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Star-Shaped Discotic Oligomesogens Based on Radial Pentakisphenylethynylbenzene Moieties

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New monodisperse star-shaped discotic oligomesogens are presented which consist of three flat radial pentaalkyne building blocks connected with a central benzene linking unit via flexible alkyl spacers. Different alkyl substituents were attached to the periphery of the pentayne units in order to modify the molecular dimensions. The thermal properties of the star oligomers in their pure state and of donor−acceptor complexes with 2,4,7-trinitrofluoren-9-one (TNF) were investigated by polarizing microscopy, differential scanning calorimetry, and X-ray scattering. The pentayne oligomers as well as the binary mixtures with TNF exhibit a nematic-columnar (N_{Col}) mesophase. On the contrary, the corresponding hydroxy-substituted pentayne monomers display a nematic-discotic (N_D) liquid crystalline phase as pure compounds, and CT interactions with TNF lead to the induction of hexagonal columnar (Col_h) mesophases. The unexpected phase behavior of the oligomers and of the CT complexes derived there from is mainly the result of the molecular architecture arising from covalent linkage of the flat anisometric moieties.

Introduction

Mesogenic self-assembly is mainly governed by the molecular shape, space-filling effects, and microsegregation of incompatible parts of the constituent molecules, whereby conventional low molar mass thermotropic liquid crystals predominantly are designed in such a way that flexible chains are attached to just one rigid anisometric calamitic or disclike core. Segregation of the flexible tails from the rigid units is the main driving force for their self-organization.

Molecular architecture can be further tailored by covalent linkage of a defined number of form anisotropic molecular subunits. Thus, certain discotic dimers have been described with two equivalent disc-shaped groups linked via suitable spacers. Examples include derivatives of triphenylene,[1,2] benzene,[3,4] and multialkynes.[5] The mesophases of these dimers are isomorphic with those of the corresponding monomers.

To the best of our knowledge, the higher monodisperse discotic oligomers reported so far have been based on either three[6] or six[7] peripheral triphenylene groups attached to a connecting unit. These triphenylene oligomers display hexagonal columnar (Col_h) liquid crystalline phases like the respective triphenylene monomers.

Novel types of mesomorphic phase structures were described for nonsymmetric discotic charge-transfer twin molecules based on either a triphenylene[8] or a pentayne[9,10] donor core decoupled from a TNF acceptor by a flexible spacer. Rather unexpected phase types may also result from covalent linkage of molecular subunits with different anisometric shapes as it was found, i.e., for trimers consisting of two triphenylene cores which are connected via a rodlike rigid group[11] and for multiyne and triphenylene based disc−rod hybrid molecules additionally comprising an intramolecular acceptor function.[12,13]

The question arises whether mesophase morphologies of disc-shaped (pentayne) mesogens can be further regulated by carefully adjusting the molecular topology. The approach we followed involves covalent linkage of a defined number of flat pentayne building blocks to a central linking unit via flexible alkyl spacers (Figure 1). We present here a new family of monodisperse star-shaped pentaalkynylbenzene trimers. We will, in particular, focus on synthesis of the pentayne oligomers **2** and the thermal properties of the pure compounds and donor−acceptor complexes with 2,4,7-trinitrofluoren-9-one (TNF).

