hexanes to give 81 mg of a faintly yellow solid (81%): mp 82 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (m, 18H), 1.50 (m, 26H), 1.72 (m, 2H), 2.84 (t, J = 7.7 Hz, 2H), 4.23 (m, 10H), 7.72 (s, 1H), 7.82 (s, 2H), 7.89 (s, 1H), 7.92 (s, 1H), 8.15 (s, 1H); MS (EI^+) m/z 742.6 (M^+). Anal. Calcd for $C_{49}H_{74}O_5$: C, 79.20; H, 10.04. Found: C, 79.24; H, 10.09.

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