

Star-Shaped π -Systems

Tristriazolotriazines with Azobenzene Arms - Acidochromic Dyes and Discotic Liquid Crystals

Marcel Sperner,^[a] Natalie Tober,^[a] and Heiner Detert^{*[a]}

Dedicated to Helmut Ringsdorf on the occasion of his 90th birthday.

Abstract: Tristriazolotriazines with azobenzene substitution and peripheral alkoxy- or alkylamino chains were prepared from the corresponding aryltetrazoles and cyanuric chloride. These star-shaped dyes are highly acidochromic. Alkoxy-substitution

allows reversible *trans-cis* photoswitching. Compounds with a 3,4-dialkoxy substitution are discotic liquid crystals that form broad and stable thermotropic mesophases. The thermal behavior was studied by DSC and polarizing optical microscopy.

Introduction

Liquid crystals (LCs) are a unique category of soft matter, which retains molecular order even in the molten state. Thus, representing an intermediate state between the isotropic fluid and that of a crystal.^[1] Rod-like liquid crystals are the most important group of LCs, especially because of their application as active compounds in LCD technology.^[2] Disc-shaped molecules constitute another class of liquid crystals (DLCs),^[3] possible applications are in optoelectronics or as sensors. Azobenzene is the working horse for research in photoactive materials, polymers,^[4] hybrid materials,^[5] and soft matter.^[6] Already Vorländer^[7] reported liquid crystalline azobenzenes.^[8] The combination of mesomorphism and photoswitching of azobenzene LCs, molecular,^[9] as units in the main chain or as side chain in polymers, is a highly active field in materials science.^[10] Possible applications are holographic displays,^[11] data storage^[12] and actuators.^[13]

Photochemical *trans-cis*-isomerization disorganizes the liquid-crystalline surrounding of the molecule. This may lead to a transformation of the LC-phase to an isotropic fluid.^[14] Smectic, columnar, and even nematic phases have been found for azobenzene-triphenylene conjugates. Uchida reported a stunning phenomenon: the photochemical switch between calamitic and discotic mesomorphism.^[15] Furthermore, isothermal phase transitions between isotropic, smectic, and columnar phases could be controlled by the intensity of the incident light. *trans-cis* Isomerization do not only provoke changes of the optical and

thermal properties, photomodulation of thin films and surfaces^[16] and nonlinear optical properties^[17] of azobenzene LCs are hot topics in material science.

Disc-shaped liquid crystals with azobenzene subunits are typically based on benzene^[18] or triphenylene as core,^[15,19] and the azobenzene carries electronically neutral or donating substituents. Tristriazolotriazines (TTTs), tetracyclic discs with a C_3 -symmetry, are heterocyclic but electron deficient analogues of triphenylene.^[20] Star-shaped molecules^[21] with this core can be mesomorphous, the LC phases are usually very broad and display hexagonal-columnar arrangements.^[22,23]

The focus of this study is on tristriazolotriazines with azobenzene arms. These molecules combine mesomorphism and photoswitching. Contrary to the usually alkyl(oxy)-substituted azobenzenes in LC materials, the TTT core and the alkoxy/amino periphery provoke an electronic donor-acceptor substitution of the azobenzene. This scarcely investigated combination^[24] adds photoswitching and non-linear optical properties^[25] to mesomorphism.

The synthesis of discotic liquid crystals composed of a TTT core with three donor-acceptor substituted azobenzene arms, their spectroscopic and thermal properties as well as photochemical switching experiments are reported.