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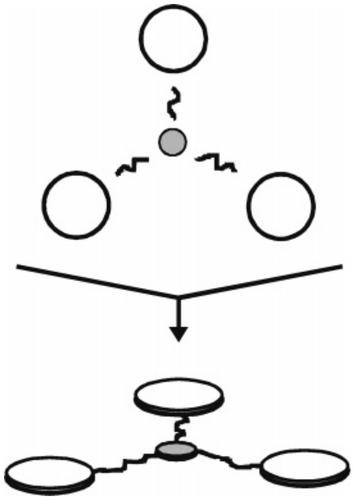
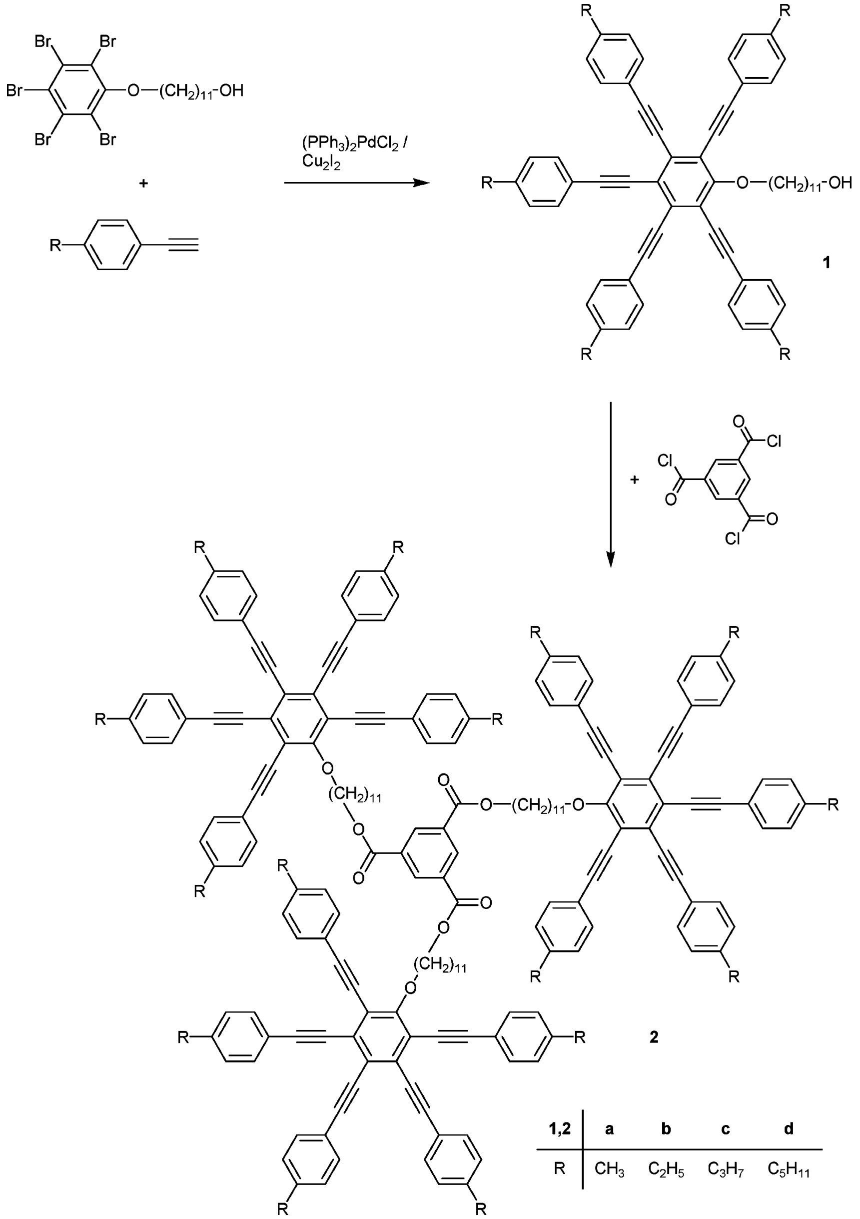


Figure 1. Starlike discotic oligomesogens with three rigid flat molecular subunits attached to a central linking unit.

Results

Synthesis. Synthesis of the new pentayne trimers **2** was carried out starting from the radial pentakis(arylethynyl)benzenes **1** carrying a terminal hydroxy substituent (Figure 2). Pentaynes **1a** and **1d** have already been described previously.[9,14] The newly synthesized 5-fold ethyl- and propyl-modified members **1b** and **1c**, respectively, were prepared by 5-fold palladium-catalyzed C,C-coupling of 11-(pentabromophenoxy)undecan-1-ol with the appropriate 4-alkyl-substituted phenylacetylenes according to the method given in ref 14. The star-shaped oligomers **2** with three multiyne groups linked to a central benzene ring via ester bonds were obtained by reaction of compounds **1** with 1,3,5-benzenetricarbonyl trichloride in the presence of pyridine and catalytic amounts of 4-(dimethylamino)pyridine.

The central linking benzene nucleus and the spacer length were kept constant for all compounds **2**, while different peripheral alkyl substituents were attached to the pentayne units in order to modify the molecular dimensions. Structural proof of the star oligomers **2** is based on spectroscopic data. No impurities could be detected by NMR spectroscopy and HPLC (i.e., compound **2c**: purity 99.75%). Full details are given in the Experimental Section.



1,2	a	b	c	d
R	CH_3	C_2H_5	C_3H_7	C_5H_{11}

Figure 2. Synthesis of the starlike pentayne trimers **2**.

