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Arylethynyl-Substituted Tristriazolotriazines: Synthesis, Optical Properties, and Thermotropic Behavior

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 85th birthday

Keywords: Liquid crystals / Conjugated oligomers / Chromophores / Fluorescence / Nonlinear optics / Heterocycles

The synthesis of C_3-symmetrical tristriazolotriazines with conjugated arms and lateral alkoxy side chains was performed by a threefold condensation of cyanuric chloride with tetrazoles. Conjugated π segments include phenyl, tolane, and its phenylethynyl-elongated homologue. Disclike and a dendritic molecule have been obtained, and two compounds with a 3,4,5-tris(octyloxy) substitution form broad thermotropic mesophases. The linear optical properties, solvatochromism of the fluorescence, acidochromism, and the two-photon absorption efficiency of selected compounds are reported.

Introduction

Star-shaped conjugated compounds are of current interest as active materials for several electronic, optical, and nonlinear optical applications. A variety of stars composed of different core systems with high symmetry and π-conjugated branches have been investigated in recent times.[1] The two-dimensional π system allows an enhanced electronic interaction,[2] and these molecules are also good candidates for mesomorphous materials. The discovery by Chandrasekhar of liquid-crystalline mesophases formed by the self-assembly of disclike molecules[3] opened a large and continuously expanding area in organic synthesis and materials science.[4–6] Whereas calamitic liquid crystals (LCs) are probably the most prominent class of organic molecules for optoelectronic devices such as liquid-crystal displays (LCDs), technologies based on discotic LCs are only at their beginning.[7] These molecules can combine several advantageous properties such as self-healing of films,[8] fluorescence, and directed charge transport.[4,9] Possible applications include xerography, field-effect transistors, photovoltaic devices,[10] optical compensation layers for LC displays,[11] and light-emitting diodes.[12] Commonly, discotic molecules that form thermotropic mesophases have a flat structure comprising a rigid core, a ring of four to nine aliphatic side chains, and a high symmetry. The core is often a polycyclic hydrocarbon such as triphenylene or hexabenzocoronene, but three to six conjugated arms on a small central ring are also sufficient to meet the steric requirements.[13] In the molecular design of new cores for discotic molecules, nitrogen-containing heterocycles are receiving increasing attention, for example, phthalocyanine,[14] hexaazatriphenylene,[15] and tricycloquinazoline[16,17] are important central units. The incorporation of nitrogen atoms into the π-conjugated core allows tailoring of the frontier orbital shapes, optical and electrical properties, and intermolecular interactions such as those between neighboring molecules in a column.[18] Depending on the nature of the heterocycle, it is possible to synthesize n- and p-type semiconducting materials in which the structural features of the parent isocyclic system are retained.[19]

A threefold annulation of 1,2,4-triazoles to a 1,3,5-triazine can result in two C_3-symmetric tristriazolotriazines (TTT), both of which have a disc-shaped geometry (Figure 1). Whereas the molecular structures of both types have C_{3h} symmetry, the shape of the threefold substituted derivatives is also C_{3h} for **1** but D_{3h} for **2**. A century ago, Hofmann reported the first synthesis of a tristriazolotriazine.[20] The initially proposed structure **2** (R = NH_2) was proved to be **1** (R = NH_2) by Kaiser in 1953.[21] Only one further report of a tristriazolotriazine appeared in the 20th century. During his investigations on the ring transformations of tetrazoles,[22] Huisgen succeeded in the formation of a triphenyl-TTT with structure **1** (R = phenyl).[23] Despite their

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intriguing structural features, research interest in TTTs has only recently seen a revival. Tartakovsky reported the first TTTs with structure **2** (R = phenyl)[24] and Gallardo[25] and we[26] recognized that the Huisgen method offers a general route for the formation of disclike molecules with the ability to form thermotropic mesophases. The tristriazolotriazine **1** represents a new core for discotic liquid crystals. Herein, we describe star-shaped molecules **3**–**10** based on the tris[1,2,4]triazolo[1,3,5]triazine core **1** with three π-conjugated branches. The branches are phenyl, tolane, or phenylethynyl-extended tolane with flexible alkoxy or dialkylamino chains on the periphery. The syntheses, optical and thermal properties, and two-photon absorption experiments are reported.

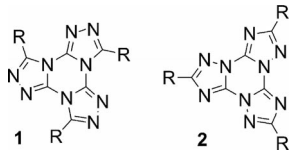


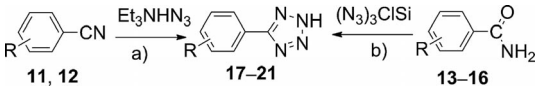
Figure 1. Isomeric tris[1,2,4]triazolo[1,3,5]triazines with C_3-symmetry **1** and **2**.

Discussion

Synthesis

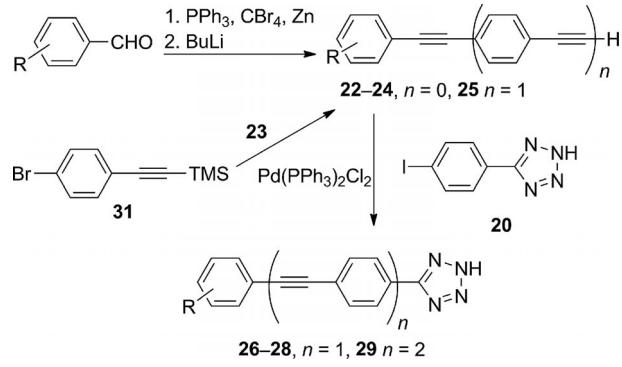
The acylation of tetrazoles with cyanuric chloride followed by threefold thermal elimination of nitrogen and ring closure to tristriazolotriazines[23] is the best available method for the synthesis of TTTs **1**. With minor modifications, this protocol proved to be suitable for the synthesis of TTTs carrying donor-substituted phenyl rings.[25,26]

The synthesis of TTTs **3**–**10** starts with typical alkylations of hydroxy- and amino-substituted benzene derivatives and their transformation to nitriles **11** and **12** or benzamides **13** and **14**.[27–29] The required phenyltetrazoles **17**–**19** can be prepared by the addition of hydrazoic acid or azides to benzonitriles;[30] for carboxylic acids as starting materials, their conversion to amides **15** and **16** followed by reaction with in situ generated triazidochlorosilane (TACS)[31] proved to be advantageous (Scheme 1). The addition of triethylammonium azide to nitriles **11** and **12** led to the tetrazoles **17** and **18** in good yields. The TACS route gave only a moderate yield of donor-substituted **19** but very good yields of iodo- and bromo-substituted tetrazoles **20** and **21**. The latter were used as synthons for the preparation of phenylethynyl-elongated tetrazoles **26**–**30** by Pd-catalyzed coupling with suitable phenylacetylenes.

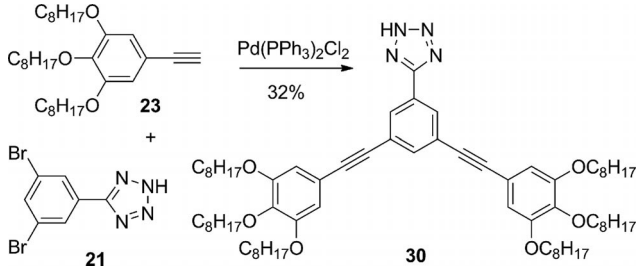


Scheme 1. Synthesis of phenyltetrazoles; R = 4-OC_6H_{13} (**17**): 68% (a), 90% (b); R = 4-N(C_6H_{13}) (**18**): 83% (a); R = 3,4,5-(OC_8H_{17})$_3$ (**19**): 47% (b); R = 4-I (**20**): 89% (b); R = 3,5-Br_2 (**21**): 95% (b).

For the synthesis of tetrazoles **26**–**30** with a larger conjugated system, the Sonogashira–Hagihara coupling of phenyl acetylenes to iodo- or bromo-substituted phenyltetrazoles **20** and **21** was chosen (Scheme 2). The donor-substituted phenylacetylenes **22**–**24** were prepared from the corresponding aldehydes[28,32–34] by ultrasound-supported Corey–Fuchs reactions. For the elongation of the conjugated system of **23** by a further phenylacetylene unit, the Pd-catalyzed coupling of **23** to trimethylsilyl-protected (TMS-protected) bromophenylacetylene **31**[35] followed by deblocking gave **25** in 46% yield (Scheme 2). A significantly higher yield (65%) of **25** was obtained when the coupling of **23** to **31** was performed under Negishi conditions. Moderate-to-good yields were obtained in the Sonogashira coupling reactions of these alkynes with iodophenyltetrazole **20** (**26**: 75%, **27**: 62%, **28**: 73%, **29**: 65%), but a yield of only 32% of the branched **26** was obtained in the twofold coupling with the less reactive **21** (Scheme 3). The lower yield for **27** results from decomposition of this compound during purification and storage.



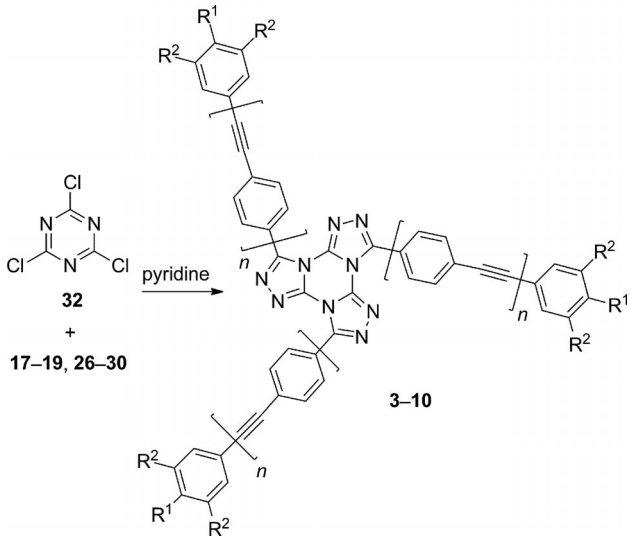
Scheme 2. Synthesis of phenylacetylenes and tolanyltetrazoles R = 4-OC_6H_{13} (**26**): 75%; R = 4-N($C_{12}H_{25}$) (**27**): 62%; R = 3,4,5-(OC_8H_{17})$_3$ (**23**): 92%, (**25**): 46% (Sonogashira), 65% (Negishi), **28**: 73%, **29**: 65%.



Scheme 3. Synthesis of branched di(phenylethynyl)phenyltetrazole **30**.

Tetrazoles **17**–**19** and **26**–**30** were dissolved in an inert solvent by the aid of a small excess of pyridine before cyanuric chloride **32** was added. Heating the mixture to reflux initiated threefold nucleophilic substitution followed by elimination of nitrogen and ring transformation (Scheme 4). The yields of the chromatographically purified products are good for alkoxyphenyl- and dihexylaminophenyl-TTTs **3**–**5**

(77–92%), moderate for the linear phenylethynyl oligomers (**6**–**9**), and only 37% for the branched di(phenylethynyl)-phenyl-TTT **10** (Table 1).



Scheme 4. Synthesis of phenyl- and tolanyl-substituted TTTs **3**–**10**.

Table 1. Synthesis of TTTs.

Entry	R^1	R^2	*n*	Yield [%]	M.p. [°C]
3	hexyl-O-	H	0	71	123
4	$hexyl_2N$-	H	0	71	168
5	octyl-O-	octyl-O-	0	74	127
6	hexyl-O-	H	1	45	245
7	$dodecyl_2N$-	H	1	38	135
8	octyl-O-	octyl-O-	1	66	81
9	octyl-O-	octyl-O-	2	38	159
10	H	3,4,5-tris(octyloxy)-phenylethynyl	0	37	90

Table 2. Linear optical properties of TTTs in different solvents and in the solid state.