Synthesis

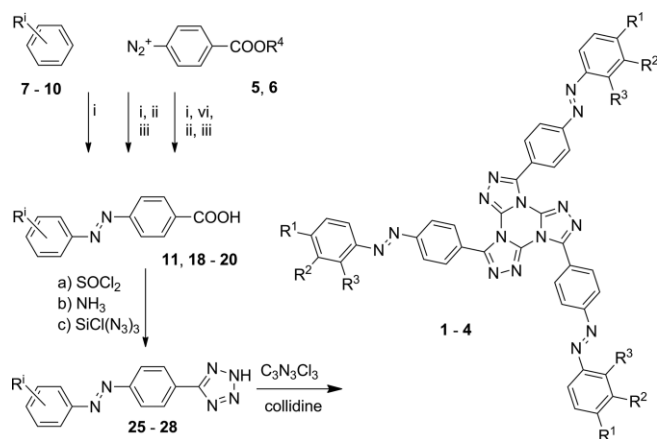
The synthesis of TTTs **1–4** follows Huisgens original procedure,^[26] threefold reaction of cyanuric chloride with tetrazoles and thermal ring transformation to form the tetracyclic tristriazolotriazine (Scheme 1). Since twelve reactions are required to form the TTT, a careful control of the reaction conditions is necessary; substituents on the tetrazole can have decisive influence on reactivity, formation of by-products, and stability of the product.^[27] The Huisgen protocol generates TTTs with a tangential orientation of the substituents, thus giving the molecule the shape of a paddle-wheel. The required tetrazoles with azo-groups were prepared from *p*-aminobenzoic acid as start-

[a] Institute for Organic Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg, 10–14, 55099 Mainz, Germany
E-mail: detert@uni-mainz.de
<https://www.blogs.uni-mainz.de/fb09ak-detert/>

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejoc.201900665>.

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ing material (Scheme 1). Diazotation to **5** ($R^4 = H$) and azo-coupling to *N,N*-dicylaniline (**7**, $R^1 = N(C_{10}H_{21})_2$, $R^2 = R^3 = H$) in acetic acid^[28] gave anilino-azo benzoic acid **11** (63 %). Due to the coupling conditions, diazotized ethyl *p*-amino-benzoate **6** ($R^4 = CH_2CH_3$) was the preferred starting material for the preparation of the 2',4'-didecyloxy-derivative (**18**, $R^1 = R^3 = OC_{10}H_{21}$, $R^2 = H$, 76 %) via a sequence involving azo-coupling with resorcinol **8** ($R^1 = R^3 = OH$, $R^2 = H$), *O*-alkylation, and alkaline hydrolysis.^[29] During the *O*-alkylation a side-reaction, additional C-alkylation on the resorcinol ring ($R^2 = C_{10}H_{21}$) occurred, which forced to extensive chromatographic purification and loss of material. The analogous coupling of **6** with catechol **9** ($R^1 = R^2 = OH$, $R^3 = H$) failed completely, even after broad variation of pH. But a detour, using 2-ethoxyphenol **10** (34 %)



Scheme 1. Synthesis of tris-triazolotriazines with azobenzene arms i) azo coupling; ii) alkyl-Br, K_2CO_3 ; iii) KOH; HCl; vi) $AlCl_3$, pyridine. **1**: $R^1 = N(C_{10}H_{21})_2$, $R^2 = R^3 = H$ (55 %); **2**: $R^1 = R^3 = OC_{10}H_{21}$, $R^2 = H$ (44 %); **3**: $R^1 = R^2 = OC_{10}H_{21}$, $R^3 = H$ (32 %); **4**: $R^1 = R^2 = OC_{12}H_{25}$, $R^3 = H$ (34 %).

as coupling partner,^[30] removal of the protecting group (76 %) and alkylation (70 %), led to the desired 3',4'-didecyloxyazobenzene **19** ($R^1 = R^2 = OC_{10}H_{21}$, $R^3 = H$) and the 3',4'-didodecyl derivative **20** ($R^1 = R^2 = OC_{12}H_{25}$, $R^3 = H$). Transformation of the carboxylic acid into tetrazole was performed by reaction with thionyl chloride, ammonolysis of the acid chloride, and a combined dehydration/azidation with in situ generated triazido-chlorosilane.^[31] Tetrazoles **25–28** were obtained in 28–65 % yield.

The convergent and most critical step for building the TTT had to be controlled carefully. Starting with an excess of tetrazole, the mixture was stirred at 25 °C and additional cyanuric chloride was added in small portions over four days. The TTTs were isolated as orange to red solids in 32–55 % yield. According to 1H -NMR spectra, chromatographically purified TTTs **1–4** are composed of solely one compound (SI). Upon storage at ambient conditions, some *cis* isomer is formed. 1H NMR reveals 4 % *cis* configured azobenzene for **2** and 8 % *cis* for **3**; the amount of *cis* in **2** to 12 % in **3** to 13 %, slowly decreasing (18 h, 27 °C) to 9 % and 12 % respectively.

