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3,5-Dialkoxy Substituted Triphenyl-tristriazolotriazines: Fluorescent Discotic Liquid Crystals

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Tristriazolotriazines with a threefold 3,5-dialkoxyphenyl substitution were prepared from the corresponding phenyltetrazoles and cyanuric chloride. These star-shaped compounds are discotic liquid crystals that form broad and stable thermotropic mesophases. The thermal behaviour was studied by DSC and polarizing optical microscopy. An increasing length of the side chains reduces the phase transition temperatures, this effect is more pronounced for the crystalline to mesophase transition than for the clearing temperature. XRD on an oriented sample revealed a hexagonal columnar structure for the mesophase. All TTTs emit a strong fluorescence in the UV-violet region.

Keywords star-shaped compounds; discotic liquid crystals; X-ray diffraction; differential scanning calorimetry; polarizing optical microscopy; fluorescence

Introduction

Thermotropic liquid crystals (LCs) are a special category of soft matter, their molecular order and dynamics are intermediate between the isotropic fluid and that of a crystal [1,2]. While calamitic liquid crystals are widely used in LC display technology, the application of discotic LCs is only at the beginning [3]. A special feature of discotic molecules is their ability to form columnar phases by self-organization processes, this can result e.g. in a highly anisotropic, one-dimensional charge carrier transport material [4]. With the observation that disk-like molecules can form liquid crystalline phases,[5] Chandrasekhar opened a new field in materials science [6]. Discotic liquid crystals with triphenylene as a mesogene have been thoroughly investigated. An alkoxy substituted derivative thereof proved to be a very efficient hole conducting material [7]. Similar polycyclic aromatic compounds with C_3-symmetry and nitrogen atoms in the core have been intensively studied as liquid crystals, as electric and as optical materials [8]. Exchange of sp^2-carbon atoms in hydrocarbon cores by nitrogen atoms receives special interest for the application in electronic devices[9] since these aza-analogues retain the structural characteristics of the respective carbocyclic molecules while the electronic properties can be shifted towards n-type[10] or p-type

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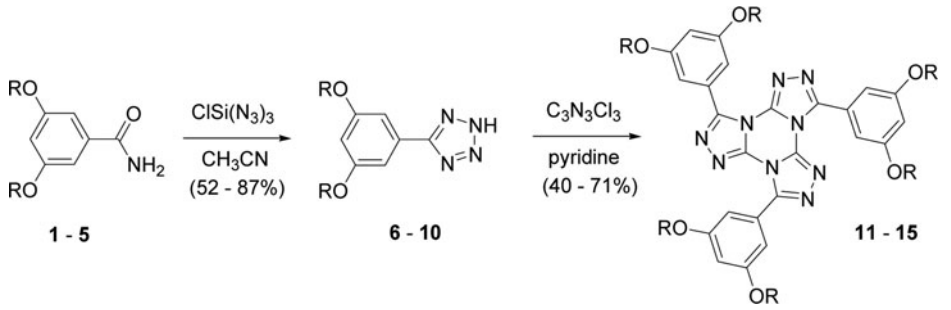
[11] semiconductors, respectively. Tristriazolotriazine (TTT), in size and symmetry closely related to triphenylene, is known for more than a century[12], but only recently Gallardo [13] and we [14] recognized the TTT as a suitable core for discotic LCs. In 1961, Huisgen reported the synthesis of triphenyl-TTT from phenyltetrazole [15]. Applying this route to alkoxy-substituted phenyltetrazoles gives alkoxyphenyl-TTTs, discotic molecules with the ability to form broad thermotropic mesophases[13, 14]. In this work, we present the synthesis of a homologous series of triphenyl-TTTs with a threefold 3,5-dialkoxyphenyl substitution and the relationship between chain length and thermal properties.

Synthesis

The acylation of tetrazoles with cyanuric chloride followed by threefold elimination of nitrogen and thermal ring transformation [15] is the best available method for the synthesis of 3,7,11-triphenyl-tris([1,2,4]triazolo)[4-*a*:4′,3′-*c*:4″,3″-*e*][1,3,5]triazines, only minor modifications were required for the synthesis of alkoxy substituted derivatives[16]. Using literature procedures, [17] ethyl 3,5-dihydroxybenzoate was converted to the 3,5-dialkoxybenzoic amides **1** – **5** via alkylation, saponification, chlorination with thionyl chloride and ammonolysis in aqueous ammonia. Condensation of amides **1** – **5** with triazidochlorosilane [18] gave the required phenyltetrazoles **6** – **10**. Cyanuric chloride was added to the suspension of tetrazoles **6** – **10** in xylenes containing small amounts of pyridine or collidine and heated to reflux for 1 h. After chromatography on silica gel, the analytically pure TTTs **11** – **15** were obtained in generally moderate yields.



Scheme 1. Synthesis of tristriazolotriazines. **11**: R = hexyl; **12**: R = heptyl; **13**: R = octyl; **14**: R = decyl; **15**: R = dodecyl.