Entry	Solvent[a,b]	λ_{max} /nm	log ε	λ^F_{max} /nm[c]	$\Delta\tilde{\nu}^{St}$ /cm^{-1}
3	cyclohexane	289	4.72	347	5784
	toluene	291	4.72	355	6195
	dichloromethane	288	4.68	367	7474
	acetonitrile	281	4.71	365	8190
	ethanol	284	4.73	381	8964
	film	280	–	368	–
4	cyclohexane	340	4.74	373	2602
	toluene	342	4.74	384	3198
	dichloromethane	348	4.71	417	4755
	acetonitrile	339	4.73	422	5802
	ethanol	343	4.73	425	5625
	film	335	–	412	–
5	cyclohexane	302	4.63	393	7667
	toluene	303	4.66	385	7029
	dichloromethane	298	4.59	410	9167
	film	293	–	395	–
6	cyclohexane	334	5.03	372	3058
	toluene	334	5.04	381	3694
	dichloromethane	331	5.05	422	6515
	acetonitrile	324	5.00	428	7500
	ethanol	326	5.01	428	7310
	film	338	–	454	–
7	cyclohexane	376	5.08	420	2786
	toluene	381	5.04	446	3825
	dichloromethane	385	5.03	515	6556
8	cyclohexane	333	5.10	401	5092
	toluene	337	5.06	422	5977
	dichloromethane	336	5.02	478	8841
	film	331	–	437	–
9	cyclohexane	347	5.32	398	3693
	toluene	349	5.26	415	4557
	dichloromethane	349	5.28	487	8119
	film	343	–	448	–
10	cyclohexane	307	5.23	421	8820
	toluene	308	5.19	419	8601
	dichloromethane	307	5.22	491	12206
	film	299	–	423	–

Optical Properties

Owing to the large number of lipophilic side chains on the periphery, all TTTs are highly soluble in nonpolar solvents. Except for **4**, **7**, and **10**, the TTTs are colorless, and all are fluorescent in the solid state as well as in solution. Their linear optical properties are collected in Table 2.

All TTTs show a strong absorption band in the UV and are intensively fluorescent with emission maxima ranging from the UV to the blue part of the visible spectrum. In solutions of the TTTs in the good solvent toluene, donor substitution and extension of the π-conjugated system cause strong redshifts of the absorption and emission maxima. TTT **3** absorbs with λ_{max} = 291 nm, an additional 3,5-dialkoxy substitution (**5**) slightly shifts the absorption band to the red ($\Delta\tilde{\nu}$ = 1361 cm^{-1}), but the absorption of **4** with the dihexylamino donor is strongly shifted to lower energy ($\Delta\tilde{\nu}$ = 5125 cm^{-1}). Like an increased donor strength, an extension of the conjugated system by one phenyleneethynylene unit results in significant bathochromic shifts of $\Delta\tilde{\nu}$ = 4424 (**3**→**6**), 2993 (**4**→**7**), and 3330 cm^{-1} (**5**→**8**). This effect decreases if a second phenyleneethynylene unit separates the donor-substituted end group and the acceptor TTT: the absorption λ_{max} of **9** is 349 nm, only 1020 cm^{-1} more on the red side than that of the lower homologue **8**. The effect of the increasing conjugation length is overcompensated by a decrease in the donor–acceptor interaction.[36] As the *meta* linkages in **10** inhibit the donor–acceptor interaction, the absorption λ_{max} is 308 nm.

The fluorescence of the TTTs in toluene is separated by large Stokes shifts $\Delta\tilde{\nu}^{St}$ from their absorption. These shifts of up to $\Delta\tilde{\nu}^{St}$ = 7029 cm^{-1} for the alkoxy-TTTs **3** and **5** decrease with extension of the π system by a phenylethynylene unit to $\Delta\tilde{\nu}^{St}$ = 3694 (**6**) and 5977 cm^{-1} (**8**) and with a further phenyleneethynylene unit to $\Delta\tilde{\nu}^{St}$ = 4557 cm^{-1} (**9**). The smallest Stokes shifts in this series were observed for the amino-substituted TTTs **4** and **7**.

The UV/Vis absorption of TTTs is only weakly influenced by solvent polarity. A small redshift from cyclohexane to toluene is generally followed by a weak negative solvatochromism. Contrary to the absorption, the fluorescence of all compounds is strongly positively solvatochromic. Comparing solutions in cyclohexane and in dichloromethane, bathochromic shifts $\Delta\tilde{\nu}$ increase with the conjugation

length (**5**: 1055 cm^{-1}, **8**: 4017 cm^{-1}, **9**: 4205 cm^{-1}) as well as with the electron-donating capability of the substituent (**3**: 1570 cm^{-1}, **4**: 2829 cm^{-1}). These data indicate a strong coupling of the lateral donors through the π bridge with the central acceptor. The strong solvatochromism of the fluorescence of these octupolar dyes can result in a localization of the excitation on one of the dipolar donor–π-bridge–triazole branches[37,38] as the electronic coupling between the arms is only small.

The huge Stokes shifts of $\Delta\tilde{\nu}$ = 8601–12206 cm^{-1} displayed by dendritic TTT **10** indicate a strong stabilization of the excited state, probably by rotation of one of the 3,5-bis-phenylethynylbenzene dendrons around the TTT–phenyl bond at the sterically congested periphery of the dendrimer.

Compared to those of the solution spectra, the absorption maxima of spin-coated films of **3**–**10** are shifted to higher energies, but the emission maxima of the films are located between the positions of the maxima recorded for the toluene and dichloromethane solutions.

The addition of up to 0.1 M of trifluoroacetic acid (TFA) to solutions of alkoxy-TTTs in dichloromethane does not significantly change the electronic spectra. However, the electronic spectra of amino-TTT **4** are sensitive towards protonation, as illustrated in Figure 2. Small amounts of TFA in dichloromethane (10^{-6} to 10^{-5} M) cause a hyperchromism of the long-wavelength absorption band (λ_{max} = 348 nm). With higher concentrations (10^{-4} to 10^{-3} M), the intensity of this band drops to the initial value combined with a small increase of the band at higher energy (λ_{max} = 268 nm). In 10^{-2} M TFA, this band becomes the main absorption, and the long-wavelength band strongly decreases in intensity and is slightly shifted to the red (λ_{max} = 358 nm); the long-wavelength band completely vanishes in 0.1 M TFA. Like the absorption, the fluorescence efficiency (λ^{F}_{max} = 420 nm) increases with small amounts of TFA and decreases with more TFA. In 10^{-3} M TFA, the band at λ^{F} = 420 nm has only 15% of the original efficiency, but simultaneously a new shoulder at λ^{F} = 518 nm is visible and becomes the main band in 10^{-2} M TFA. As the absorption band at λ = 350 nm vanishes in 0.1 M TFA, no emission of **4** could be observed upon excitation with λ^{exc} = 350 nm, but irradiation into the high-energy maximum (λ^{exc} = 270 nm) gives a new emission in the UV at λ^{F}_{max} = 345 nm. The same emission is observed if **4** in 10^{-2} M TFA is excited at λ^{exc} = 270 nm. The absorption maximum of protonated **4** (λ_{max} = 268 nm) corresponds to that of a tristriazolotriazine with simple octyl side chains (λ_{max} = 248 nm),[39] and the emission maximum matches that of a TTT with three *m*-tolyl substituents (λ^{F}_{max} = 346 nm).[39]

The changes in the absorption spectra of **4** result from simultaneous protonation of the peripheral amino groups; this inverts the donor effect of the amine to a weakly accepting ammonium group. The effect of TFA on the emission is more interesting: in 10^{-2} M TFA, excitation at λ^{exc} = 350 nm gives an emission at λ^{F}_{max} = 520 nm, shifted by $\Delta\tilde{\nu}$ ≈ 4579 cm^{-1} to the red. This emission can be attributed to a species with a protonated triazole ring and, therefore, a strengthened donor–acceptor substitution. Similar protonations of aniline-substituted "nonbasic" heterocycles have been observed recently.[40] On the other hand, excitation with λ^{exc} = 250 nm under the same conditions causes exclusively an emission at λ^{F}_{max} = 350 nm from a species with a protonated amino group. The emission bands of the two protonated species of **4** in 10^{-2} M TFA are separated by ca. 9340 cm^{-1}, without an indication for a proton transfer in the excited state [excited-state intramolecular proton transfer (ESIPT)].

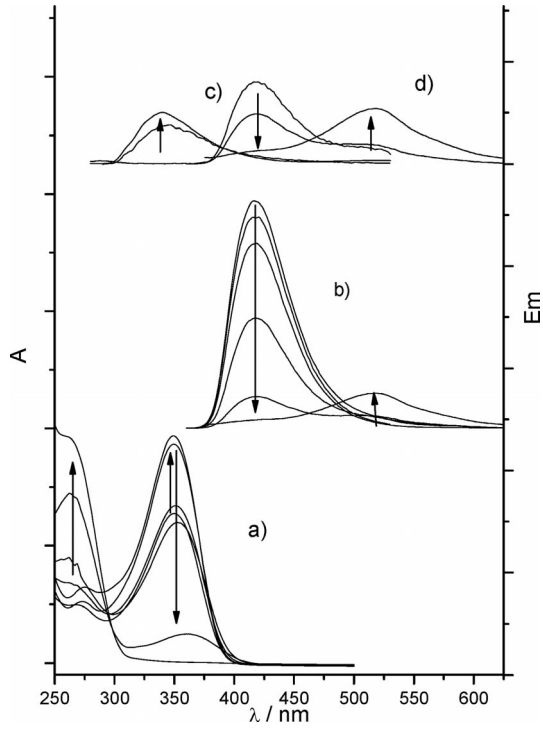


Figure 2. Electronic spectra of **4** in dichloromethane with increasing concentrations of TFA (10^{-5} to 10^{-1} M): (a) absorption spectra, dichloromethane, 10^{-1} M TFA; (b) fluorescence in dichloromethane and 10^{-2} M TFA, excitation at 345 nm; (c) fluorescence in 10^{-3} to 10^{-1} M TFA, excitation at 270 nm; (d) fluorescence in 10^{-4} to 10^{-2} M TFA, excitation at 345 nm.

Two-Photon Absorption

The large π systems of TTTs **8** and **9** together with their solvatochromic fluorescence are good prerequisites for efficient two-photon absorption properties. The two-photon-induced fluorescence measurements (TPIF) were performed with solutions of **8** and **9** in cyclohexane (CH) and dichloromethane (DCM); fluorescein (in H_2O, pH = 12) and rhodamine B (in methanol) were used as reference substances (R). The available two-photon excitation range was 735–810 nm. To determine the two-photon cross-section of the sample (S), it is necessary to compare its efficiency with that of a reference sample (R) by using the following relationship for a two-photon absorption cross-section [Equation (1)]:[41]

$$\sigma^{S}_{TPA} = \sigma^{S}_{TPA}\frac{\langle F\rangle_S C_R \eta_R n_S^2}{\langle F\rangle_R C_S \eta_S n_R^2} \quad (1)$$

$<F>$ is the fluorescence signal collected by the detector, C is the compound concentration, η is the fluorescence quantum yield, and n is the refractive index of the solution. The used $<F>$ value is corrected for the detector response curve, the filter transmittance, and the reabsorption of the emission spectrum.

The one- and two-photon absorption (TPA) spectra of **9** in dichloromethane are shown in Figure 3. In the wavelength range studied, the TPA spectra of both TTTs **8** and **9** show the same trend as the linear absorption spectra, but the available excitation range was not wide enough to reach maxima in the TPA spectra. This is more evident for **8** as its linear absorption peaks deeper in the UV region.

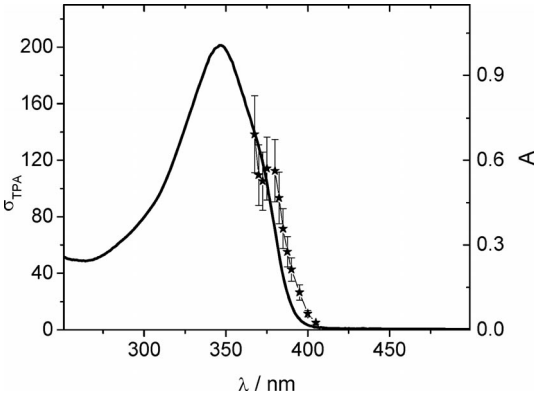


Figure 3. One- (–) and two-photon (∗) absorption spectra of TTT **9**; two-photon absorption spectrum with half-wavelength scale.