Optical Spectroscopy

TTTs **1–4** are orange to dark red compounds, in the solid state and in solution. The length of alkyl chains has no effect on optical properties (**3**: decyl vs. **4**: dodecyl). The solution spectra are dominated by an intense band with maximum in the violet (**1**) to near UV range (**2–4**). Spectroscopic data are collected in Table 1, the spectra are depicted in the supporting information.

The stronger donor-effect of the 2,4-dialkoxy substitution in **2** compared to the 3,4-substituted congeners **3**, **4** shifts the

Table 1. Photophysical data of TTTs **1–3**.^[a]

	TTT 1 / nm ($\epsilon / 10^3 M^{-1} cm^{-1}$)	TTT 2 λ_{max} / nm ($\epsilon / 10^3 M^{-1} cm^{-1}$)	TTT 3 λ_{max} / nm ($\epsilon / 10^3 M^{-1} cm^{-1}$)
cyclohexane	441 (106)	387 (78)	382 (61)
toluene	450 (110)	390 (83)	387 (67)
dichloromethane	474 (106)	392 (90)	385 (79)
acetonitrile	495 (76)	389 (66)	387 (53)
ethanol	510 (85)	386 (57)	386 (52)
cyclohexane	441 (106)	387 (78)	382 (61)
solvatochromic shift [#]	3068 cm^{-1}	-67 cm^{-1}	338 cm^{-1}
neat film	464	393	388
film with PS	458	393	388
film with CA	470	393	388
film CA + TFA	532, 574	393, 500 sh	388, 542 sh
10^{-6} M TFA/DCM	477 (107)	392 (99)	385 (77)
10^{-5} M TFA/DCM	477 (111)	392 (93)	385 (75)
10^{-4} M TFA/DCM	477 (114)	393 (106)	385 (71)
10^{-3} M TFA/DCM	479 (106)	393 (87), 470 sh (30)	n.d.
5×10^{-3} M TFA/DCM	488 (92) 562 sh (45)	405 (64), 487 (85)	385 (95)
10^{-2} M TFA/DCM	565 (164)	492 (136), 405 sh (52)	385 (71), 517 (49)
10^{-1} M TFA/DCM	563 (205)	487 (179)	397 (48), 541 (109)
1 M TFA/DCM	557 (224)	484 (183)	538 (191)
acidochromic shift [§]	3351 cm^{-1}	4890 cm^{-1}	7356 cm^{-1}

[a] #: cyclohexane/ethanol; § dichloromethane/0.1 M TFA; sh: shoulder.

absorption maximum to longer wavelengths; the 4'-amino group in **1** provokes the largest redshift and hyperchromism. Furthermore, the optical spectra of these TTTs are influenced by the environment. Solvatochromism is connected with changes in dipole moments, a necessary prerequisite for non-linear optical phenomena.^[32] A selection of different solvents from non-polar to polar-protic was used for **1–3**. Whereas solvent-induced spectroscopic shifts of alkoxy substituted azo-TTTs (**2–4**) are only weak ($\Delta\lambda < 5$ nm), the efficient dialkylamino donor in amino-TTT **1** provokes a strong and positive solvatochromism (cyclohexane/ethanol: $\Delta\lambda = 69$ nm, $\Delta\tilde{\nu} = 3068$ cm⁻¹), indicating a polarity-enhanced charge transfer from the amino group to the acceptor azophenyltriazole. This screening shows the largest change of dipole moment from ground to excited state in **1**.

In thin spin-coated films, the absorption spectra of the neat compounds peak at slightly higher wavelengths compared to solution in cyclohexane, this holds for pristine and annealed films. In films composed of **1–3** and a polymer matrix, only amino-TTT **1** shows an impact of the matrix on the excitation (Figure 1). With polystyrene, cellulose acetate and polyvinyl alcohol, three polymers of very different polarity were chosen, their impact on the absorption of **1** combines polarity of the matrix and its ability to act as host for **1** in competition with self-organization of **1**. Whereas $\lambda_{max} = 458$ nm in polystyrene is red-shifted compared to toluene solution ($\lambda = 450$ nm), the spectrum of **1** in polyvinyl alcohol peaks at $\lambda = 488$ nm – about $\Delta\lambda = 22$ nm at higher energies relative to ethanol solution. These shifts indicate a significant aggregation of **1** as in the neat film ($\lambda = 464$ nm).