Optical Properties

TTTs **11** – **15** are colorless and fluorescent, in solution as well as in the solid state. In cyclohexane, the absorption spectrum of TTT **13** peaks at $\lambda = 281$ nm, increasing solvent polarity shifts the absorption maximum to higher energies (dichloromethane: $\lambda_{max} = 275$ nm, methanol: $\lambda_{max} = 272$ nm). Contrary to the absorption spectra, fluorescence is positive solvatochromic: The emission maximum of TTT **13** appears at $\lambda^{F}_{max} = 373$ nm in cyclohexane, in toluene at $\lambda^{F}_{max} = 376$ nm, in dichloromethane at $\lambda^{F}_{max} = 385$ nm and in ethanol at $\lambda^{F}_{max} = 394$ nm. With deviations of $\Delta\lambda < 2$ nm, these data have been found for the other members in this series. The pronounced positive solvatochromism of the fluorescence corresponds to a higher dipole moment of the excited state[19]. Spin-coated

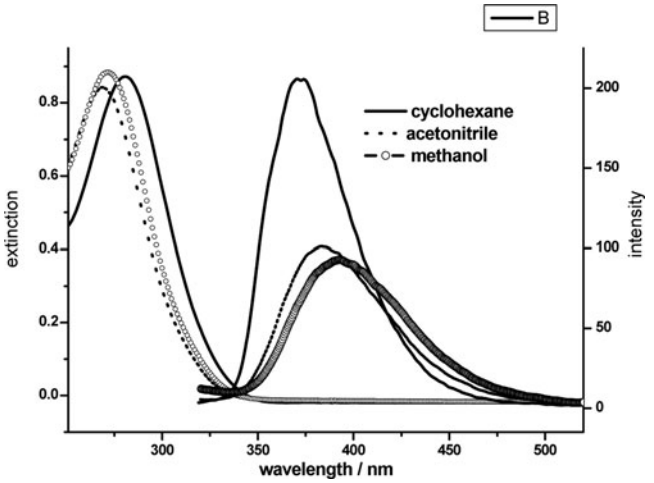


Figure 1. Electronic spectra of **13** in solution.

films show similar optical properties, the absorption maximum of **13** appears at $\lambda = 283$ nm and the emission peaks at $\lambda^F = 373$ nm – in the pristine film as well as after heating into the mesophase for 30 min. Figure 1 shows representative absorption and emission spectra of **13**.

Thermal Properties

The liquid crystal properties of the title compounds (**11** – **15**) were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Birefringent

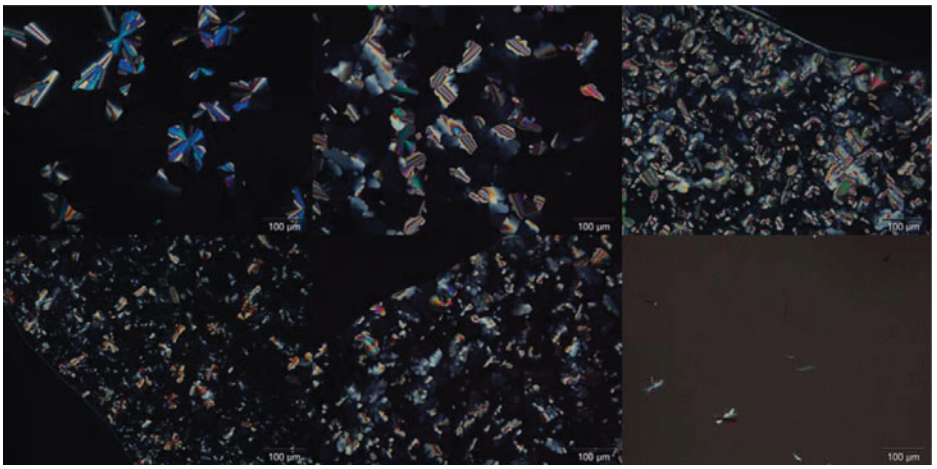


Figure 2. POM textures of TTTs **1** – **5** in the mesophase under crossed polarizers. a) TTT **11**: fast cooling (20 $Kmin^{-1}$), 180°C; b) TTT **12**: fast cooling (20 $Kmin^{-1}$), 160°C; c) TTT **13**: fast cooling (20 $Kmin^{-1}$), 150°C; d) TTT **14**: fast cooling (20 $Kmin^{-1}$), 140°C; d) TTT **15**: fast cooling (20 $Kmin^{-1}$), 130°C; f) TTT **14**: slow cooling (5 $Kmin^{-1}$), 140°C.