The similarity of the one- and two-photon spectra confirms the prediction for non-centrosymmetric molecules: the same electronic levels are allowed by one- and two-photon absorption processes.[38] The extension of the conjugated system of **8** with an additional phenyleneethynylene segment (**9**) results in a significantly enhanced linear extinction coefficient ε_{max}, but this is strongly superseded by the increase of the two-photon absorption cross-sections (within the available excitation range). The Φ_F and σ_{TPA} values of **8** and **9** are summarized in Table 3. Contrary to the hypochromism of the linear absorption as the solvent polarity increases, the maximum TPA values for both stars in cyclohexane are lower than the values measured in the dipolar solvent dichloromethane. The two-photon excited fluorescence spectra of these compounds were identical for three different excitation wavelengths (λ^{TPA} = 750, 760, and 780 nm) and also very similar to the one-photon emission spectra recorded with a common spectrofluorometer.

Table 3. Average fluorescence quantum yields Φ_F and two-photon absorption cross-sections σ_{TPA} at λ_{TPA} = 740 nm.

Entry	Solvent	ε_{max} /L mol^{-1} cm^{-1}	Φ_F	σ_{TPA} /GM
8	CH	$1.25\times10^5 \pm 7.50\times10^3$	0.5 ± 0.02	20 ± 2
8	DCM	$1.05\times10^5 \pm 6.30\times10^3$	0.77 ± 0.04	58 ± 6
9	CH	$2.11\times10^5 \pm 1.27\times10^3$	0.50 ± 0.09	140 ± 27
9	DCM	$1.90\times10^5 \pm 1.14\times10^4$	0.59 ± 0.09	200 ± 33

Thermal Properties

The thermal properties of the TTTs were studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Disclike molecules with a balanced ratio between the size of the rigid core and the flexible side chains can form thermotropic mesophases. Whereas a single hexyloxy chain per phenyl group on a TTT (**3**) is not sufficient for liquid-crystalline behavior, a threefold 3,4-didodecyloxy substitution results in the formation of a broad (92.2–207.6 °C) mesophase with Col_h structure.[25a] Accordingly, the TTTs with hexyl chains (**4** and **6**) are not mesomorphous. However, the second DSC heating scan of TTT **5** reveals a transition into a mesophase at 126 °C (ΔH = 22.8 kJ mol^{-1}) and a second endothermic transition (184 °C, ΔH = 5.6 kJ mol^{-1}) to the isotropic melt. Upon cooling, the LC–crystalline transition was shifted to 105 °C. Though this compound carries the same number of sp^3 carbon atoms in the periphery as the LC with a 3,4-didodecyloxy substitution of Gallardo,[25a] the mesophase of **5** is only half as broad (48 vs. 115 °C). This can be attributed to the higher symmetry of **5** and the shorter side chains. Polarized optical microscopy of **5** (Figure 4) showed fan-shaped textures below the clearing point, and X-ray diffraction on oriented fibers led to the assignment of the mesophase as a disordered hexagonal columnar structure. The cell parameter a was calculated to be 25.2 Å, significantly smaller than the van der Waals diameter of the molecule in the most extended conformation (AM1: 34 Å). This indicates either interdigitation or partial folding of the chains. The core–core mean distance was found to be d = 3.9 Å, suitable for π stacking. In addition, the main characteristics of the X-ray diffractogram of **5** in the mesophase (145 °C) also appear at room temperature; this indicates that the columnar structure is retained in the crystalline phase (a = 3.5 Å, d = 27.8 Å).

Contrary to the tris(octyloxy)phenyl TTT **5**, its phenyleneethynylene-elongated congener **8** as well as didodecylamino-substituted **7** did not give any indication for mesomorphous behavior by DSC and POM. However, **9**, the next member in this homologous series, showed two transitions in the DSC curve (159 and 204 °C, ΔH < 1 kJ mol^{-1}) and optical birefringence under crossed polarizers. X-ray scattering in the mesophase (165 °C) of an oriented sample of **9** gives a strong reflection in the small-angle region (d = 40.2 Å). Three reflections in the wide-angle region have been found and correspond to d = 14.1, 8.5 (very weak reflection), and 4.5 Å. Like for **5**, the calculated diameter of **9** (AM1: 54 Å) is significantly higher than the spacing d = 40.2 Å obtained from X-ray scattering. With minor variation, the last three distances (d = 15.45, 8.96, and 4.4 Å) have also been observed by powder diffraction at 20 °C. The small transition enthalpy ($\Delta H \leq$ 1 kJ/

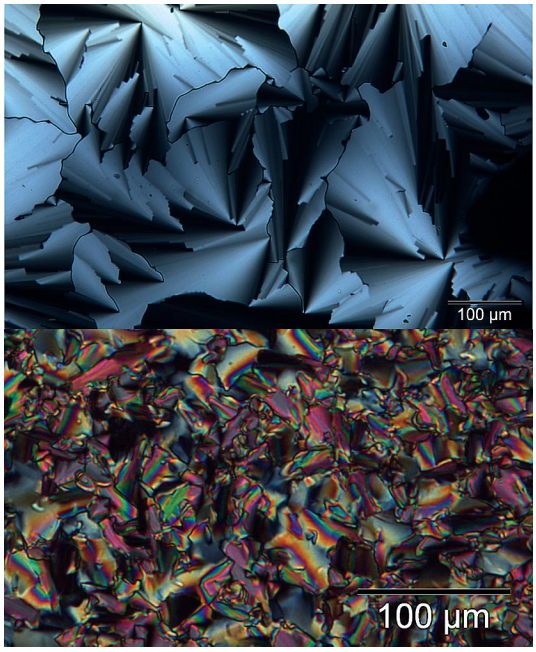


Figure 4. Texture (crossed polarizers) after cooling from the isotropic melt. Top: **5** at 180 °C, bottom: **9** at 165 °C.

mol), the observed schlieren texture, and the diffuse cyclic X-ray reflections (see Supporting Information) indicate a lower-order structure of the mesophase of **9**.

Conclusions

The convergent synthesis of star-shaped tristriazolotriazines with three π-conjugated branches is reported. The π segments are benzene, tolane, and di(phenylethynyl)benzene with one to three alkoxy or alkylamino chains on the lateral rings. Owing to the donor–acceptor character of the three branches, the fluorescence of these dyes is positively solvatochromic. Owing to their non-centrosymmetric structures, the two-photon absorption spectra of **8** and **9** are similar to their linear absorption spectra, and cross-sections of up to 200 GM were found. Tris-tris(octyloxy)phenyl-TTT **5** forms a hexagonal columnar thermotropic LC phase between 126 and 184 °C; its phenyleneethynylene homologue is not mesomorphous, but the next homologue **9** forms a mesophase of similar width but lower order.

Experimental Section

General Information: All reactions were performed under dry argon or nitrogen unless otherwise indicated. Commercially available reagents were used without further purification unless otherwise indicated; solvents and gases were dried by standard procedures, yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 300 (300 MHz), Bruker AV 400 (400 MHz), and Bruker ARX 400 (400 MHz) spectrometers; the solvents were $CDCl_3$, CD_3OD, C_6D_6, and [D_6]dimethyl sulfoxide ([D_6]DMSO). Chemical shifts δ are expressed in ppm, and coupling constants are given in Hz. ^{1}H and ^{13}C NMR signals were assigned on the basis of DEPT, COSY 45, heteronuclear multiple quantum coherence (HMQC), and HMBC experiments. Abbreviations used for assignment of spectra: Ph phenyl, Tet tetrazole, TTT tristriazolotriazine, Tin 1,3,5-triazine, Tol 1,2,4-triazole, In ethynyl, sup. superimposed signals, n.d. not detected owing to poor solubility and/or broad signal, hyphenation of phenyl and ethynyl from the core (In, Tet, TTT) to the rim. Melting points were determined with a Büchi HWS SG 200 or Stuart Scientific SMP3 instrument. DSC was performed with a Perkin–Elmer DSC 7 instrument at a heating rate of 10 °C/min. IR spectra were recorded with a JASCO 4100 FTIR (ATR) or Perkin–Elmer Paragon 500 (KBr) spectrometer. FD-MS was performed with a Mat 95 (Finnigan) spectrometer. HRMS (ESI) was performed with a Q-TOF-ULTIMA 3, Lock Spray device (Waters-Micromass) with NaI/CsI as reference. UV/Vis spectra were recorded with Perkin–Elmer Lambda 16 spectrophotometer. Fluorescence spectra were recorded with a Perkin–Elmer LS 50B spectrometer. TPIF measurements were conducted with a Ti-sapphire laser system (Coherent, mod. Mira Optima 900-F), which delivers pulses with a duration of ca. 150 fs in the wavelength range 735–810 nm with a 76 MHz repetition rate and ca. 10 nJ pulse energy at 800 nm. The beam is focused through a 40 cm lens onto a 10 mm cuvette containing the sample solution. Elemental analyses were conducted with a Vario EL analyzer. Polarized microscopy was performed with an Olympus BX51 microscope with a ColorView Olympus camera equipped with a Linkam LTS 350 heating stage. Wide-angle X-ray scattering (WAXS) measurements were performed with a Cu anode (2.2 kW), a pinhole-collimator, an Osmic CMF15-sCu6 mirror, and a Bruker 1024 × 1024 pixel detector (Highstar). Silver behenate was used as the calibration standard,[42] and the date were analyzed with the Datasqueeze software (http://www.datasqueezesoftware.com/). Starting materials were prepared according to the literature: 4-(hexyloxy)-benzonitrile,[27] 4-(hexyloxy)benzaldehyde,[34] 4-(hexyloxy)benzamide[28d] (**13**), 4-(dihexylamino)benzaldehyde,[43] 4-iodobenzamide[44] (**15**), 3,5-dibromobenzamide[45] (**16**), [4-(hexyloxy)phenyl]-acetylene[46] (**22**), [4-(didodecylamino)phenyl]acetylene[47] (**24**), [3,4,5-tris(octyloxy)phenyl]acetylene[48] (**23**), 3,4,5-tris(octyloxy)-benzaldehyde,[49] and 2-(4-bromophenyl)ethynyltrimethylsilane[35] (**31**).

General Procedure A for the Synthesis of Alkoxy-Substituted Benzamides: To a solution of the corresponding hydroxybenzoic acid ester (1 equiv.) in acetonitrile were added K_2CO_3 (1.1 equiv./hydroxy group) and the alkyl bromide (1.1 equiv./hydroxy group), and the solution was heated to reflux and stirred for 2 h. The solution was filtered, the residue was washed with ethyl acetate, and the combined organic solutions were concentrated and washed with NaOH (1 N) and brine. The solvent was evaporated, the product was dissolved in methanol/2-propanol, and KOH (3 equiv.) was added. After 45–60 min at reflux, the starting material was consumed and acidified with HCl (2 N). The product was extracted with chloroform, and the solution was dried ($MgSO_4$) and concentrated. The acid was dissolved in toluene, $SOCl_2$ (3 equiv.) and *N*,*N*-dimethylformamide (DMF; 0.5 mL) were added, and the mixture was heated to reflux for 6 h. The solution was concentrated and poured into aqueous ammonia (28%, –10 °C). The mixture was stirred for 10 min, and the product was isolated by suction filtration, washed with water and petroleum ether (PE), and dried in vacuo.