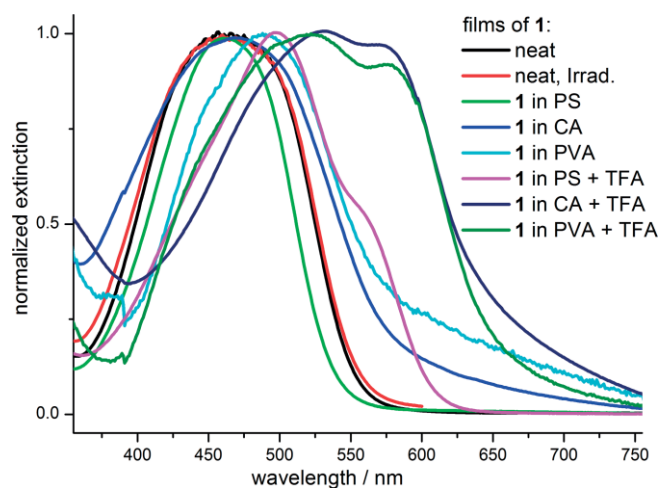


Figure 1. UV/Vis spectra of **1** in neat and polymer supported films normalized to identical absorption.

Monochromatic irradiation ($\lambda = 545$ nm) into the long-wavelength tail of the absorption band of neat **1** (film) results in a successive reduction of the main absorption band and a small increase of the absorption around $\lambda = 370$ nm. Two isosbestic points ($\lambda = 335$ nm, 397 nm) indicate a homogeneous reaction (SI). The same experiments performed with **2** and **3** and irradiation at $\lambda = 445$ nm resulted only in weak (**2**) or nearly negligible (**3**) reduction of the λ_{max} extinction. Upon irradiation into the

high-energy flank of the main absorption band of **1** ($\lambda = 400$ nm), **2**, **3** ($\lambda = 366$ nm), **3** shows photoswitching in contrast to **1**, **2**. The photochemical equilibrium is reached in less than 10 min; thermal relaxation at 300 K occurs with $t_{1/2} \approx 90$ min.

Irradiation of solutions of **1–3** with UV-light completely changes the behavior. Variation of the exciting light in seven steps from $\lambda = 366$ to 445 nm amino-TTT **1** gives the identical UV/Vis spectra. On the other hand, the alkoxy-TTTs **2**, **3** are highly reactive upon UV irradiation (Figure 2, SI). Within less than 10 min, the photostationary *cis-trans* equilibrium (**2**: $\lambda_{max} = 393$ nm; $I/I_0 = 0.56$; **3**: $\lambda_{max} = 388$ nm, $I/I_0 = 0.43$) was reached, with isosbestic points for **2** at $\lambda = 322$ nm and for **3** at $\lambda = 318$ and 468 nm. Irradiation of these solutions with $\lambda = 400$ nm induces the way back to the *trans* form. This process is much faster, new photostationary equilibria are established within 1 min – the extinctions at λ_{max} indicate significant amount of *cis* isomers (**2**: $I/I_0 = 0.78$; **3**: $\lambda_{max} = 388$ nm; $I/I_0 = 0.67$). The thermal way back is also possible but with $t_{1/2} \approx 1$ h at 300 K.

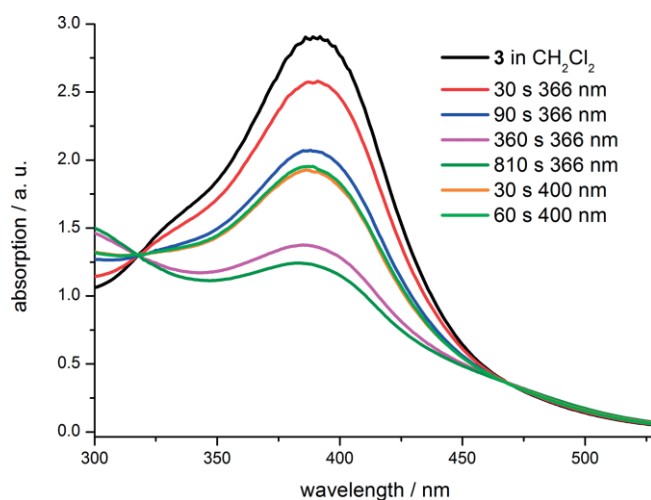


Figure 2. Reversible photoswitching of **3** upon irradiation with $\lambda = 366$ nm and $\lambda = 400$ nm.