Table 1. DSC transition temperatures and enthalpies, onset temperatures of 2nd heating curve, values in brackets: onset temperatures from cooling curve; n.d. not determined, Col_h: mesophase with columnar hexagonal structure according to SAXS (vide infra), M: mesophase, probably columnar hexagonal structure according to POM

	T_m / °C	ΔH / kJ mol^{-1}		T_c / °C	ΔH / kJ mol^{-1}
11	136.4(118)	17.4	M	187.2(181)	4.2
12	122.2(116)	11.1	Col_h	178.8(171)	n.d.
13	91.6(86)	10.0	M	151.7(155)	5.5
14	72.9(72)	8.4	M	147.0(134)	2.9
15	74.0(69.5)	6.8	Col_h	142.5(143.2)	5.9

mesophases were observed by polarized optical microscopy for all TTTs. Upon cooling (20 Kmin^{-1}) TTTs **1** – **5** from the isotropic melt below their clearing temperature, birefringent textures appeared under crossed polarizers (Fig. 2 (a) – (e)). The observed textures, small pseudo-focal conic fan-shaped domaines and large branched leaf-like domains are characteristic for discotic liquid crystals with columnar mesophases [20]. Furthermore, the size of the fan-shaped domains decreases with increasing chain length of the alkyl chains. Slow cooling (5 Kmin^{-1}) intensifies the homeotropic alignment of the columns, as indicated by texture f) of **14**, representative for all TTTs **11** – **15**.

DSC investigation on this homologous series of alkoxy-TTTs shows that the triphenyltristriazolotriazine is an excellent core for discotic liquid crystals. All five members of this homologous series form thermotropic mesophases, from TTT **11** with hexyloxy side chains to TTT **15** with the long dodecyloxy chains (Table 1). Extension of the length of the alkoxy chains permits the regulation of the width of the LC phase. With an elongation of the aliphatic chains from hexyl to decyl, the Cr→M transition temperature drops from T_m = 136°C to T_m = 73°C and the clearing temperature is shifted from T_c = 187°C to T_c = 147°C. The effect of a further elongation to dodecyl chains (**15**: Cr74M142I is only small. Since the depression of the transition temperatures is more pronounced for the Cr→M transition than for the M→I transition, the width of the mesophase increases from ΔT = 51°C (**11**:

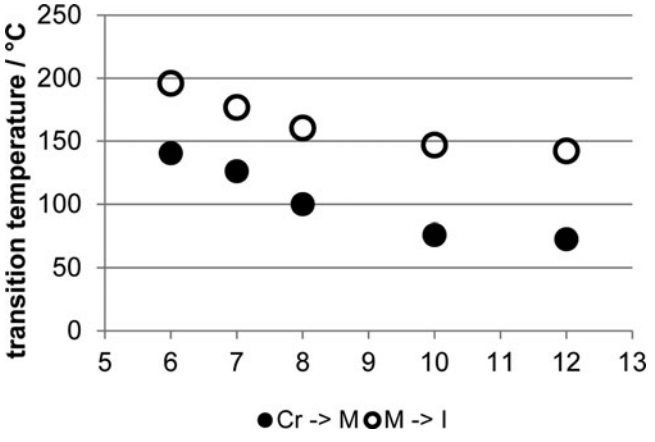


Figure 3. Chain length dependencies of the transition temperatures.

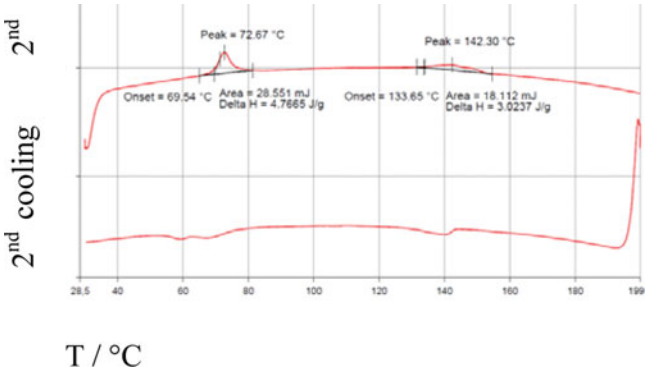


Figure 4. DSC traces of TTT **15**.

O-hexyl) to $\Delta T = 74°C$ (**14**: O-decyl) (Fig. 3.). A similar behaviour has been observed in the series of hexaalkanoyltriphenylenes[21] and hexa(3,4-alkoxyphenyl]triphenylenes[22] whereas in the triphenylene hexaether series the width of the mesophase decreases with increasing length of the side chains.

While TTTs **12** – **14** show only the melting and clearing transitions, a second peak appeared in the DSC traces of **11** and **15**. The second heating curve of **11** shows a shoulder 5°C above the melting point, the cooling scan of **15** (Fig. 4) exhibits a broad exothermic crystallization signal, the main peak, centered at 68°C, is followed by a weaker peak at 59°C. These additional peaks are attributed to the formation of a second, narrow (crystalline) phase. Polymorphism in star-shaped liquid crystals has recently been observed in the oligobenzoate series [17].