General Procedure B for the Synthesis of Substituted 5-Phenyltetrazoles from Benzamides: NaN_3 (6.6 equiv.) was suspended in anhydrous acetonitrile, $SiCl_4$ (2.2 equiv.) was added, and the mixture was stirred for 45 min. The benzamide (1 equiv.) was then added, and the mixture was stirred for 16 h. Further NaN_3 (3 equiv.) and

$SiCl_4$ (1 equiv.) were added, and the stirred mixture was heated to 50 °C until the starting material had disappeared. Water was added, and the suspension was extracted with $CHCl_3$. The pooled organic solutions were washed with brine and dried ($MgSO_4$). Basic alumina was added, the solvent was evaporated, and the residue was placed at the top of a chromatography column (SiO_2, toluene). The byproducts were eluted with toluene, followed by toluene/ethyl acetate (1:1), and after the addition of 0.5% glacial acetic acid to the eluent, the tetrazoles were eluted.

General Procedure C for the Synthesis of Substituted Phenyltetrazoles from Benzonitriles: A suspension of the nitrile (1 equiv.), NaN_3 (3.5 equiv.), and triethylammonium chloride (3.5 equiv.) in xylenes was heated to reflux. When the starting material had disappeared (1–5 d, TLC), petroleum ether was added, and the solid was isolated by suction filtration, washed with petroleum ether, and dissolved in water. Hydrochloric acid (2 N) was added to pH 3, and the product was collected by filtration, dried, and recrystallized.

General Procedure D for the Sonogashira–Hagihara Coupling with Iodo- and Bromophenyl-Substituted Tetrazoles: Under nitrogen, aryl halide, $Pd(PPh_3)_2Cl_2$, and CuI were added to the deaerated solvent (three freeze–pump–thaw cycles) in a Schlenk flask. The solution of the alkyne was added, and the mixture was heated to 70 (piperidine as solvent) or 85 °C (DMF/1 M K_2CO_3) until complete conversion (TLC). The solvent was evaporated, and the residue was dissolved in ethyl acetate. The solution was filtered through Celite, washed twice with HCl (2 N) and brine, and dried ($MgSO_4$). The solution was then concentrated, and the product was purified by flash chromatography.

General Procedure E for the Synthesis of Tristriazolotriazines: The tetrazole (3.3 equiv.) was suspended in xylenes or $CHCl_3$, pyridine (6 equiv.) was added, and the mixture was stirred for 30 min. Compound **32** (1 equiv.) was added, and the stirred solution was slowly heated to reflux and kept at this temperature for 1 h. The cooled mixture was diluted with ethyl acetate, washed twice with HCl (2 N) and brine, and dried (Na_2SO_4). The product was purified by column chromatography.

Tris(4-hexyloxyphenyl)tris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*]-[1,3,5]triazine (3): According to the general procedure E, **3** was obtained from **17** (212 mg) in xylenes (50 mL) and pyridine (0.5 mL) and **32** (55 mg, 0.3 mmol) as a colorless amorphous solid (155 mg, 71%); m.p. 123–124 °C (ref. 127 °C).[25a]

Tris(4-dihexylaminophenyl)tris[1,2,4]triazolo[4,3-a:4′,3′-c:4′′,3′′-*e*]-[1,3,5]triazine (4): According to the general procedure E, **4** was obtained from **18** (271 mg) as an amorphous solid (155 mg, 58%); m.p. 156 °C (DSC).[26c] R_f = 0.25 (toluene/ethyl acetate 10:1). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.08 (d, ^3J = 8.9 Hz, 6 H, 2-H, 6-H Ph), 6.74 (d, ^3J = 8.9 Hz, 6 H, 3-H, 5-H Ph), 3.34 (t, ^3J = 8.5 Hz, 12 H, NCH_2), 1.60 (m, 12 H, β-CH_2), 1.29 (m, 36 H, CH_2), 0.92 (t, ^3J = 7.0 Hz, 18 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 151.5, 150.3, 140.3, 131.5, 110.6, 109.3, 51.1 (NCH_2), 31.6, 27.1, 26.7, 22.7 (CH_2), 14.0 (CH_3) ppm. FD-MS: *m*/*z* (%) = 498.8 (5) $[M]^{2+}$, 979.5 (100) $[M]^+$.

Tris[3,4,5-tris(octyloxy)phenyl]tris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (5): According to the general procedure E, **5** was obtained from **19** (212 mg) as a colorless solid in 74% yield (140 mg); m.p. 127 °C (DSC). ^{1}H NMR (400 MHz, C_6D_6): δ = 8.15 (s, 6 H, 2-H, 6 Ph), 4.33 (br t, ^3J = 6.4 Hz, 6 H, OCH_2), 4.18 (br t, ^3J = 6.4 Hz, 12 H, OCH_2), 1.91–2.01 (m, 6 H, CH_2), 1.73–1.85 (m, 12 H, CH_2), 1.57–1.68 (m, 6 H, CH_2), 1.43–1.52 (m, 12 H, CH_2), 1.17–1.42 (m, 72 H, CH_2), 0.83–0.98 (m, 27 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 153.6 (C-3, C-5 Ph), 150.7 (C-5 Tol), 142.1 (C-4 Ph), 140.5 (C-3 Tol), 119.3 (C-1 Ph), 109.4 (C-2, C-6 Ph),73.5, 69.4 (OCH_2), 32.0, 30.8, 29.7, 29.6, 29.5, 26.4, 26.3, 22.8 (CH_2), 14.1 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2920, 2853, 1583, 1486, 1466, 1430, 1385, 1339, 1283, 1228, 1112, 1007, 975, 868, 835, 718, 702, 671 cm^{-1}. FD-MS: *m*/*z* (%) = 790.8 (23), 791.6 (10) $[M]^{2+}$, 1581.2 (97), 1582.2 (100), 1583.2 (55), $[M]^+$. $C_{96}H_{159}N_9O_9$ (1583.39): calcd. C 72.82, H 10.12, N 7.96; found C 72.59, H 10.52, N 8.00.

Tris{4-[2-(4-hexyloxyphenyl)ethynyl]phenyl}tris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (6): According to the general procedure E, **26** (229 mg, 0.66 mmol) and **32** (37 mg, 0.2 mmol) in xylenes (25 mL) and pyridine (0.5 mL) gave **6** as colorless amorphous solid (90 mg, 45%); m.p. 245 °C. R_f = 0.33 (toluene/ethyl acetate 20:1). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 8.41 (d, ^3J = 8.4 Hz, 6 H, 2-H, 6-H Ph), 7.75 (d, ^3J = 8.4 Hz, 6 H, 3-H, 5-H Ph), 7.12 (d, ^3J = 8.8 Hz, 6 H, 2-H, 6-H Ph′), 6.73 (d, ^3J = 8.8 Hz, 6 H, 3-H, 5-H Ph′), 3.53 (t, ^3J = 6.5 Hz, 6 H, OCH_2), 1.49–1.61 (m, 6 H, β-CH_2), 1.11–1.35 (m, 18 H, CH_2), 0.88 (t, ^3J = 7.2 Hz, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 159.5 (C-4 Ph′), 150.5 (C-5 Tol), 140.5 (C-2 Tin), 132.1, 131.4, 130.0, (C-2, C-3, C-5, C-6 Ph, C-2, C-6 Ph′), 127.4 (C-1 Ph), 122.7 (C-4 Ph), 114.5 (C-3 Ph′), 114.4 (C-1 Ph′), 92.5 (C-2 In), 87.4 (C-1 In), 68.1 (OCH_2), 31.6, 29.5, 29.1, 25.7, 22.6 (CH_2), 14.1 (CH_3) ppm. IR (neat, ATR): $\tilde{\nu}$ = 2960, 2924, 2854, 2220, 1584, 1507, 1476, 1417, 1393, 1286, 1246, 1173, 1139, 1088, 1018, 946, 834 cm^{-1}. FD-MS: *m*/*z* (%) = 515.5 (41) $[M]^{2+}$, 1029.8 (100) $[M]^+$. $C_{66}H_{63}N_9O_3$ (1030.30): calcd. C 76.94, H 6.16, N 12.24; found C 76.54, H 6.17, N 12.12.

Tris{4-[2-(4-didodecylaminophenyl)ethynyl]phenyl}tris[1,2,4]-triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (7): According to the general procedure E, a solution of **27** (209 mg, 0.9 mmol), **32** (20 mg, 0.11 mmol), and pyridine (0.5 mL) in xylenes (50 mL) gave **7** as a yellow solid (75 mg, 38%); m.p. 135 °C. R_f = 0.35 (toluene/ethyl acetate 20:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.17 (d, ^3J = 8.4 Hz, 6 H, 2-H, 6-H Ph), 7.62 (d, ^3J = 8.4 Hz, 6 H, 3-H, 5-H Ph), 7.30 (d, ^3J = 8.8 Hz, 6 H, 2-H, 6-H Ph′), 6.49 (d, ^3J = 8.8 Hz, 6 H, 3-H, 5-H Ph′), 3.19–3.24 (m, 12 H, NCH_2), 1.52–1.54 (m, 12 H, β-CH_2), 1.24–1.29 (m, 108 H, CH_2), 0.84–0.89 (m, 18 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 150.7 (C-4 Ph′), 148.2 (C-5 Tol), 140.5 (C-2 Tin), 133.0 (C-2, C-6 Ph′), 131.1, 129.9 (C-2, C-3 Ph), 128.2 (C-1 Ph), 122.2 (C-4 Ph), 111.1 (C-3, C-5 Ph′), 107.8 (C-′1 Ph′), 94.1 (C-2 In), 86.8 (C-1 In), 50.9 (NCH_2), 31.9, 29.7, 29.5, 29.3, 27.1, 22.7 (CH_2, sup.), 14.1 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2852, 2362, 2207, 1599, 1518, 1470, 1423, 1403, 1369, 1320, 1302, 1195, 1137, 1013, 949, 838, 814, 728 cm^{-1}. FD-MS: *m*/*z* (%) = 893.4 (77) $[M]^{2+}$, 1785.9 (100) $[M]^+$. HRMS (ESI): calcd. for $C_{120}H_{175}N_{12}$ $[M + H]^+$ 1784.4062; found 1784.4075.

Tris{4-[2-[3,4,5-tris(octyloxy)phenyl]ethynyl]phenyl}tris[1,2,4]-triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (8): According to the general procedure E, a solution of **28** (631 mg, 1 mmol), **32** (55 mg, 0.3 mmol), and pyridine (0.5 mL) in xylenes (35 mL) gave **8** as a colorless solid (371 mg, 66%); m.p. 81 °C. R_f = 0.36 (toluene/ethyl acetate 16:1). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 8.63 (d, ^3J = 8.4 Hz, 6 H, 2-H, 6-H Ph), 7.89 (d, ^3J = 8.4 Hz, 6 H, 3-H, 5-H Ph), 6.92 (s, 6 H, 2-H, 6-H Ph′), 4.07 (t, ^3J = 6.5 Hz, 6 H, OCH_2), 3.67 (t, ^3J = 6.4 Hz, 12 H, OCH_2), 1.77–1.83 (m, 6 H, β-CH_2), 1.52–1.64 (m, 18 H, β-CH_2), 1.27–1.32 (m, 84 H, CH_2), 0.91–0.95 (m, 27 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 153.0 (C-3, C-5 Ph′), 150.5 (C-5 Tol), 140.7 (C-2 Tin), 139.1 (C-4 Ph′), 131.5 (C-3, C-5 Ph), 130.1 (C-2, C-6 Ph), 127.1, 123.2 (C-1, C-4 Ph), 117.2 (C-1 Ph′), 110.1 (C-2, C-6 Ph′), 92.8, 87.5 (C-1, C-2 In), 73.6, 69.1 (OCH_2), 32.0, 31.9, 30.3, 29.6, 29.4, 26.1, 22.7 (CH_2,

sup.), 14.1 (CH_3, sup.) ppm. IR (neat): $\tilde{\nu}$ = 2926, 2855, 2208, 1590, 1499, 1469, 1421, 1354, 1256, 1232, 1115, 1014, 837, 728, 563 cm^{-1}. FD-MS: *m/z* (%) = 942.0 (11) $[M]^{2+}$, 1885.7 (100) $[M]^+$. $C_{120}H_{171}N_9O_9$ (1883.76): calcd. C 76.51, H 9.15, N 6.69; found C 76.46, H 9.14, N 6.73.