Table 1. Phase-Transition Temperatures (°C) for the Hydroxy-Substituted Pentaalkynylbenzene Compounds 1 and Star-Shaped Pentayne Oligomers 2 Determined by Differential Scanning Calorimetry on Second Heating (10 K min^{-1})[a]

compound	phase transitions				
1a[9]	Cr	171.6 (43.9)	N_D	226.6 (0.5)	I
1b	Cr	122.2 (26.3)	N_D	147.3 (0.2)	I
1c	Cr	90.0 (19.3)	N_D	135.5 (0.1)	I
1d[14]	Cr	67.0 (25.8)	N_D	94.2 (0.2)	I
2a	Cr	173.6 (68.4)			I
	Cr	[148.0 (28.9)]	N_{Col}	[172.9 (0.4)]	I
2b	Cr	110.8 (45.0)	N_{Col}	157.9 (0.4)	I
2c	T_g	24.0	N_{Col}	141.9 (0.6)	I
2d	T_g	−12.43	N_{Col}	23.6 (4.7)	I

[a] Transition enthalpies (kJ mol^{-1}) are given in parentheses and monotropic phase transitions in square brackets. Cr = crystalline; T_g = glass temperature; N_D = nematic discotic; N_{Col} = nematic columnar; I = isotropic.

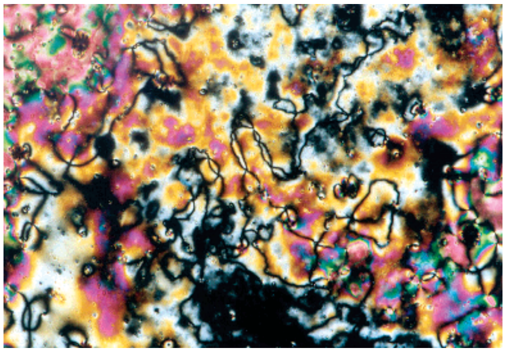


Figure 3. Photomicrograph of the mesophase texture of oligomer **2b** at 155.6 °C; first cooling at 1 K min^{-1}.

Thermal Properties of the Pentayne Monomers 1 and Star Oligomers 2. The hydroxy-substituted pentaalkynes **1a−d** exhibit an enantiotropic nematic-discotic (N_D) mesophase within the temperature range given in Table 1. The melting as well as isotropization temperatures decrease with increasing chain length of the peripheral alkyl chains.

The starlike multiyne oligomers **2** exhibit Schlieren textures between crossed polarizers on cooling from the isotropic melts (Figure 3). The thermal fluctuations are quite similar to those observed microscopically for the monomers **1** and point to a low viscosity within the mesophases. This behavior contrasts that of mesomorphic polymers which usually exhibit high viscous mesophases.

In contrast to the appropriate monomer **1a,** the methyl-substituted pentayne oligomer **2a** exhibits only a monotropic mesophase on cooling from the isotropic liquid. Increasing the chain length of the peripheral alkyl substituents leads to enantiotropic mesomorphism in the case of the higher homologues **2b−d**. The ethyl-modified multiyne oligomer **2b** forms a crystalline solid when it is cooled from the mesophase.

Further elongation of the flexible alkyl chain leads to suppression of crystallization. The liquid crystalline phases of **2c** and **2d** can be quenched into a glassy state. However, the glass-transition as well as isotropization temperatures are very low for the pentyl-substituted compound **2d**. An endotherm is detectable for the propyl-substituted star-shaped multiyne **2c** by DSC at 51 °C on heating, which is due to thermally induced crystallization. The endotherm is followed by remelting to the mesophase before the transition to the isotropic phase occurs. However, without thermal treatment we found the anisotropic glassy state to be stable for several months.

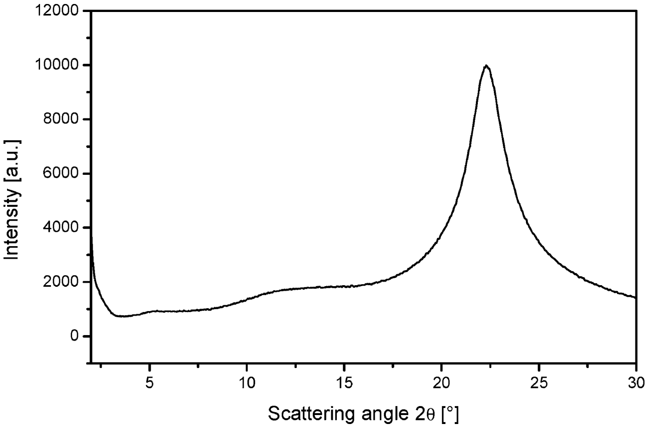


Figure 4. Wide-angle X-ray diffractogram of the propyl-substituted star-shaped pentaalkyne trimer **2c**.