The isosbestic points and the reversibility of the photoisomerization prove homogeneous reactions and that the molecules **2**, **3** are composed of three identical and independent triazolyl-azobenzene subunits.

Despite considerable interest in the photoisomerization of azobenzenes, there is only scant information concerning the interconversion of derivatives having both electron-donor and electron-acceptor substituents in a conjugative relationship.^[33] This substitution reduces the bond order of the azo group and thus enhances the *cis-trans* isomerization rate. The half-lives of the *cis* isomers of several 4-amino-4'-nitro-azobenzenes at 293 °C were determined as 1 s or less.^[34] Whereas TTT **1** belongs to this group, only one electron pair donating alkoxy group in **3** is in direct conjugation with the triazole acceptor and the half-life greatly increases. In the solid film, azobenzene units are buried in the viscous bulk, the photo-responsiveness is usually remarkably weakened^[35] or even completely suppressed, e.g. due to severe H-aggregation.^[16a]

Like methyl red or similar indicator dyes, the optical spectra of azo-TTTs are sensitive towards protonation. Addition of tri-

fluoroacetic acid (TFA) to solutions of TTTs in dichloromethane changes the absorption spectra significantly (Figure 3 and SI). Common features are that the absorption band around 400 nm vanishes and a new band in the green-yellow region appears. The spectra of the transition from neutral to protonated form show isosbestic points, indication of a simultaneous protonation of all three azobenzene units. Amino-TTT **1** has a transition point at 5×10^{-4} M TFA in dichloromethane, the 2,4- and the 3,4-didecyloxy derivatives **2** and **3**, **4** are about 1 or 2 pK units less basic. Noteworthy, the red shifts of the absorption maxima increase in this series ($\Delta\tilde{\nu} = 3351$ (**1**); 4980 (**2**); 7356 (**3**) cm^{-1}) and extinction coefficients of the protonated forms are about twice as high as of the neutral molecules.

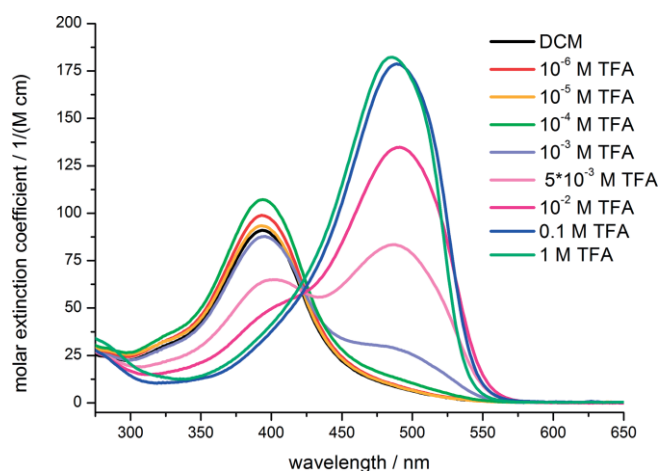


Figure 3. Absorption spectra of TTT **2** in dichloromethane with increasing TFA concentration.

Irradiation of protonated azo-TTTs **1** ($\lambda = 445$ nm) and **2**, **3** ($\lambda = 400$ nm) does not change the electronic spectra but **1** + H^+ exhibits a very weak fluorescence with $\lambda_{\text{max}} = 610$ nm. Proton-induced spectral changes are also possible in polymer-supported films (Figure 1 and SI). Cellulose acetate provided the best combination of film stability and dye sensitivity.