Tris[4-(2-{4-[2-[3,4,5-tris(octyloxy)phenyl]ethynyl]phenyl}ethynyl)-phenyl]tris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (9): According to the general procedure E, a solution of **29** (117mg, 0.16 mmol), **32** (9 mg, 0.05 mmol), and pyridine (0.5 mL) in xylenes (25 mL) gave **9** as a colorless wax (41 mg, 38%); m.p. 159 °C. R_f = 0.29, (toluene/ethyl acetate 50:1). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.29 (d, 6 H, 2-H, 6-H Ph), 7.69 (d, ^3J = 8.3 Hz, 6 H, 3-H, 5-H Ph), 7.50 (s, 12 H, 2-H, 3-H, 5-H, 6-H Ph′), 6.61 (s, 6 H, 2-H, 6-H Ph′′), 3.85 (br t, 18 H, OCH_2), 1.64–1.70 (m, 18 H, β-CH_2), 1.29–1.41 (m, 90 H, CH_2), 0.87–0.90 (m, 27 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 152.7 (C-3, C-5 Ph′′), 150.1 (C-5 Tol), 140.7 (C2 Tin), 138.4 (C-4 Ph′′), 131.5, 131.6, 131.7 (C-2 Ph, C-3 Ph′, C-4 Ph′), 130.3 (C-3 Ph), 126.4 (C-4 Ph), 123.8 (C 2 Ph), 122.4, 123.5 (C-1 Ph′, C-4 Ph′), 117.5 (C-1 Ph′′), 109.6 (C-2, C-6 Ph′′), 91.9 (C-2 In′), 91.7 (C-1 In′), 90.6, 88.0 (C-1, C-2 In), 68.9, 73.6 (OCH_2), 32.0, 31.9, 30.2, 29.5, 29.3, 29.1, 26.0, 22.7 (CH_2, sup.), 14.1 (CH_3, sup.) ppm. IR (Nujol): $\tilde{\nu}$ = 2207, 1591, 1509, 1257, 1234, 1115, 1016, 973, 837, 722 cm^{-1}. FD-MS: *m/z* (%) = 728.5 (13) $[M]^{3+}$, 1093.1 (100) $[M]^{2+}$, 2187.6 (23) $[M^+]$. $C_{144}H_{183}N_9O_9$ (2184.12): calcd. C 79.19, H 8.45, N 5.77; found C 78.98, H 8.28, N 5.96.

Tris{3,5-bis[2-[3,4,5-tris(octyloxy)phenyl]ethynyl]phenyl}tris[1,2,4]-triazolo[4,3-*a*:4′,3′-*c*:4′′,3′′-*e*][1,3,5]triazine (10): According to the general procedure E, a solution of **30** (167mg, 0.15 mmol), **32** (8 mg, 0.043 mmol), and pyridine (0.5 mL) in xylenes (35 mL) gave **10** as a slightly brown solid (55 mg, 37%); m.p. 88–91 °C. R_f = 0.39 (toluene/ethyl acetate 40:1). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.98 (s, 6 H, 2-H, 6-H Ph), 8.25 (3 H, C-4 Ph), 6.94 (s, 12 H, 2-H, 6-H Ph′), 4.11 (t, ^3J = 6.4 Hz, 12 H, OCH_2), 3.67–3.70 (m, 24 H, OCH_2), 1.86–1.88 (m, 12 H, β-CH_2), 1.28–1.66 (m, 204 H, CH_2), 0.90–0.94 (m, 54 H, CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 153.4 (C-3, C-5 Ph′′), 148.9 (C-5 Tol), 140.8 (C-2 Tin), 139.8 (C-4 Ph′′), 137.4 (C-1 Ph), 132.6 (C-3, C-5 Ph), 125.0, 126.4 (C-2, C-6 Ph), 117.4 (C-1 Ph′), 110.5 (C-2, C-6 Ph′), 92.3 (C-2 In), 87.1 (C-1 In), 73.4, 68.8 (OCH_2), 32.1, 32.0, 30.7, 29.9, 29.8, 29.6, 29.5, 26.4, 26.2, 22.8 (CH_2 sup.), 14.1 (CH_3 sup.) ppm. IR (neat): $\tilde{\nu}$ = 2924, 2855, 2725, 2214, 1574, 1499, 1458, 1377, 1235, 1115, 1038, 882, 831, 722 cm^{-1}. FD-MS: *m/z* (%) = 3340.3 (100) $[M]^+$, 5011.8 (49) $[M_3]^{2+}$, 6681.5 (25) $[M_2]^+$. $C_{216}H_{327}N_9O_{18}$ (3338.06): calcd. C 77.72, H 9.87, N 3.78; found C 77.50, H 10.02, N 3.96.

4-(Dihexylamino)benzonitrile (12):[29] Aqueous ammonia (30 mL, 28%) was added to a vigorously stirred solution of (dihexylamino) benzaldehyde[34] (1.40 g, 4.84 mmol) in THF (25 mL), and iodine was added in small portions until the starting material had disappeared. Diethyl ether (50 mL) was added, and the mixture was washed with aqueous $NaHSO_3$ (50 mL, 5%) and brine (3 × 50 mL) and dried (Na_2SO_4). Purification by column chromatography gave **12** (1.16 g, 83%) as a yellowish, fluorescent oil. R_f = 0.65 (toluene). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.5 (C-4 Ph), 133.5 (C-2, C-6 Ph), 120.9 (C_q), 111.0 (C-3, C-5), 96.1 (C_q), 51.0, (N-CH_2) 31.9, 27.1, 26.8, 22.6, (CH_2), 14.0 (CH_3) ppm.

5-(4-Hexyloxyphenyl)-2*H*-tetrazole (17):[50] According to the general procedure C, a suspension of 4-(hexyloxy)benzonitrile[27] (**11**) (4.07 g, 20 mmol), NaN_3 (2.72 g, 40 mmol) and Et_3NHCl (5.51 g, 40 mmol) for 5 d gave **17** (3.36 g, 68%) as a colorless solid; m.p. 163 °C. The same product was obtained in 90% yield from benzamide[42] **13** and TACS (procedure B). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.95 (d, ^3J = 8.3 Hz, 2 H, 2-H, 6-H), 7.14 (d, ^3J = 8.3 Hz, 2 H, 3-H, 5-H), 4.05 (t, ^3J = 6.2 Hz, 2 H, OCH_2), 1.76–1.67 (m. 2 H, CH_2), 1.44–1.30 (m, 6 H, CH_2),0.88 (t, ^3J = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 160.0 (C-1, Tet), 154.7 (C-4 Ph), 127.9 (C-2, C-6 Ph), 116.4 (C-1 Ph), 114.6 (C-3, C-5 Ph), 67.1 (OCH_2), 30.4, 27.9, 24.6, 21.5 (CH_2), 13.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3077, 2924, 2853, 1611, 1582, 1499, 1256, 840 cm^{-1}. FD-MS: *m/z* (%) = 246.2 (100) $[M]^+$, 493.6 (5) $[M_2 + H]^+$. HRMS (ESI): calcd. for $C_{13}H_{18}ON_4Na$ $[M + Na]^+$ 2691378; found 2691383.

5-(4-Dihexylaminophenyl)-2*H*-tetrazole (18): According to the general procedure C, nitrile **12** gave **18** in 74% yield; m.p. 73–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, ^3J = 8.5 Hz, 2 H, 2-H, 6-H), 6.63 (d, ^3J = 8.5 Hz, 2 H, 3-H, 5-H), 3.26 (t, 4 H, NCH_2), 1.58 (m, 4 H, β-CH_2), 1.29 (m, 12 H, CH_2), 0.92 (t, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.0 (C-5 tet), 150.4 (C-4 Ph), 129.1 (CH), 111.5 (CH), 108.6 (C-1 Ph), 51.0 (NCH_2), 31.7, 27.1, 26.8, 22.7 (CH_2), 14.0 (CH_3) ppm. FD-MS: *m/z* (%) = 329.4 (100) $[M]^+$, 659.8 (24) $[M_2 + H]^+$.

5-[3,4,5-Tris(octyloxy]phenyl-2*H*-tetrazole (19): According to the general procedure B, a suspension of 3,4,5-tris(octyloxy)benzamide[28] (**14**) (2.53 g, 5 mmol), NaN_3 (2.05 g, 31.5 mmol), and $SiCl_4$ (1.20 mL, 10.5 mmol) was heated to afford **19** (1.24 g, 47%) as colorless solid; m.p. 94 °C. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.82 (s, 2 H, 2-H, 6-H Ph), 4.22 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 3.92 (t, ^3J = 6.3 Hz, 4 H, OCH_2), 1.89 (m, 2 H, β-CH_2), 1.68 (m, 4 H, β-CH_2), 1.59 (m, 2 H, CH_2), 1.20–1.41 (m, 34 H, CH_2), 0.86–0.94 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 157.8 (C-5, Tet), 154.1 (C-3, C-5 Ph), 140.6 (C-4 Ph), 120.9 (C-1 Ph), 105.9 (C-2, C-6 Ph), 69.4, 73.5 (OCH_2), 31.9, 29.7, 29.5, 26.3, 26.2, 22.8 (CH_2, sup.), 14.1 (CH_3, sup.) ppm. IR (ATR): $\tilde{\nu}$ = 2952, 2919, 2850, 1584, 1502, 1464, 1443, 1382, 1307, 1247, 1115, 1081, 1051, 991, 948, 871, 844, 824 cm^{-1}. FD-MS: *m/z* (%) = 502.1 (4) $[M - N_2]^+$, 530.1 (100) $[M]^+$, 1062.3 (7) $[M_2]^+$. HRMS (ESI): calcd. For $C_{31}H_{54}O_3N_4Na$ $[M + Na]^+$ 553.4094; found 553.4111.

5-[4-Iodo(phenyl)-2*H*-tetrazole] (20): Following the general procedure B, *p*-iodobenzamide[44] **15** (6.67 g, 27 mmol), NaN_3 (7.15 g, 110 mmol), and $SiCl_4$ (4.24 mL, 37 mmol) gave **20** (6.56 g, 89%) as a colorless solid; m.p. 275–278 °C (ref. 271 °C).[51] ^{1}H NMR (400 MHz, 25 °C, [D$_6$]DMSO): δ = 7.98 (d, ^3J = 8.6 Hz, 2 H), 7.80 (d, ^3J = 8.6 Hz, 2 H) ppm. ^{13}C NMR δ = (100 MHz, $CDCl_3$, 25 °C): δ = 155.2 (C-5 tet), 138.3 (CH), 128.7 (CH), 123.3 (C-1), 98.5 (C-4) ppm. IR (ATR): $\tilde{\nu}$ = 2447, 1909, 1604, 1556, 1477, 1431, 1271, 1165, 1058, 1006, 984, 826, 743 cm^{-1}.