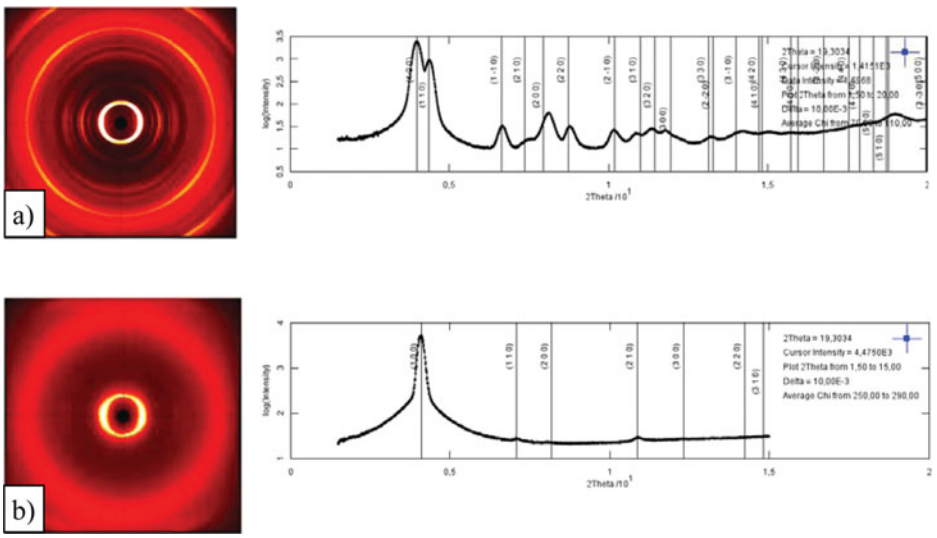


Figure 5. 2DSAXS patterns and equatorial integration of TTT **12** recorded: a) at 55°C and b) in the mesophase (150°C).

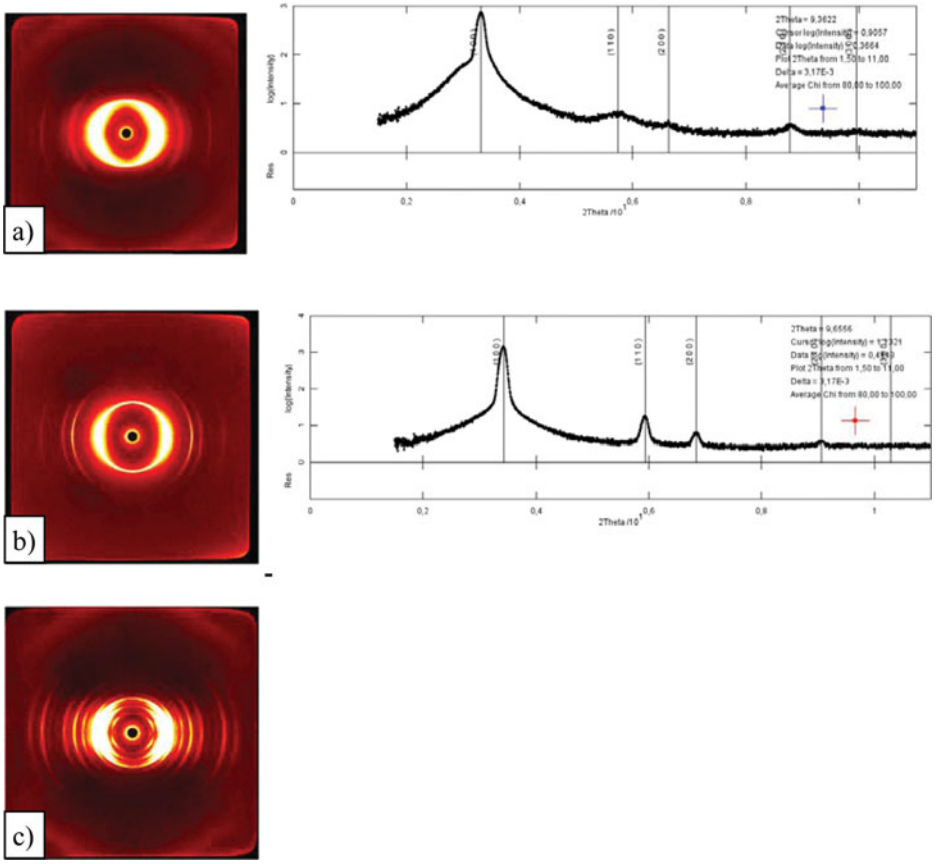


Figure 6. 2DSAXS patterns and equatorial integration of TTT **15** recorded: a) at 55°C, b) in the mesophase (115°C), and c) after slow cooling to 25°C.

X-ray Scattering

In their mesophase, TTTs **11** – **15** are birefringent, viscous oils; the textures observed under crossed polarizers are typical for a columnar arrangement of discotic materials. To get more structural information, we have performed X-ray scattering experiments on two compounds: TTT **12** with short heptyl chains and TTT **15** with long dodecyl chains. Using a custom-made extruder, the compounds were heated about 20°C above their melting point and pressed to a filament. Small angle X-ray scattering on **12** at 100°C (22°C below the melting point) gave a highly structured diffractogram corresponding to a rhombohedral columnar structure with a = 24.2 Å and $\gamma = 66.8°$. Figure 5 shows the diffractogram and the integration along the equatorial plane together with the calculated reflections for a rhombohedral lattice.

Upon heating the filament of **12** to 150°C (20°C above the m.p.) the diffractogram changes completely. An intense reflection at $2\Theta = 4.05°$ and two weak reflections at $2\Theta = 7.03°$, $10.81°$ can be attributed to the 100, 110, and 210 reflections of a hexagonal lattice with a = 24.9 Å. WAXS revealed a broad halo with a maximum at $2\Theta = 19.8°$ (d = 4.5 Å), resulting from the disordered alkyl chains.