The optical textures observed for the oligomeric pentaalkynylbenzene derivatives **2** may be indicative of a nematic-discotic (N_D) but also for a nematic-columnar (N_{Col}) liquid crystalline phase. X-ray investigations were performed to determine the phase type in detail. Figure 4 shows the wide-angle X-ray diffractogram of the propyl-substituted member **2c**.

One distinct reflection is present in the wide-angle region corresponding to a spacing of 0.39 nm. Only a diffuse halolike reflection with low intensity is found in the small-angle regime.

For a more quantitative analysis on the extent of order within the mesophase, the correlation length l, as a measure of the length scale of the positional order, was calculated using the Scherrer equation $l = 0.9\lambda/w_{1/2} \cos \theta$.[15] λ is the wavelength of the incident X-ray beam (Cu Kα = 0.154 nm). $w_{1/2}$ is the full-width at half-maximum of the reflection, and the diffraction angle θ is the maximum of the reflection. Both values are easily determined after fitting the X-ray pattern with Lorentzian profiles. Accordingly, analysis of the wide-angle reflection gives a correlation length of 5.78 nm. This value is significantly larger than the correlation length reported for the low-ordered nematic-discotic (N_D) phase,[16] but it is of the same order of magnitude as correlation lengths for columnar phases along the columnar direction.[17] Therefore, it is most reasonable to suggest that the wide-angle reflection is mainly governed by a close face-to-face packing of the aromatic pentayne cores rather than by the liquidlike ordered flexible alkyl segments.

Taking all these findings into account we propose that the pentayne star trimers **2** display a nematic-columnar (N_{Col}) liquid crystalline phase.[17−19] This conclusion is further supported by the fact that the enthalpy for the transition of compounds **2** from their mesophases to the isotropic liquid are of the same order of magnitude as those found for the clearing transitional enthalpies of charge-transfer-induced

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Table 2. Phase-Transition Data for Selected Binary Mixtures of the Pentaynes 1 and 2 with 2,4,7-Trinitrofluoren-9-one (TNF); Data from DSC, Second Heating at 10 K min^{-1} [a]

mixture	phase transitions						
1a/TNF (1:1)[10]	Cr	119.9 (7.1)	N_D	219.3 (0.1)			I
1b/TNF (1:1)	Cr	104.9 (18.8)[b]	Col_h	140.5 (0.8)	N_D	152.3 (0.2)	I
1c/TNF (1:1)	T_g	−14.3	Col_h	134.5 (3.0)			I
1d/TNF (1:1)[14]	Cr		Col_h	110.0 (4.7)			I
2a/TNF (1:3)	Cr	150.7 (9.2)	N_{Col}	166.9 (1.1)			I
2b/TNF (1:3)	T_g	30.7	N_{Col}	111.5 (1.2)			I
2c/TNF (1:2)	T_g	13.2	N_{Col}	97.7 (0.5)			I
2c/TNF (1:1)	T_g	15.0	N_{Col}	102.1 (0.38)			I
2d/TNF (1:3)	T_g	−15.6	N_{Col}	28.5 (0.7)			I

[a] Transition enthalpies (kJ mol^{-1}) in brackets. Cr = crystalline; N_D = nematic discotic; N_{Col} = nematic columnar; Col_h = hexagonal columnar; I = isotropic. [b] Polymorphism was observed in the solid state. The phase-transition temperature is given for the highest melting modification. The enthalpy value was obtained by integration of the broad unresolved peak.

nematic-columnar phases formed by binary mixtures of multiethynylbenzene compounds with TNF.[14,19]

Binary Mixtures of the Pentaalkynes 1 and Star-Shaped Oligomesogens 2 with Electron Acceptors. Radial multialkynylbenzene compounds are known to form charge-transfer (CT) complexes with electron acceptors such as 2,4,7-trinitrofluoren-9-one (TNF).[20]

The equimolar mixture of the methyl-modified pentayne **1a** and TNF exhibits a nematic-discotic (N_D) mesophase but with a broader temperature range than the pure compound **1a**.[10] The 1:1 composition **1b**/TNF displays an induced hexagonal columnar (Col_h) liquid crystalline phase followed by a N_D phase at more elevated temperatures. Doping with one equivalent of TNF leads to induction of a Col_h mesophase, exclusively, in the case of the higher homologues **1c** and **1d** substituted with peripheral propyl and pentyl chains, respectively.The mixtures of the pentayne star oligomers **2** with TNF show Schlieren textures between crossed polarizers similar to the optical textures of the pure compounds **2**. Therefore, induction of higher ordered columnar mesophases with parallel alignment of the columns on a two-dimensional lattice can be excluded.