3,5-Dibromophenyl-2*H*-tetrazole (21): Following the general procedure B, 3,5-dibromobenzamide[45] **16** (3.5 g, 12 mmol), NaN_3 (3.12 g, 48 mmol), and $SiCl_4$ (1.9 mL, 16 mmol) gave **21** (3.43 g, 95%) as a colorless solid; m.p. 242 °C (dec). ^{1}H NMR (400 MHz, 25 °C, [D$_6$]DMSO): δ = 8.21 (d, ^4J = 2.1 Hz, 2 H, 2-H, 6-H), 8.08 (t, ^4J = 2.1 Hz, 1 H, 4-H) ppm. IR (KBr): $\tilde{\nu}$ = 3446, 3079, 2736, 1654, 1553, 1382, 1244, 1103, 1025, 863, 666 cm^{-1}. FD-MS: *m/z* (%) = 302.1 (100) [M].$^+$

5-[4-(2-*p*-Hexyloxy)phenylethynyl]phenyl-2*H*-tetrazole (26): According to the general procedure, heating a suspension of tetrazole **20** (272 mg, 1 mmol), alkyne[46] **22** (202 mg, 1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg), CuI (4 mg), and 1 drop of trihexylamine in DMF (20 mL) and aqueous K_2CO_3 (1 M, 20 mL) gave **26** (262 mg, 75%) as a colorless solid after chromatography (SiO_2, toluene/ethyl acetate 20:1, R_f = 0.33); m.p. 199 °C. ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.96 (d, ^3J = 8.4 Hz, 2-H, 6-H, Ph), 7.50 (d, ^3J = 8.6 Hz, 3-H, 5-H, Ph), 7.35 (d, ^3J = 8.8 Hz, 2-H, 6-H, Ph′), 6.77 (d, ^3J = 8.8 Hz, 3-H. 5-H Ph′), 3.85 (t, ^3J = 6.6 Hz, 6 H,OCH_2), 1.65 (m, 2 H, β-

CH_2), 1.33 (m, 2 H, CH_2), 1.11–1.25 (m, 4 H, CH_2), 0.77–0.80 (m, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 159.5 (C-4 Ph′), 133.0, 131.9, 127.1 (C-2, C-3, C-5, C-6 Ph, C-2, C-6 Ph′), 126.3 (C-1 Ph), 123.6 (C-4 Ph), 114.5 (C-3, C-5 Ph′), 114.4 (C-1 Ph′), 91.3 (C-2 In), 87.3 (C-1 In), 68.0 (OCH_2), 31.6, 29.0, 25.6, 22.5 (CH_2), 13.9 (CH_3) ppm (C-5 Tet n.d.). IR (ATR): $\tilde{\nu}$ = 2920, 2857.0 2210, 1603, 1513, 1470, 1431, 1385, 1353, 1294, 1250, 1162, 1110, 1061, 1035, 989, 836, 759 cm^{-1}. FD-MS: *m*/*z* (%) = 346.3 (100) [M$^+$]. $C_{21}H_{22}N_4O$ (364.41): calcd. C 72.81, H 6.40, N 16.17; found C 72.46, H 6.68, N 15.76.

5-{4-[2-(4-Didodecylaminophenyl)ethynyl]phenyl}-2*H*-tetrazole (27): According to the general procedure D, tetrazole **20** (462 mg, 1.7 mmol), alkyne[47] **24** (817 mg, 1.8 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg), CuI (15 mg), PPh_3 (21 mg), and one drop of trihexylamine in piperidine (50 mL) gave **27** (625 mg, 62%) as a yellow solid. R_f = 0.28 (toluene/ethyl acetate 15:1). Compound **27** turned green within 1 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, ^3J = 8.3 Hz, 2 H, 2-H, 6-H Ph), 7.59 (d, ^3J = 8.3 Hz, 2 H, 3-H, 5-H Ph), 7.35 (d, ^3J = 8.8 Hz, 2 H, 2-H, 6-H Ph′), 6.56 (d, ^3J = 8.8 Hz, 2 H, 3-H, 5-H Ph′), 3.26 (m, 4 H, NCH_2), 1.56 (m,4 H, β-CH_2), 1.24–1.29 (m, 36 H, CH_2), 0.86 (m, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2853, 2207, 1603, 1560, 1521, 1466, 1400, 1369, 1197, 1133, 845, 812, 721 cm^{-1}. FD-MS: *m*/*z* (%) = 597.5 (100) [M]$^+$.

5-{4-[2-[3,4,5-Tris(octyloxy)phenyl]ethynyl]phenyl}-2*H*-tetrazole (24): According to procedure D, **20** (544 mg, 2 mmol), alkyne **23** (1.07 g, 2.2 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg), CuI (8 mg), PPh_3 (10 mg), and one drop of trihexylamine in DMF/aq. K_2CO_3 (9:1, 70 mL) gave **24** (960 mg, 73%) as a colorless solid; m.p. 79 °C. R_f = 0.35 (SiO_2, toluene/ethyl acetate 20:1). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.88 (d, ^3J = 8.3 Hz, 2 H, 2-H, 6-H Ph), 7.50 (d, ^3J = 8.3 Hz, 2 H,3-H, 5-H Ph), 6.66 (s, 2 H, 2-H, 6-H Ph′), 4.05 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 3.87 (t, ^3J = 6.5 Hz, 4 H,OCH_2), 1.79–1.86 (m, 2 H, β-CH_2), 1.68–1.73 (m, 4 H,β-CH_2), 1.25–1.48 (m, 30 H, CH_2), 0.86 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 153.0 (C-3, C-5 Ph′), 138.1 (C-4 Ph′), 132.6 (C3, C-5 Ph), 127.2 (C-2, C-6 Ph), 126.3 (C-4 Ph), 123.3 (C-1 Ph), 117.8 (CC-1 Ph′), 109.7 (C-2, C-6 Ph′), 87.5 (C-1 In), 92.8 (C-2 In), 69.1, 73.6 (OCH_2), 32.0, 31.9, 30.3, 29.6, 29.4, 26.1, 22.7 (CH_2, sup.), 14.1 (CH_3, sup.) ppm (C-5 Tet n.d.). IR (neat): $\tilde{\nu}$ = 2922, 2853, 2719, 2610, 2203, 1606, 1570, 1504, 1465, 1428, 1416, 1352, 1256, 1235, 1157, 1113, 1028, 993, 844, 750, 699 cm^{-1}. FD-MS: *m*/*z* (%) = 630.9 (100) [M]$^+$, 1263.1 (10) [M_2]$^+$. HRMS: calcd. for $C_{39}H_{58}N_4O_3Na$ [M + Na]$^+$ 653.4407, found 653.4387.

5-[4-(2-{4-[2-[3,4,5-Tris(octyloxy)phenyl]ethynyl]phenyl}ethynyl)-phenyl]-2*H*-tetrazole (29): According to procedure D, diyne **25** (176 mg, 0.3 mmol), **20** (76 mg, 0.28 mmol), $Pd(PPh_3)_2Cl_2$ (11 mg), CuI (6 mg), PPh_3 (8 mg), and one drop of trihexylamine in DMF/aq. K_2CO_3 (9:1, 70 mL) gave **29** (133 mg, 65%) as a light yellow solid; m.p. 163 °C. R_f = 0.25 (toluene/ethyl acetate 15:1). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.97 (d, ^3J = 8.2 Hz, 2 H, 2-H. 6-H Ph), 7.53 (d, ^3J = 8.2 Hz, 2 H, 3-H, 5-H Ph), 7.42 (s, 4 H, 2-H, 3-H, 5-H, 6-H Ph′), 6.69 (s, 2 H, 2-H, 6-H, Ph′′), 4.06 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 3.90 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 1.70–1.80 (m, 6 H, β-CH_2), 1.44 (m, 6 H, CH_2) 1.27 (m, 24 H, CH_2), 0.85–0.88 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 156.3 (C-5 Tet), 152.9 (C-3, C-5 Ph′′), 138.0 (C-4 Ph′′), 132.2 (C-3, C-5 Ph), 131.5, 131.6 (C-2, C-3, C-5, C-6 Ph′), 127.4 (C-2, C-6 Ph), 126.2 (C-4 Ph), 123.5 (C-1 Ph, C-4 Ph′), 122.4 (C-1 Ph′), 118.1 (C-1 Ph′′), 109.7 (C-2, C-6 Ph′′), 91.7 (C-1, C-2 In′, sup.), 90.2 (C-1 In), 88.1 (C-2 In), 69.0, 74.3 (OCH_2), 31.9, 31.8, 30.3, 29.7, 29.5, 29.3, 29.2, 26.1, 22.7, 22.6, (CH_2, sup.), 14.1 (CH_3, sup.) ppm. IR (KBr): $\tilde{\nu}$ = 3427, 2926, 2855, 2210, 1654, 1611, 1573, 1511, 1465, 1421, 1382, 1354, 1255, 1115, 838 cm^{-1}. FD-MS: *m*/*z* (%) = 731.2 (100) [M]$^+$, 1464.6 (6) [M_2]$^+$. $C_{47}H_{62}N_4O_3$ (731.04): calcd. C 77.22, H 8.55, N 7.66; found C 76.97, H 8.34, N 7.47.

3,5-Bis[2-[3,4,5-tris(octyloxy)phenyl]ethynyl]phenyltetrazole (30): According to procedure D, tetrazole **21** (152 mg, 0.5 mmol), alkyne **23** (535 mg, 1.1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg), CuI (4 mg), and one drop of trihexylamine in DMF/aq. K_2CO_3 (9:1, 50 mL) gave **30** (181 mg, 32%) as a colorless wax; m.p. 111 °C. R_f = 0.19 (toluene/ethyl acetate 25:1). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 7.91 (br s, 2 H, 2-H, 6-H Ph), 7.69 (m, 1 H, 4-H Ph), 6.68 (s, 4 H, 2-H, 6-H Ph′), 4.06 (t, ^3J = 6.1 Hz, 4 H, OCH_2), 3.92 (t, ^3J = 6.1 Hz, 8 H, OCH_2), 1.69–1.82 (m, 12 H, β-CH_2), 1.20–1.49 (m, 60 H, CH_2), 0.83–0.87 (m, 18 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, $CDCl_3$): δ = 155.3 (br, C-5 tet), 152.8 (C-3, C-5 Ph′), 138.4 (C-4 Ph′), 136.3 (C-3, C-5, Ph), 129.5 (C-1 Ph), 125.1 (C-2 Ph), 124.7 (C-4 Ph), 117.6 (C-1 Ph′), 110.0 (C-2, Ph′), 91.5, 86.3 (C-1, C-2 In), 69.1, 74.2 (OCH_2), 31.8, 30.1, 29.5, 29.3, 26.0, 22.0 (CH_2 sup.), 14.1 (CH_3 sup.) ppm. FD-MS: *m*/*z* (%) = 1116.9 (100) [M]$^+$. HRMS: calcd. for $C_{71}H_{111}N_4O_6$ [M + H]$^+$ 1115.8504; found 1115.8472.

3,4,5-Tris(octyloxy)-ω,ω-dibromostyrene (23a): Zinc powder (2.87 g, 44 mmol) and PPh_3 (9.96 g, 44 mmol) were added to a solution of CBr_4 (14.59 g, 44 mmol) in CH_2Cl_2 (150 mL), which was degassed by purging with N_2. At 0 °C, the mixture was sonicated for 1 h (sonotrode, external cooling) and 3,4,5-tris(octyloxy)benzaldehyde[33] (5.40 g, 11 mmol) in anhydrous CH_2Cl_2 (50 mL) was added dropwise to the stirred suspension. Stirring was continued for 15 min at 0 °C and 1.5 h at 25 °C. The liquid was decanted and concentrated to 100 mL. Water (50 mL) and methanol (50 mL) were added, and the aqueous layer was extracted with petroleum ether (3 × 75 mL). The combined organic solutions were washed with brine (3 × 50 mL) and dried ($MgSO_4$). Column chromatography gave **23a** as colorless oil (5.80 g, 82%). R_f = 0.39 (toluene/petroleum ether 1:3). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 7.26 (s, 1 H, 1-H vin), 6.72 (s, 2 H, 2-H, 6-H Ph), 4.19 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 3.76 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 1.88 (m, 2 H, β-CH_2), 1.55–1.70 (m, 6 H, CH_2), 1.24–1.44 (m, 32 H, CH_2), 0.89–0.93 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, C_6D_6): δ = 153.3 (C-3, C-5 Ph), 139.6 (C-4 Ph), 137.3 (α-C vin), 130.0 (C-1 Ph), 107.5 (C-2, C-6 Ph), 88.2 (β-C vin), 69.0, 73.2 (OCH_2), 32.0, 31.9, 30.7, 29.7, 29.5, 29.4, 26.3, 26.2, 22.8, (CH_2 sup.), 14.1 (CH_3 sup.) ppm. IR (film): $\tilde{\nu}$ = 2926, 2855, 1576, 1501, 1466, 1428, 1381, 1331, 1239, 1115, 866, 836, 722 cm^{-1}. FD-MS: *m*/*z* (%) = 646.9 (100) [M]$^+$. $C_{32}H_{54}Br_2O_3$ (646.59): calcd. C 59.44, H 8.42; found C 59.35, H 8.36.