Contrary to the rhombohedral structure in the pristine filament of **12** at 25°C, SAXS on the pristine filament of **15** (25°C) gave a hexagonal lattice ("A") with a = 30.5 Å. At elevated temperatures, the reflections became increasingly sharp. Figure 6 shows the diffractogram 6a of **15** at 55°C and the integration along the equator ($80° < \chi < 100°$). Signals at $2\Theta = 3.33°$, 5.80°, 6.71°, and 8.86° are attributed to the 100, 110, 200, and 210 reflections of a columnar hexagonal structure with a = 30.8 Å.

The very similar diffractogram 6b in Fig. 6 was obtained from **15** in the LC phase (115°C). The reflections appear at slightly larger angles (100: 3.40°, 110: 5.96°, 200: 6.88°, 210: 9.15°) and fit to a hexagonal columnar structure with a = 29.8 Å. WAXS gives a halo with maximum at $2\Theta = 19.5°$ (a = 4.54 Å) due to the alkyl chains and a reflection centered at $2\Theta = 25.5°$ (a = 3.48 Å) corresponding to the stacking distances between the π-systems. A large number of reflections are obtained after slow cooling of **15** from the mesophase to room temperature (6c, Fig. 6). Attempts to evaluate the diffraction pattern led to a superposition of two hexagonal lattices (A, B), one with a = 30.8 Å (A) and the second with a = 33.8 Å (B). The first (A) lattice constant is identical to that found for the pristine filament at 55°C, obtained by fast cooling from the LC phase to room temperature, thus quenching the crystallization process in the highly viscous material. The slow cooling process after the measurement at 115°C to the one at 25°C allowed an improved organization of the molecules. DSC (Fig. 4, 2nd cooling) gives two exothermic peaks with maxima at 68.1°C and 58.9°C, indicating either transitions from the mesophase to a crystalline phase A and thereafter to the crystalline phase B or, due to viscosity, slow and incomplete transition from the mesophase to a crystalline phase A and, at lower temperatures, from the residual, supercooled melt to a crystalline phase B. This thermal history of **15** results in the coexistence of two hexagonal columnar lattices, as can be deduced from the superposition of their reflections in the SAXS diffractogram.

Conclusion

A series of five 3,5-dialkoxyphenyl substituted tristriazolotriazines has been prepared from the corresponding tetrazoles and cyanuric chloride. These fluorescent compounds form broad enantiotropic mesophases with a hexagonal columnar structure. Increasing length of the side chains from hexyl to decyl lowers the clearing point and more pronounced the melting point, thus enhancing the width of the LC phase.

Experimental Part

^{1}H and ^{13}C NMR spectra: Bruker AC 300 (300 MHz), Bruker AV 400 (400 MHz), and Bruker ARX 400 (400 MHz), solvents were $CDCl_3$, C_6D_6, DMSO-d_6. Chemical shifts are expressed as δ values in ppm, coupling constants are given in Hz. Assignments of ^{1}H and ^{13}C signals on the basis of HSQC and HMBC experiments. Abbreviations used for assignment of spectra: ph: phenyl, tet: tetrazole, tria: triazole, TTT: tristriazolotriazine. Melting points: Büchi HWS SG 200, Stuart Scientific SMP3. DSC: Perkin Elmer, DSC 7, Perkin Elmer Pyris Software (4.01), IR: JASCO 4100 FT-IR (ATR), FD-MS: Mat 95 (Finnigan), HR-ESI: Q-TOF-ULTIMA 3, Lock Spray device (Waters-Micromass), NaICsI as reference, UV-vis: Perkin-Elmer Lambda 16. Fluorescence: Perkin-Elmer LS 50B. Polarized microscopy: Olympus BX51, ColorView Olympus camera, heattable Linkam LTS 350 for temperature regulation. DSC: Perkin Elmer DSC7, heating rate: 10 $Kmin^{-1}$, SAXS and WAXS measurements were performed using Bruker Nanostar (copper anode X-ray tube), calibration with silver behenate. Analysis of the diffractograms with

datasqueeze (http://www.datasqueezesoftware.com/). The sample was prepared extrusion using a custom-built mini-extruder heated 20°C above the respective melting point. The filament was positioned perpendicular to the incident X-ray beam and horizontal to the 2D detector. Benzamides **1** – **5** were prepared from 3,5-dihydroxybenoic acid using a procedure described in ref. 14d.

General Procedure for the Synthesis of (3,5-dialkoxyphenyl)tetrazoles

Sodium azide (0.066 mol) (toxic!) was suspended in anhydrous acetonitrile and $SiCl_4$ (0.022 mol) was added. The mixture was stirred for 45 min and the corresponding benzoic amide (10 mmol) was added. After stirring for 16 h, a second portion of NaN_3 and $SiCl_4$ was added and the mixture heated to 50°C until the starting material has been consumed (TLC). The cooled mixture was diluted with $CHCl_3$, extracted with brine (3 × 50 mL) (Formation of toxic and explosive hydrazoic acid is possible), and dried (Na_2SO_4). Alumina (basic, 15 g) was added to the filtered solution and the solvent was evaporated. The residue was placed on a silica gel column. Elution of by-products was possible with toluene/ethyl acetate (1/1), the tetrazoles were eluted after addition of 0.5% glacial acetic acid to the eluent. Solvents for optical spectroscopy: spectroscopic grade (Sigma-Aldrich, Fisher Scientific), solvents for synthesis and chromatography: analytical grade. Silica gel (60 – 230) and basic alumina (Brockmann activity 1) were obtained from Macherey-Nagel.