The monotropic phase of the pure oligomesogen **2a** is replaced by an enantiotropic mesophase in the case of mixtures with TNF. Interaction with the acceptor leads to a broadening of the mesomorphic temperature range for the ethyl-substituted oligomer **2b**. However, the clearing temperatures of oligomers **2a**−**c** in mixtures with TNF are lower compared with the pure compounds. On the other hand, glass-forming tendencies are enhanced and no thermally induced recrystallization is observed for mixtures **2b**−**d**/TNF upon heating. Remarkably, we do not find a significant dependence of the phase-transition temperatures of the mixed systems **2**/TNF on the concentration of the TNF dopant.

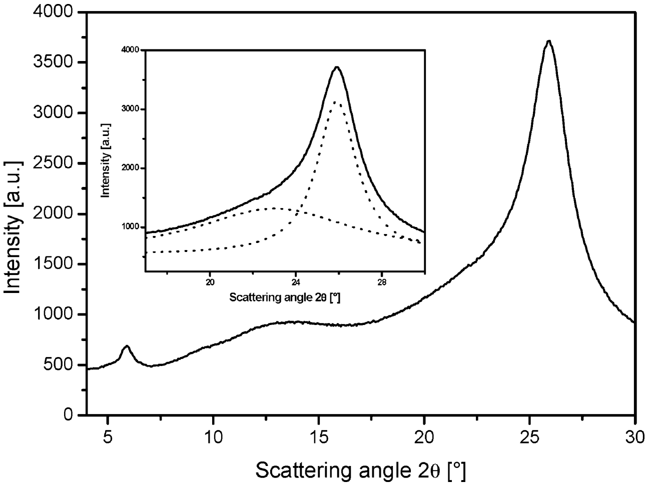

Figure 5. WAXS diffractogram of the (1:2) CT complex of the star-shaped pentayne oligomer **2c** with the acceptor TNF. The inset shows the splitting of the wide-angle reflection into two separate maxima.

Figure 5 displays the wide-angle X-ray diffractogram of the (1:2) mixture of the propyl-substituted pentaalkyne trimer **2c** with TNF. One distinct but relatively broad reflection is visible in the small-angle region corresponding to a spacing of 1.5 nm which can be attributed to the side-by-side distance of the aromatic cores. Similar values have been reported for the mean intercolumnar distances of pentayne-based donor−acceptor twin and triple mesogens.[10,12] The intense wide-angle reflection could be analyzed as consisting of two maxima (inset in Figure 5). The broad halo with a maximum at a scattering angle of $2\theta = 23°$ originates from the liquidlike ordering of the flexible alkyl segments. The second reflection is indicative of a close face-to-face packing of the aromatic pentayne cores with a distance of 0.35 nm.

The WAXS diffractograms of both the undoped and the doped oligomer **2c** additionally display a diffuse halo in the intermediate scattering range indicative of the presence of short-range order. A tentative interpretation might be that the halo around 12° reflects a liquidlike packing of the benzene linker, connected with the flexible alkyl spacers, with a mean periodicity of about 0.7 nm. A more detailed interpretation would require a pair correlation analysis, which would become difficult due to the presence of the columnar reflections.

Most probably, the liquid crystalline structure of the CT complexes can be identified as a N_{Col} phase with a periodical distance of the donor and acceptor discs of 0.35 nm in the nematic columns. The intracolumnar correlation length evaluated from the separated intracolumnar reflection amounts to 7.3 nm. Hence, the CT interactions lead to a decrease of intracolumnar periodicity compared with the pure pentayne trimers **2**, the intracolumnar correlation length increases, and, as evident from the distinct small-angle reflection, the lateral correlation of the columns increases. It must be noted that the lateral distances are slightly smaller than the diameter of the pentayne cores (ca. 1.8 nm as estimated from CKP models). It suggests that the cores are interdigitated to some extent.[21]

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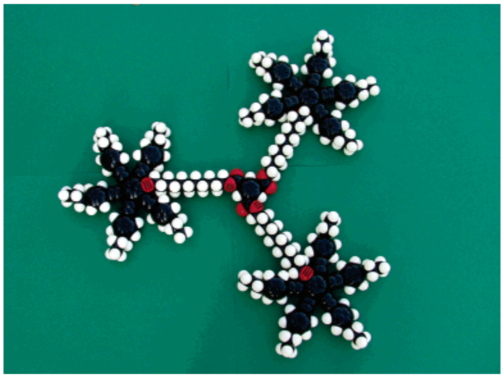

Figure 6. CPK model of the propyl-substituted star-shaped pentayne trimer **2c** with an all-trans conformation of the undecyl spacers.