[3,4,5-Tris(octyloxy)phenyl]acetylene (23): 3,4,5-Tris(octyloxy)-ω,ω-dibromstyrol (**23a**) (3.88 g, 6 mmol) was dissolved in anhydrous THF (220 mL) in a Schlenk flask, and the solution was deaerated by three freeze–pump–thaw cycles. At –78 °C, *n*BuLi (2.5 M, 8.4 mL) was added, and the mixture was stirred (24 h at –78 °C and 24 h at r.t.). NH_4Cl (satd. aq., 50 mL) was added, and the organic layer was separated, washed with brine (3 × 30 mL), dried ($MgSO_4$), and concentrated. The residue was filtered through silica gel to give **23** as a colorless oil (2.69 g, 92%). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 6.87 (s, 2 H, 2-H, 6-H Ph), 4.15 (t, ^3J = 6.4 Hz, 2 H, 2 H, OCH_2), 3.56 (t, ^3J = 6 Hz, 4 H, 4 Hz, OCH_2), 2.80 (s, 1 H, Ph-CC-H), 1.86 (qui, 2 H, β-CH_2), 1.57–1.60 (m, 8 H, CH_2), 1.24–1.32 (m, 26 H, CH_2), 0.89–0.93 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, 25 °C, C_6D_6): δ = 153.4 (C-3, C-5 Ph), 140.2 (C-4), 117.0 (C-1 Ph), 111.0 (C-2, C-6 Ph), 84.3 (C-2 In), 76.1 (C-1 In), 68.7, 73.2 (OCH_2), 32.0, 31.9, 30.7, 29.7, 29.5, 29.4, 26.3, 26.1, 22.8 (CH_2 sup.), 14.1 (CH_3 sup.) ppm. IR (film): $\tilde{\nu}$ = 3313, 2926, 2855, 2105,

1573, 1499, 1467, 1420, 1381, 1332, 1233, 1115, 958, 897, 832, 722, 645, 595 cm^{-1}. FD-MS: *m/z* (%) = 486.6 (100) $[M]^+$.

(2-{4-[2-[3,4,5-Tris(octyloxy)phenyl]ethynyl]phenyl}ethynyl)trimethylsilane (25a): (a) According to procedure D, **31** (177 mg, 0.7 mmol), **23** (399 mg, 0.82 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg), CuI (8 mg), PPh_3 (10 mg), and one drop of trihexylamine in DMF/1 M K_2CO_3 (aq., 70 mL) gave **25a** as a colorless oil (270 mg, 50%). R_f = 0.30 (PE/Tol, 10:1). (b) *n*BuLi (0.75 mL, 2.5 M) was added to a cooled (–78 °C) solution of **23** (730 mg, 1.5 mmol) in THF (10 mL), and $ZnBr_2$ (anhydrous, 440 mg, 1.95 mmol) was added. The mixture was warmed to 25 °C and transferred by cannula to a stirred solution of $Pd(PPh_3)_2Cl_2$ (135 mg, 0.13 mmol), PPh_3(79 mg, 0.3 mmol), and **31** (658 mg, 2.6 mmol) in absolute THF (15 mL). After completion of the reaction, NH_4Cl (satd. aq., 100 mL) was added, and the mixture was extracted with ethyl acetate (2 × 50 mL). The combined organic solutions were washed with water and brine and dried ($MgSO_4$). Purification by chromatography (R_f = 0.29 PE/Tol. 10:1) gave a colorless oil (712 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (s, 4 H, Ph), 6.70 (s, 2 H, 2-H, 6-H Ph′), 3.95 (m, 6 H, OCH_2), 1.70–1.80 (m, 6 H, CH_2), 1.41–1.46 (m, 6 H, CH_2), 1.26–1.29 (m, 24 H, CH_2), 0.85–0.88 (m, 9 H, CH_3), 0.23 (s, 9 H, Si-CH_3) ppm. ^{13}C NMR (75 MHz, in $CDCl_3$): δ = 153.0 (C-3, C-5, Ph′), 139.2 (C-4 Ph′), 131.8, 131.3 (C-2, C-3, C-5, C-6 Ph), 123.4, 122.7 (C-1, C-4 Ph), 117.3 (C-1 Ph′), 110.1 (C-2, C-6 Ph′), 104.7 (C-2 In), 96.2 (C-1 In), 91.7 (C-2 In′), 87.8 (C-1 In′), 73.5, 69.1 (OCH_2), 31.9, 31.8, 30.3, 29.5, 29.3, 26.1, 26.1, 22.7 (CH_2), 14.1 (CH_3), 0.02 ($SiCH_3$) ppm. IR (film): $\tilde{\nu}$ = 2954, 2926, 2855, 2208, 2157, 1574, 1509, 1469, 1418, 1383, 1354, 1250, 1232, 1115, 1019, 863.5, 841, 760, 723, 629 cm^{-1}. FD-MS: *m/z* (%) = 659.1 (100) $[M]^+$, 660.1 (54), 1319.6 (1) $[M_2]^+$.

5-[2-(4-Ethynylphenyl)ethynyl]-1,2,3-tris(octyloxy)benzene (25): K_2CO_3 (44 mg, 0.2 mmol) was added to a solution of **25a** (231 mg. 0.35 mmol) in dichloromethane/methanol (1:1, 30 mL), and the suspension was stirred under N_2 for 16 h at 25 °C. The mixture was washed with water and brine, dried ($MgSO_4$), concentrated, and filtered through silica gel to yield **25** as a yellow oil (185 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 4 H, Ph), 6.71 (s, 2 H, 2-H, 6-H Ph′), 3.96 (m, 6 H, OCH_2), 3.15 (s, 1 H, CC-H), 1.70–1.80 (m, 6 H, CH_2), 1.41–1.46 (m, 6 H, CH_2), 1.26–1.29 (m, 24 H, CH_2), 0.85–0.88 (m, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0 (C-3, C-5, Ph′), 139.3 (C-4 Ph′), 131.3, 132.0 (C-2, C-3, C-5, C-6 Ph), 123.8, 121.7 (C-1, C-4 Ph), 117.3 (C-1 Ph′), 110.1 (C-2, C-6 Ph′), 91.9 (C-2 In′), 87.6 (C-1 In′), 83.2 (C-2 In), 78.9 87.8 (C-1 In), 73.5, 69.1 (OCH_2), 31.9, 31.8, 30.3, 29.5, 29.3, 26.1, (22.7, CH_2), 14.1 (CH_3) ppm. IR (film): $\tilde{\nu}$ = 3302, 2926, 2209, 1731, 1573, 1508, 1467, 1419, 1383, 1353, 1255, 1233, 1115, 837, 722 cm^{-1}. FD-MS: *m/z* (%) = 586.9 (100) $[M]^+$.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra and UV/Vis/fluorescence spectra of **1**–**12**.

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[1] a) H. Detert, M. Lehmann, H. Meier, *Materials* **2010**, *3*, 3218–3330, and references cited therein; b) M. Quintiliani, J. Pérez-Moreno, I. Asselberghs, P. Vázquez, K. Clays, T. Torres, *J. Chem. Phys.* **2010**, *114*, 6309–6315; c) S. Ren, D. Zeng, H. Zhong, Y. Wang, S. Qian, Q. Fang, *J. Phys. Chem. B* **2010**, *114*, 10374–10383; d) W.-Y. Lai, R. Xia, Ruidong, D. D. C. Bradley, W. Huang, *Chem. Eur. J.* **2010**, *16*, 8471–8479.

[2] a) H. C. Jeong, M. J. Piao, S. H. Lee, M.-Y. Jeong, K. M. Kang, G. Park, S.-J. Jeon, B. R. Cho, *Adv. Funct. Mater.* **2004**, *14*, 64–70; b) C. Le Droumaguet, O. Mongin, M. H. V. Werts, M. Blanchard-Desce, *Chem. Commun.* **2005**, 2802–2804; c) C. Katan, S. Tretiak, M. H. V. Werts, A. J. Bain, R. J. Marsh, N. Leonczek, N. Nicolaou, E. Badaeva, O. Mongin, M. Blanchard-Desce, *J. Phys. Chem. B* **2007**, *111*, 9468–9483; d) F. Terenziani, C. Le Droumaguet, O. Mongin, C. Katan, M. Blanchard-Desce, *Nonlinear Optics, Quantum Opt.* **2006**, *35*, 69–81.

[3] S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana* **1977**, *9*, 471–480.

[4] W. Pisula, M. Zorn, J. Y. Chang, K. Müllen, R. Zentel, *Macromol. Rapid Commun.* **2009**, *30*, 1179–1202, and references cited therein.

[5] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887; *Angew. Chem.* **2007**, *119*, 4916–4973, and references cited therein.

[6] R. J. Bushby, O. R. Lozman, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 343–54, and references cited therein.

[7] a) J. Arines, *Materials* **2009**, *2*, 549–561, DOI: 10.3390/ma2020549; b) B. R. Kaafarani, *Chem. Mater.* **2011**, *23*, 378–396.

[8] a) V. de Cupere, J. Tant, P. Viville, R. Lazzaroni, W. Osikowicz, W. R. Salaneck, Y. H. Geerts, *Langmuir* **2006**, *22*, 7798–7806; b) A. J. J. M. van Breemen, P. T. Herwig, C. H. T. Chlon, J. Sweelssen, H. F. M. Schoo, S. Setayesh, W. M. Hardeman, C. A. Martin, D. M. de Leeuw, J. J. P. Valeton, C. W. M. Bastiaansen, D. J. Broer, A. R. Popa-Merticaru, S. C. J. Meskers, *J. Am. Chem. Soc.* **2006**, *128*, 2336–2345.

[9] a) G. Hughes, M. R. Bryce, *J. Mater. Chem.* **2005**, *15*, 94–107; b) L. J. Lever, R. W. Kelsall, R. J. Bushby, *Phys. Rev. B* **2005**, *7*, 035130–1–035130–11; c) M. Talarico, R. Termine, E. M. Garcia-Frutos, A. Omenat, J. L. Serrano, B. Gomez-Lor, A. Golemme, *Chem. Mater.* **2008**, *20*, 6589–6591; d) M. P. de Jong, W. Osikowicz, S. L. Sorensen, S. Sergeyev, Y. H. Geerts, W. R. Salaneck, *J. Phys. Chem. C* **2008**, *112*, 15784–15790; e) N. Boden, R. J. Bushby, J. Clements, B. Movaghar, *J. Mater. Chem.* **1999**, *9*, 2081–2086; f) J. Cornil, V. Lemaur, J.-P. Calbert, J.-L. Bredas, *Adv. Mater.* **2002**, *14*, 726–729; g) V. Lemaur, D. A. da Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts, J. Piris, M. G. Debije, A. M. van de Craats, K. Senthilkumar, L. D. Siebbeles, J. M. Warman, J. L. Brédas, J. Cornil, *J. Am. Chem. Soc.* **2004**, *126*, 3271–3279.

[10] a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122; b) G. Hennrich, E. Cavero, J. Barberá, B. Gómez-Lor, R. E. Hanes, M. Talarico, A. Golemme, J. L. Serrano, *Chem. Mater.* **2007**, *19*, 6068–6070; c) S. Leng, L. H. Chan, J. Jing, J. Hu, R. M. Moustafa, R. M. Van Horn, M. J. Graham, B. Sun, M. Zhu, K.-U. Jeong, B. R. Kaafarani, W. Zhang, F. W. Harris, S. Z. D. Cheng, *Soft Matter* **2010**, *6*, 100–112; d) S.-J. Jeong, Y.-H. Kwon, B.-D. Choi, H. Ade, Y.-S. Han, *Appl. Phys. Lett.* **2010**, *96*, 183305/1–183305/3.

[11] a) K. Kawata, *Chem. Rec.* **2002**, *2*, 59–80; b) I. Seguy, P. Jolinat, P. Destruel, *J. Appl. Phys.* **2001**, *89*, 5442–5448; c) H.-S. Lin, K.-H. Wang, Z. Zhang, Q. Chen, Innolux Display Corp., CN 101614911, **2009**; d) T. Imai, Fuji Photo Film Co. Ltd., Japan, JP 2007217519, **2007**.