General Procedure for the Synthesis of Tristriazolotriazines

The tetrazole (3.3 mmol) was suspended in dry xylenes (30 mL) and pyridine (0.8 mL) was added. After 10 min stirring, cyanuric chloride (1 mmol) was added. Over 1.5 h, the stirred mixture was gradually heated to reflux and after 1 h, the mixture was cooled, diluted with ethyl acetate (30 mL) and extracted with hydrochloric acid (2N, 2 × 30 mL), brine (2x 30 mL), and dried ($MgSO_4$). Purification by chromatography on silica gel.

5-(3,5-Dihexyloxyphenyl)tetrazole

Yield: 81%, colorless solid, mp = 80°C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (t, 6 H, $J = 6.6$ Hz, CH_3), 1.27 – 1.37 (m, 8 H, CH_2), 1.37 – 1.49 (m, 4 H, CH_2), 1.75 (qui, 4 H, = 6.5 Hz, β-CH_2), 3.96 (t, 4 H, $J = 5.9$ Hz, OCH_2), 6.60 (t, 1 H, $J = 2.2$ Hz, 4-H ph), 7.19 (d, 2 H, $J = 2.2$ Hz, 2-H, 6-H ph); **^{13}C-NMR** (75 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.6, 25.6, 29.1, 31.5 (CH_2), 68.5 (OCH_2), 105.0 (C-4 ph), 105.5 (C-2, C-6 ph), 125.0 (C-1 ph), 156.9 (C-5 tet), 160.9 (C-3, C-5 ph); **IR** (ATR): $\tilde{\nu} = 2953$, 2931, 2854, 1601, 1562, 1454, 1166, 1052, 858, 846, 681; **FD-MS:** m/z (%): 348.3 (5) $[M]^+$.

5-(3,5-Diheptyloxyphenyl)tetrazole

Yield: 88%, colorless solid, mp = 84°C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (t, 6 H, $J = 6.6$ Hz, CH_3), 1.14 – 1.32 (m, 12 H, CH_2), 1.33 – 1.44 (m, 4 H, CH_2), 1.75 (m, 4 H, β-CH_2), 3.92 (t, 4 H, $J = 6.5$ Hz, OCH_2), 6.58 (t, 1 H, $J = 1.9$ Hz, 4-H ph), 7.23 (d, 2 H, $J = 1.8$ Hz, 2-H, 6-H ph); **^{13}C-NMR** (75 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 22.8, 26.1, 29.2, 29.3, 31.9 (CH_2), 68.7 (OCH_2), 105.4 (C-4 ph), 105.7 (C-2, C-6 ph), 124.8 (C-1 ph), 156.9 (C-5 tet), 161.2 (C-3, C-5 ph); **IR** (ATR): $\tilde{\nu} = 3049$, 2921, 2850, 1602, 1566, 1449, 1396, 1286, 1170, 1053, 845, 760, 682; **FD-MS:** m/z (%): 375.4 (35) $[M+H^+]$, 749.6 $[2M + H^+]$.

5-(3,5-Dioctyloxyphenyl)tetrazole

Yield: 65%, colorless solid, mp = 85°C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, 6 H, $J = 6.4$ Hz, CH_3), 1.17 – 1.35 (m, 16 H, CH_2), 1.35 – 1.47 (m, 4 H, CH_2), 1.68 – 1.82 (m, 4 H, β-CH_2), 3.96 (t, 4 H, $J = 6.8$ Hz, OCH_2), 6.60 (t, 1 H, 4-H ph), 7.23 (d, 2 H, 2-H, 6-H ph); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.4$ (CH_3), 23.0, 26.3, 29.5, 29.6, 29.7, 32.2 (CH_2), 68.8 (OCH_2), 105.6 (C-4 ph), 105.9 (C-2, C-6 ph), 125.1 (C-1 ph), 157.2 (C-5 tet), 161.4 (C-3, C-5 ph); IR (ATR): $\tilde{\nu} = 2992$, 2928, 2857, 1612, 1559, 1448, 1389, 1286, 1170, 1053, 841, 753; FD-MS: m/z (%) = 403.5 (46) [M+H$^+$], 805.8 [2M + H$^+$]; EA: $C_{23}H_{38}N_4O_2$ (402.3) calcd.: 68.62% C, 9.10% H, 13.92% N, found: 68.49% C, 9.40% H, 13.73% N.