Discussion

Radial symmetric hexaalkynylbenzene compounds bearing six peripheral long flexible chains[22,23] and 5-fold alkyl-substituted pentakis(phenylethynylbenzene) ethers[14,24,25] are well established to exhibit a thermotropic nematic-discotic (N_D) phase in their pure states. Doping with an electron acceptor such as TNF leads to induction of a hexagonal columnar (Col_h) liquid crystalline phase.[20] The same phase behavior is valid for the hydroxyundecyloxy-modified pentaynes **1** used here as the starting materials, except the N_D phase-forming CT complex of the methyl-substituted compound **1a**. A nematic-columnar mesophase has been reported for an LC polymer attached with pentaalkyne side groups[21] and for CT complexes of peripherally unsubstituted pentakis-(phenylethynyl)benzene derivatives.[14,19,26] Yet, the N_{Col} phases identified for the pure star pentaynes **2** and for their donor−acceptor complexes with TNF differ from the phase behavior known so far for structurally related alkyl-substituted low molar mass pentaalkynes.

Obviously the formation of columns of the oligomesogens **2** is not predominantly effected by the anisometric shape of the pentayne moieties but by the covalent linkage of the flat enlarged building blocks via flexible spacers to the central benzene nucleus. Thus, the molecular topology preorganizes the mesogenic units and a columnar arrangement is preferred over the nematic-discotic phases exhibited by the pentayne monomers themselves.

As evident from CPK models (Figure 6), the undecyl spacer and the bulky phenyl linking unit exceed the diameter of the individual pentayne building blocks. Accommodation of the linker into a hexagonal lattice would require a random distribution around the column axis to provide a circular shape of the individual columns. However, the mobility of the pentaalkyne subunits within the columns is reduced owing to their starlike covalent linkage.

Moreover, the flexibility of the spacers within the mesophase most likely causes a steric repulsion between the periphery of the pentayne fragments and the benzene linker. The steric stress partly can be avoided by tilting of the pentayne moieties out of the plane of the whole molecule, which additionally disfavors a parallel columnar alignment. This assumption is further supported by the strong decrease of the mesophase stability found for the pentyl-substituted homologue **2d**. Increasing the diameter of the pentayne cores by keeping constant the spacer length should increase the steric frustration and, therefore, the out-of-plane tilt of the anisometric cores. Thus, the spacers along with the linking units act as an element of steric disturbance[19,26] which prevents a parallel packing of the columns. Instead, the columns order in a nematic manner. The structural model for the nematic-columnar mesophase displayed by the star oligomers is presented schematically in Figure 7.

Figure 7. Structural model for the nematic-columnar mesophase formed by the star-shaped pentayne oligomers **2**.

The color change from a blue fluorescence to orange that appears by mixing pentaynes **1** and **2** with the acceptor clearly indicates a charge transfer. However, both attractive interactions provided by electron donor−acceptor interactions perpendicular to the planes of the aromatic cores[27] and attractive electrostatic quadrupole interactions[28] may contribute to attractive interactions between the components. An intercalated structure with close face-to-face contacts between the pentayne donor groups of compounds **1** and **2** and the electron acceptor TNF is strongly preferable. Therefore, it is most likely that intracolumnar interactions through doping with TNF are enhanced not only in the case of the monomers **1** but also for the pentayne oligomers **2**. It is, however, apparent that even for the doped systems **2**/TNF the steric repulsion between the individual columns due to the benzene linking units dominates, not allowing for a parallel columnar alignment on a two-dimensional lattice.

Thus, the thermal behavior of binary mixtures of the pentayne star oligomers **2** with electron-deficient TNF confirms the role of the central benzene linker with respect to suppression of a higher ordered columnar mesophase very distinctly.