[12] a) I. H. Stapff, V. Stümpflen, J. H. Wendorff, D. B. Spohn, D. Möbius, *Liq. Cryst.* **1997**, *23*, 613–617; b) H. Mao, Z. He, J. Wang, C. Zhang, P. Xie, R. Zhang, *J. Lumin.* **2007**, *122–123*, 942–945.

[13] S. Kumar, in: *Chemistry of Discotic Liquid Crystals*, CRC Press, Boca Raton, **2011**.

[14] a) C. Deibel, D. Janssen, P. Heremans, V. De Cupere, Y. Geerts, M. L. Benkhedir, G. J. Adriaenssens, *Org. Electron.* 2006, *7*, 495–499; b) I. H. Bechtold, J. Eccher, G. C. Faria, H. Gallardo,

F. Molin, N. R. Gobo, K. T. de Oliveira, H. v. Seggern, *J. Phys. Chem. B* **2012**, *116*, 13554–13560.
[15] a) P. Secondo, F. Fages, *Org. Lett.* **2006**, *8*, 1311–1314; b) T. Ishi-i, K.-I. Murakami, Y. Imai, S. Mataka, *Org. Lett.* **2005**, *7*, 3175–3178; c) M. Lehmann, G. Kestemont, A. Gómez Aspe, C. Buess-Herman, M. H. Koch, M. G. Debije, J. Piris, M. P. de Haas, J. M. Warman, M. D. Watson, V. Lemaur, J. Cornil, Y. H. Geerts, R. Gearba, D. A. Ivanov, *Chem. Eur. J.* **2005**, *11*, 3349–3362.
[16] a) E. Keinan, S. Kumar, S. P. Singh, R. Ghirlando, E. J. Wachtel, *Liq. Cryst.* **1992**, *11*, 157–163; b) S. Kumar, E. J. Wachtel, E. Keinan, *J. Org. Chem.* **1993**, *58*, 3821–3827.
[17] a) H. K. Bisoyi, V. A. Rangunatha, S. Kumar, *Chem. Commun.* **2004**, 66–67; b) N. Boden, R. J. Bushby, K. Donovan, Q. Liu, Z. Lu, T. Kreouzis, A. Wood, *Liq. Cryst.* **2001**, *28*, 1739–1748.
[18] a) S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902–1929; b) R. Cristiano, D. M. P. O. Santos, H. Gallardo, *Liq. Cryst.* **2005**, *32*, 7–12; c) B. Gómez-Lor, B. Alonso, A. Omenat, J. L. Serrano, *Chem. Commun.* **2006**, 5012–5014.
[19] K. Pieterse, A. Lauritzen, A. P. H. J. Schenning, J. A. J. M. Wekemans, E. W. Meijer, *Chem. Eur. J.* **2000**, *6*, 5597–5604.
[20] a) K. A. Hofmann, O. Erhardt, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2713–2717; b) K. A. Hofmann, O. Erhardt, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 2731–2736.
[21] D. W. Kaiser, G. A. Peters, V. P. Wystrach, *J. Org. Chem.* **1953**, *18*, 1610–1615.
[22] a) R. Huisgen, J. Sauer, M. Seidel, *Chem. Ber.* **1960**, *93*, 2885–2891; b) R. Huisgen, H. J. Sturm, J. H. Markgraf, *Chem. Ber.* **1960**, *93*, 2106–2124; c) J. Sauer, R. Huisgen, H. J. Sturm, *Tetrahedron* **1960**, *11*, 241–251.
[23] R. Huisgen, H. J. Sturm, M. Seidel, *Chem. Ber.* **1961**, *94*, 1555–1562.
[24] V. A. Tartakovsky, A. E. Frumkin, A. M. Churakov, Y. A. Strelenko, *Russ. Chem. Bull.* **2005**, *54*, 719–725.
[25] a) R. Cristiano, H. Gallardo, A. J. Bortoluzzi, I. H. Bechtold, C. E. M. Campos, R. L. Longo, *Chem. Commun.* **2008**, 5134–5136; b) R. Cristiano, J. Eccher, I. H. Bechtold, C. N. Tironi, A. A. Vieira, F. Molin, H. Gallardo, *Langmuir* **2012**, *28*, 11590–11598.
[26] a) S. Glang, V. Schmitt, H. Detert, *Proc. 36th German Topical Meeting Liquid Crystals* **2008**, 125–128; b) K. Herget, D. Schollmeyer, H. Detert, *Acta Crystallogr., Sect. E* **2013**, *69*, o365–o366; c) S. Glang, D. Borchmann, T. Rieth, H. Detert, *Adv. Sci. Technol.* **2013**, *77*, 118–123.
[27] a) R. Ferroni, D. Simoni, S. Manfredini, M. Guarneri, P. Orlandini, *Arzneim.-Forsch.* **1995**, *45*, 665–669; b) H. Gallardo, M. Begnini, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1995**, *258*, 85–94.
[28] a) C. K. Lai, A. G. Serrette, T. M. Swager, *J. Am. Chem. Soc.* **1992**, *114*, 7948–7949; b) C. K. Lai, F.-G. Chen, Y. Ku, C.-H. Tsai, R. Lin, *J. Chem. Soc., Dalton Trans.* **1997**, *2*, 4683–4688; c) T. Ishi-i, R. Kuwahara, A. Takata, Y. Jeong, K. Sakurai, S. Mataka, *Chem. Eur. J.* **2006**, *12*, 763–776; d) U. Beginn, G. Lattermann, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1994**, *24*, 215–220.
[29] N. P. Reddy, M. Tanaka, *Tetrahedron Lett.* **1997**, *38*, 4807–4810.
[30] a) R. M. Herbst, K. Wilson, *J. Org. Chem.* **1957**, *22*, 1142–1144; b) A. Kraft, F. Osterod, R. Froehlich, *J. Org. Chem.* **1999**, *64*, 6425–6433; c) H. Detert, D. Schollmeier, *Synthesis* **1999**, 999–1004.
[31] A. El-Ahl, S. Elmorsy, A. Elbeheery, *Tetrahedron Lett.* **1997**, *38*, 1257–1260.
[32] C. Gosse, A. Boutorine, I. Aujard, M. Chami, A. Kononov, E. Cogne-Laage, J.-L. Allemand, J. Li, L. Jullien, *J. Phys. Chem. B* **2004**, *108*, 6485–6497.
[33] H. C. Holst, T. Pakula, H. Meier, *Tetrahedron* **2004**, *60*, 6765–6776.
[34] a) V. Ulian, *Farmaco Ed. Sci.* **1969**, *24*, 518–521; b) R. Brettle, D. A. Dunmur, N. J. Hindley, C. M. Marson, *J. Chem. Soc. Perkin Trans. 1* **1993**, 775–782.
[35] a) C. Dufraisse, A. Dequesnes, *Bull. Soc. Chim. Fr.* **1931**, *49*, 1880–1882; b) A. Gorgues, *C. R. Seances Acad. Sci., Ser. C* **1974**, *278*, 287–290.
[36] H. Meier, J. Gerold, H. Kolshorn, W. Baumann, M. Bletz, *Angew. Chem. Int. Ed.* **2002**, *41*, 292–295; *Angew. Chem.* **2002**, *114*, 302.
[37] a) C. E. M. Carvalho, I. M. Brinn, A. V. Pinto, M. d. C. F. R. Pinto, *J. Photochem. Photobiol. A: Chem.* **2000**, *136*, 25–33; b) F. Terenziani, A. Painelli, C. Katan, M. Charlot, M. Blanchard-Desce, *J. Am. Chem. Soc.* **2006**, *128*, 15742–15755.
[38] F. Terenziani, C. Le Droumaguet, C. Katan, O. Mongin, M. Blanchard-Desce, *ChemPhysChem* **2007**, *8*, 723–734.
[39] H. Detert, V. Schmitt, T. Glang, T. Schnitzler, R. Müller-Seipel, presented at the GDCh General Meeting, Düsseldorf, **2005**.
[40] a) S. Achelle, A. Barsella, C. Baudequin, B. Caro, F. Robin-le Guen, *J. Org. Chem.* **2012**, *77*, 4087–4096; b) V. Schmitt, S. Moschel, H. Detert, *Eur. J. Org. Chem.* **2013**, 5655–5669.
[41] M. Rumi, J. E. Ehrlich, A. A. Heikel, J. W. Perry, S. Barlow, Z. Y. Hu, D. McCord-Maughon, T. C. Parker, H. Rockel, S. Thayumanavan, S. R. Marder, D. Beljonne, J. L. Bredas, *J. Am. Chem. Soc.* **2000**, *122*, 9500–9510.
[42] C. Huang, H. Toraya, T. N. Blanton, J. Wu, *J. Appl. Crystallogr.* **1993**, *26*, 180–184.
[43] a) H. Meier, E. Karpuk, H. C. Holst, *Eur. J. Org. Chem.* **2006**, 2609–2617; b) V. Schmitt, S. Moschel, H. Detert, *Eur. J. Org. Chem.* **2013**, 5655–5669.
[44] a) I. Remsen, E. E. Reid, *Am. Chem. J.* **1899**, *21*, 284–348; b) R. J. Weikert, S. Bingham, M. A. Emanuel, E. B. Fraser-Smith, D. G. Loughhead, P. H. Nelson, A. L. Poulton, *J. Med. Chem.* **1991**, *34*, 1630–1633.
[45] a) J. Sudborough, L. Jackson, *J. Chem. Soc.* **1897**, *71*, 229–234; b) D. Alagille, H. Dacosta, G. D. Tamagnan, Y. Chen, K. Hemstapat, A. Rodriguez, J. P. Conn, R. M. Baldwin, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 3243–3247.
[46] P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *J. Mater. Chem.* **2003**, *13*, 458–469.
[47] a) H. Meier, J. Gerold, H. Kolshorn, B. Mühling, *Chem. Eur. J.* **2004**, *10*, 5445–5449; b) H. Meier, B. Muehling, H. Kolshorn, *Eur. J. Org. Chem.* **2004**, 1033–1042.
[48] a) R. P. Hsung, C. E, D. Chidsey, L. R. Sita, *Organometallics* **1995**, *14*, 4808–4815; b) C. Grave, D. Lentz, A. Schaefer, P. Samori, J. P. Rabe, P. Franke, A. D. Schlüter, *J. Am. Chem. Soc.* **2003**, *125*, 6907–6918; c) S. Hoeger, V. Enkelmann, *Angew. Chem. Int. Ed. Engl.* **1996**, *34*, 2713–2716; *Angew. Chem.* **1995**, *107*, 2917–2919.
[49] H. C. Holst, T. Pakula, H. Meier, *Tetrahedron* **2004**, *60*, 6765–6776.
[50] H. Gallardo, R. Magnano, A. J. Bortoluzzi, *Liq. Cryst.* **2001**, *28*, 1343–1352.
[51] a) S. A. Lang, *J. Heterocycl. Chem.* **1975**, *12*, 1143–1153; b) J. Bonnamour, C. Bolm, *Chem. Eur. J.* **2009**, *15*, 4543–4545.

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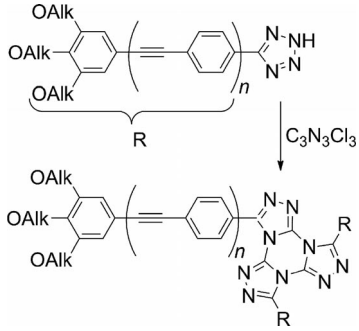
Dendritic Molecules

Star-shaped and dendritic molecules with a triphenyl-tristriazolotriazine core and flexible side chains are prepared from tetrazoles and cyanuric chloride. The optical, nonlinear optical, and thermotropic properties of these compounds as well as their phenylethynyl homologues are reported.



Keywords: Liquid crystals / Conjugated oligomers / Chromophores / Fluorescence / Nonlinear optics / Heterocycles