5-(3,5-Didecyloxyphenyl)tetrazole

Yield: 71%, colorless solid, mp = 79°C; ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, 6 H, CH_3), 1.14 – 1.34 (m, 24 H, CH_2), 1.34 – 1.43 (m, 4 H, CH_2), 1.64 – 1.76 (m, 4 H, β-CH_2), 4.00 (t, 4 H, $J = 6.4$ Hz, OCH_2), 6.66 (t, 1 H, $J = 2.1$ Hz, 4-H ph), 7.15 (d, 2 H, J = 2.1 Hz, 2-H, 6-H ph); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.2, 25.5, 28.6, 28.8, 29.0, 29.1, 29.2, 31.4 (CH_2), 68.0 (OCH_2), 103.8 (C-4 ph), 105.3 (C-2, C-6 ph), 125.7 (C-1 ph), 155.3 (C-5 tet), 160.6 (C-3, C-5 ph); IR (ATR): $\tilde{\nu} = 2918$, 2851, 1602, 1569, 1467, 1385, 1336, 1170, 1078, 1058, 999, 851; FD-MS: m/z (%) = 458.3 (100) [M$^+$], 917.7 [2M + H$^+$]; EA: $C_{27}H_{46}N_4O_2$ (445.3) calcd.: 72.83% C, 10.41% H, 12.58% N, found: 72.40% C, 9.99% H, 12.73% N.

5-(3,5-Didodecyloxyphenyl)tetrazole

Yield: 52%, colorless powder, mp 123 – 125°C (ethanol); ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, $^3J = 6.8$ Hz, 6 H, 18-H, CH_3) , 1.47 – 1.16 (m, 36 H, 9-H – 17-H, CH_2), 1.76 (qui, $^3J = 6.6$ Hz, 4 H, 8-H, CH_2), 3.95 (t, $^3J = 6.6$ Hz, 4 H, 7-H, OCH_2), 6.52 (t, $^4J = 2.2$ Hz, 1 H, 4-H, Ph), 7.21 (d, $^4J = 2.2$ Hz, 2 H, 2-H, 6-H, ph); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.46$ (CH_3), 23.04, 26.33, 29.50, 29.71, 29.75, 29.93, 29.99, 30.03, 32.27 (superimposed, CH_2), 68.84 (OCH_2), 105.63 (C-4), 105.84 (C-2, C-6), 125.10 (C-1), 157.7 (C-5, tet), 161.35 (C-3, C-5, ph); IR (ATR): $\tilde{\nu} = 2921$, 2857, 1608, 1559, 1468, 1389, 1290, 1167, 1057, 845, 749, 686; FD-MS: m/z (%) = 515.6 (87) [M$^+$], 1030.3 (100) [M_2^+]; HR-ESI calcd. for: $C_{31}H_{54}N_4O_2 + H^+$: 515.4325, found: 515.4332.

Tri(3,5-dihexyloxyphenyl)-tris[1,2,4]triazolo[4,3-a:4′,3′-c:4″,3″-e]-[1,3,5]triazine

Yield: 62% of a colorless solid with mp = 200°C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 6.7$ Hz, 18H, CH_3), 1.28 – 1.38 (m, 24H, CH_2), 1.40 – 1.52 (m, 12H, CH_2), 1.73 – 1.86 (m, 12H, β-CH_2), 4.02 (t, $J = 6.5$ Hz, 12H, O$-CH_2$),6.69 (s, 3H, *p*-CH), 7.26 (s, 6H, *o*-CH); ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 14.39$ (CH_3), 22.95, 26.04, 29.48, 31.92 (CH_2), 68.78 (O$-CH_2$), 105.79 (C-2, C-6 ph), 108.81 (C-4 ph), 125.45 (C-1 ph), 140.84 (C-3 triazol), 151.25 (C-5 triazol), 160.52 (C-3, C-5 ph); IR (ATR): $\tilde{\nu} = 2931$, 2864, 1587, 1523, 1464, 1428, 1386, 1336, 1265, 1163, 1057, 838, 717, 682 cm^{-1}; FD-MS: m/z (%) = 515.2 (12) [M]$^{2+}$, 1030.1 (100), [M]$^+$; EA: $C_{60}H_{87}N_9O_6$ (1030.1) calcd.: 69.94% C, 8.51% H, 12.23% N, found: 69.79% C, 9.01% H, 12.15% N.

Tri(3,5-diheptyloxyphenyl)-tris[1,2,4]triazolo[4,3-a:4′,3′-c:4′′,3′′-e]-[1,3,5]triazine

Yield: 52% of a colorless solid with mp = 180°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.5 Hz, 18H, CH_3), 1.15 – 1.37 (m, 36H, CH_2), 1.38 – 1.50 (m, 12H, CH_2), 1.69 – 1.84 (m, 12H, β-CH_2), 3.92 – 4.07 (t, J = 6.5 Hz, 12H, O—CH_2), 6.67 (s, 3H, *p*-CH), 7.23 (s, 6H, *o*-CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.44 (CH_3), 22.96, 26.33, 29.41, 29.52, 32.13 (CH_2), 68.78 (O-CH_2), 105.78 (C-2, C-6 ph), 108.82 (C-4 ph), 125.45 (C-1 ph), 140.84 (C-2 triazol), 151.27 (C-5 triazol), 160.53 (C-3, C-5 ph); IR (ATR): $\tilde{\nu}$ = 3115, 2925, 2857, 2587, 1520, 1464, 1436, 1386, 1336, 1265, 1163, 1057, 862, 841, 714, 682 cm^{-1}; FD-MS: m/z (%) = 557.2 (9) $[M]^{2+}$, 1114.4 (100) $[M]^+$.