Conclusions

We synthesized the first members of a new family of monodisperse star-shaped discotic oligomesogens which are composed of three flat radial pentaalkyne building blocks linked to a central benzene moiety via alkyl spacers. The

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compounds display a nematic-columnar (N_{Col}) phase. Even attractive interactions with TNF acting as an electron acceptor do not favor a columnar mesophase with the columns aligned parallel on a two-dimensional lattice. Mixtures of the pentayne oligomers with TNF display N_{Col} phases as well. The nematic-columnar arrangement of the pentayne blocks is mainly governed by the reduced intramolecular mobility of the anisometric subunits due to the covalent linkage and steric repulsion between the periphery of the mesogenic cores and the bulky linker which frustrates regular packing of the columns into highly ordered arrays. The N_{Col} phase is intermediate in the transition from nematic-discotic to hexagonal-columnar organization. Regarding the N_D phase forming radial multialkynes grafted with peripheral flexible tails the N_{Col} phase of the oligomers means an upgrading of the mesomorphic order. With respect to CT-induced Col_h mesophases of multialkynes, a downgrading of the molecular order is provided. The star-shaped molecular topology of the new oligomesogens, thus, offers new access toward controlling liquid crystalline structures of multiyne-based mesogens.

Experimental Section

Preparation of the Hydroxy-Substituted Pentakis(phenylethynyl)benzene Derivatives 1. Compounds **1a** and **1d** have been described previously.[9,14] The new homologues **1b,c** were prepared as follows.

A 2.30 g (3.5 mmol) amount of 11-(pentabromophenoxy)-undecanol,[14] 35 mmol of 5-ethylphenylacetylene or 5-propylphenylacetylene (both purchased from SYNTHON Chemicals GmbH, Wolfen), 350 mg of triphenylphosphine, 175 mg of copper(I) iodide, and 175 mg of bis(triphenylphosphine)palladium(II) chloride in 35 mL of dry triethylamine were stirred for 24 h at 100 °C under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into a mixture of 130 mL of ice/water and 130 mL of hydrochloric acid. Extraction with dichloromethane, drying of the organic solution with sodium sulfate, and evaporation of the solvent gave the crude products. Purification was performed by flash chromatography (Kieselgel 60, 230−400 mesh, E. Merck, Darmstadt) with light petroleum/ethyl acetate (10:3) as eluent followed by recrystallization from ethanol.

11-{Pentakis[(4-ethylphenyl)ethynyl]phenoxy}undecan-1-ol, ***1b.*** Yield: 59%, $C_{67}H_{68}O_2$ (M_W 905.3). IR (KBr): $\nu = 2200$, 1510, 1420 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.26$ (t, 3H, CH_3, $J = 7.5$ Hz), 1.29−1.63 (m, 16H, CH_2), 1.92 (m, 2H, CH_2), 2.68 (q, 10H, CH_2, $J = 7.5$ Hz), 3.62 (t, 2H, CH_2−OH, $J = 6.5$ Hz), 4.36 (t, 2H, CH_2−O−phenyl, $J = 6.3$ Hz), 7.18−7.24 (m, 10H, phenyl), 7.51−7.56 (m, 10H, phenyl) ppm.

11-{Pentakis[(4-propylphenyl)ethynyl]phenoxy}undecan-1-ol, ***1c.*** Yield: 54%, $C_{72}H_{78}O_2$ (M_W 975,4). IR (KBr): $\nu = 2200$, 1510, 1420, 1340 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.96$ (t, 15H, CH_3, $J = 7.3$ Hz), 1.21−1.71 (m, 10H, CH_2, propyl and 16H, CH_2, undecyl), 2.62 (t, 10H, CH_2, $J = 7.5$ Hz), 3.63 (t, 2H, CH_2−OH, $J = 6.6$ Hz), 4.36 (t, 2H, CH_2−O−phenyl, $J = 6.4$ Hz), 7.16−7.19 (m, 10H, phenyl), 7.51−7.56 (m, 10H, phenyl) ppm.

Synthesis of Star-Shaped Oligomesogens 2. A 1.2 mmol amount of the appropriate 5-fold alkyl-substituted hydroxyundecyloxy pentakis(phenylethynylphenyl) ether **1** was dissolved in 10 mL of dry dichloromethane followed by addition of 5 mL of dry pyridine and 10 mg (0.1 mmol) of 4-(dimethylamino)pyridine. Under nitrogen atmosphere a solution of 100 mg (3.77 mmol) of 1,3,5-benzenetricarbonyl trichloride and 10 mL of dry dichloromethane was added dropwise with stirring at room temperature. Stirring was continued at room temperature for 24 h. The mixture was washed one time with water, three times with 1 N hydrochloric acid, and again two times with water. The organic solution was dried with sodium sulfate, and the solvent was evaporated under reduced pressure. Purification was performed by flash chromatography using Kieselgel 60, 230−400 mesh (E. Merck, Darmstadt). Details are given below.