Tri(3,5-dioctyloxyphenyl)-tris[1,2,4]triazolo[4,3-a:4′,3′-c:4′′,3′′-e]-[1,3,5]triazine

Yield: 41% of a colorless solid with mp = 160°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.8 Hz, 18H, CH_3), 1.30 (m, 48H, CH_2), 1.45 (m, 12H, CH_2), 1.72 – 1.86 (m, 12H, β-CH_2), 4.02 (t, J = 6.5 Hz, 12H, O-CH_2), 6.70 (t, J = 4.6 Hz, 3H, *p*-CH), 7.25 (d, J = 2.0 Hz, 6H, *o*-CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 14.45 (CH_3), 23.00, 26.38, 29.52, 29.59, 29.70, 32.16 (CH_2), 68.79 (O—CH_2), 105.78 (C-2, C-6 ph), 108.83 (C-4 ph), 125.45 (C-1 ph), 140.85 (C-3 triazole), 151.27 (C-5 triazole), 160.53 (C-3, C-6 ph); IR (ATR): $\tilde{\nu}$ = 2925, 2854, 1595, 1523, 1436, 1389, 1336, 1269, 1163, 1057, 838, 717, 682 cm^{-1}; FD-MS: m/z (%): 599.1 (6) $[M]^{2+}$, 1199.0 (100) $[M]^+$; EA: $C_{72}H_{111}N_9O_6$ (1198.7) calcd.: 72.14% C, 9.33% H, 10.52% N, found: 72.37% C, 9.42% H, 10.32% N.

Tri(3,5-didecyloxyphenyl)-tris[1,2,4]triazolo[4,3-a:4′,3′-c:4′′,3′′-e]-[1,3,5]triazine

Yield: 71% of a colorless solid with mp = 73°C; ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.92 (broad t, 18H, CH_3), 1.21–1.33 (m, 72H, CH_2), 1.36-1.45 (m, 12H, CH_2), 1.68-1.76 (m, 12H, β-CH2), 3.97 (t, ^{3}J = 6.4 Hz, 12H, O-CH2), 6.98 (t, ^{4}J = 2.2 Hz, 3H, *p*—CH), 7.93 (d, ^{4}J = 2.2 Hz, 6H, 2-H, 6-H ph); ^{13}C-NMR (75 MHz, C_6D_6): δ = 14.1 (CH_3), 22.8, 26.1, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0 (CH_2), 68.3 (O-CH_2), 105.4 (*p*-CH), 108.9 (*o*-CH), 126.5 (C-1 ph), 140.3 (C-2 triazole), 150.3 (C-5 triazole), 160.7 (C-3, C-5 ph); IR (ATR): $\tilde{\nu}$ = 2921, 2853, 2358, 1594, 1522, 1463, 1435, 1389, 1337, 1272, 1165, 1056, 838, 716, 703, 684, 659 cm^{-1}; FD-MS: m/z (%) = 683.2(17) $[M]^{2+}$, 1366.4(100) $[M]^+$; EA: $C_{84}H_{135}N_9O_6$ (1367.07) calcd.: 73.80%, C 9.95% H, found: 73.83% C, 9.83% H.

Tri(3,5-didodecyloxyphenyl)-tris[1,2,4]triazolo[4,3-a:4′,3′-c:4′′,3′′-e]-[1,3,5]triazine

Yield: 29% of a colorless powder with mp = 72°C; R_f = 0.50 (toluene/ethyl acetate 40/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz, 6 H, CH_3), 1.47 – 1.16 (m, 36H, CH_2), 1.79 (qui, ^3J = 6.6 Hz, 4 H, 8-H, CH_2), 4.01 (t, ^3J = = 5 Hz, 4 H, 7-H, OCH_2), 6.67 (t, ^4J = 2.1 Hz, 1 H, 4-H, ph), 7.29 (d, ^4J = 2.2 Hz, 2 H, 2-H, 6-H, ph); ^{13}C-NMR (75 MHz, $CDCl_3$): 14.4 (C-18, CH3), 23.0, 32.26, 29.97, 29.77, 29.69, 29.53, 26.37 (CH_2), 68.77 (OCH2), 105.74 (C-3, C-5 ph), 108.70 (C-4 ph), 125.48 (C-1 ph), 140.80 (C-3, tri), 151.15 (C-5, tri), 160.48 (C-3, C-5, ph); IR (ATR): $\tilde{\nu}$ = 2918, 2854, 1595, 1523, 1459, 1442, 1389, 1340, 1265, 1170, 1053, 851, 720, 686 cm^{-1}; FD-MS: m/z (%) = 1536,5 (100) $[M^+]$, 768,1 (21) $[M^{2+}]$; EA: $C_{97}H_{161}N_9O_6$ (1535,35) calcd.: 75.10% C, 10.44% H, 8.21% N, found: 75.47% C, 10.09% H, 7.75% N.

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