Tris{11-[pentakis-(4′-methylphenylethynyl)phenoxy]undecyl}-trimesate, ***2a.*** One flash chromatogram with CH_2Cl_2/light petroleum (10:5) as eluent. Yield: 59%, $C_{195}H_{174}O_9$ (M_W 2661.6). IR (KBr): $\nu = 2200$ (C≡C), 1720 (C═O) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta =$ 1.25−1.93 (m, 54H, CH_2, undecyl), 2.37 (s, 45H, CH_3), 4.31−4.36 (m, 6H, CH_2−O−CO and 6H, CH_2−O−phenyl), 7.15 (m, 30H, phenyl), 7.49 (m, 30H, phenyl), 8.83 (s, 3H, phenyl) ppm.

Tris{11-[pentakis-(4′-ethylphenylethynyl)phenoxy]undecyl}trimesate, ***2b.*** One flash chromatogram with light petroleum/ethyl acetate (10:4) as eluent; one chromatogram with the same eluent system (10:2). Yield: 56%, $C_{210}H_{204}O_9$ (M_W 2871.9). IR (KBr): $\nu = 2206$ (C≡C), 1726 (C═O) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.26$ (t, 35H, CH_3, $J = 7.5$ Hz), 1.30−1.97 (m, 54H, CH_2, undecyl), 2.70 (q, 30H, CH_2, $J = 7.5$ Hz), 4.37 (m, 6H, CH_2−O−CO and 6H, CH_2−O−phenyl), 7.20−7.29 (m, 30H, phenyl), 7.53−7.58 (m, 30H, phenyl), 8.86 (s, 3H, phenyl) ppm.

Tris{11-[pentakis-(4′-propylphenylethynyl)phenoxy]undecyl}-trimesate, ***2c.*** One flash chromatogram with light petroleum/ethyl acetate (10:2) as eluent; one chromatogram with the same eluent system starting with 20:1 and then changing to 10:3. Yield: 68%, $C_{225}H_{234}O_9$ (M_W 3082.4). IR (KBr): $\nu = 2200$ (C≡C), 1725 (C═O) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.95$ (t, 45H, CH_3, $J = 7.3$ Hz), 1.25−1.91 (m, 30H, propyl and 54H, undecyl), 2.60 (t, 30H, propyl, $J = 7.5$ Hz), 4.35 (m, 6H, CH_2−O−CO and 6H, CH_2−O−phenyl), 7.15−7.17 (m, 30H, phenyl), 7.49−7.54 (m, 30H, phenyl), 8.83 (s, 3H, phenyl) ppm.

Tris-{11-[pentakis-(4′-pentylphenylethynyl)phenoxy]undecyl}-trimesate, ***2d.*** One flash chromatogram with light petroleum/ethyl acetate (10:1) as eluent. Yield: 63%, $C_{255}H_{294}O_9$ (M_W 3503.2). IR (KBr): $\nu = 2200$ (C≡C), 1730 (C═O) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, 45H, CH_3, $J = 6.5$ Hz), 1.26−1.91 (m, 90H, CH_2, pentyl and 54H, CH_2, undecyl), 2.62 (t, 30H, CH_2, pentyl, $J = 7.5$ Hz), 4.31−4.37 (m, 6H, CH_2−O−CO and 6H, CH_2−O−phenyl), 7.15−7.17 (m, 30H, phenyl), 7.49−7.54 (m, 30H, phenyl), 8.83 (s, 3H, phenyl) ppm.

Instrumental Details. IR spectra were obtained with an M80 spectrometer (Carl Zeiss Jena). ^{1}H NMR spectra were recorded using a Bruker AMX 300 spectrometer. HPLC was performed with a RP-18 column (250 × 4) using THF/H_2O (80/20 v/v) as the isocratic eluent at a flow rate of 0.7 mL/min and with an UV detector at 250 nm. Texture observations were made with an Olympus polarizing microscope fitted with a Linkam TMH/S 600 hot stage in conjunction with a Linkam TP 92 control unit. Photomicrographs were obtained with an Olympus OM-4 Ti system camera. Calorimetric investigations were performed with a Netzsch DSC 204 Phoenix. Wide-angle X-ray scattering analysis was carried out with a Siemens 5000 diffractometer.

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