Thermal Properties

The thermal behavior of azo-TTTs **1–4** was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Whereas TTTs with didecylamino group (**1**) or 2,4-didecyloxy substitution (**2**) are not mesomorphous (**1**: m.p. 132 °C, **2**: m.p. 134 °C), the 3,4-dialkoxy substitution leads to liquid crystalline behavior. POM reveals pseudo-focal conical textures of the mesophases (Figure 4). The schlieren texture after shearing, and the restoration of the pseudo-focal conical texture are strong indicators of mesomorphism. The observed pseudo focal conical textures are characteristic for discotic liquid crystals with columnar arrangement in the mesophase.^[36] These textures are stable even under prolonged illumination with unfiltered visible light. A resistance of mesomorphism towards azo-*cis-trans* isomerization has recently reported for related stars with a trimesic triamide core.^[37]

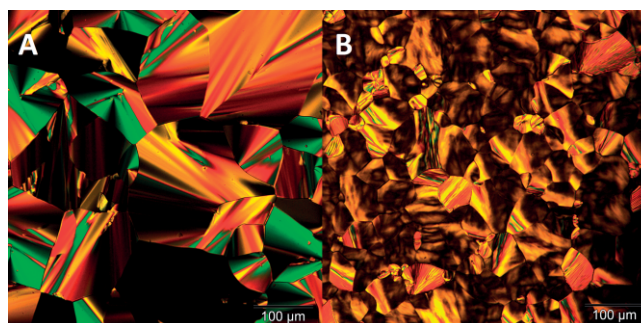


Figure 4. POM textures of TTTs **3** (140 °C), **4** (120 °C) in the mesophase under crossed polarizers.

Since POM revealed that the 3,4-dialkoxy substituted azo-TTTs **3** and **4** form birefringent and liquid phases at elevated temperatures, we used DSC to get further information about the thermal behavior. TTT **3** melts at 56 °C and the mesophase is stable up to 143 °C ($\Delta H = 1.2$ kJ mol^{-1}). Upon cooling, the material becomes mesomorphous, but a crystallization of these star-shaped molecules from the viscous mesophase was not observed. Accordingly, the second heating scan revealed only the clearing transition, but a third heating scan of this sample, performed after a several months, revealed both transitions again (SI). Similarly, DSC of freshly prepared TTT **4** showed no melting transition but a clearing point at 171 °C ($\Delta H = 2.5$ kJ mol^{-1}). A third heating experiment on the thermally equilibrated sample revealed three transitions: 61 °C ($\Delta H = 8.5$ kJ mol^{-1}), 111 °C ($\Delta H = 6.3$ kJ mol^{-1}) and the clearing point at 171 °C. The first transition corresponds to Cr→Cr and the second to Cr→M. Upon cooling, the viscous LC phase solidified to a plastic phase. It should be noted that the elongation of the alkyl chain about an ethylene unit raises the clearing point about 30 °C!

Conclusions

A series of threefold azobenzene substituted triazolotriazines has been prepared via Huisgen reaction. These star-shaped dyes are solvatochromic and acidochromic, UV and visible light allow photochemical switching between *cis*- and *trans*-alkoxy TTTs. A 3,4-dialkoxy substitution results in discotic LCs that form broad enantiotropic mesophases, though the viscosity of the LC phase strongly hampers crystallization. The LC phases are stable under illumination with sunlight. Increasing length of the side chains to dodecyl enhances the width of the LC phase.

Experimental Section

Experimental Details: ^1H 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 , $[\text{D}_6]\text{DMSO}$. Chemical shifts are expressed as δ values in ppm, coupling constants are given in Hz. Calibration on the residual ^1H signal of the solvent, in $\text{CDCl}_3/\text{DMSO}$ mixtures calibration on DMSO. Assignments of ^1H 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: triazolotriazine. 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), NaCl sI as reference. UV/Vis: Perkin-Elmer Lambda 16. Fluorescence: Perkin-Elmer LS 50B; Photochemistry: LOT Xe-arc lamp, 300 W, equipped with IR-filter and color filters. Polarized microscopy: Olympus BX51, ColorView Olympus camera, heatable Linkam LTS 350 for temperature regulation. DSC: Perkin Elmer DSC7, heating rate: 10 K min⁻¹. Details for synthesis of intermediates are collected in the SI.

General Procedure for the Synthesis of Azo-tris(triazolotriazines):

A solution of the tetrazole (ca. 400 mg, 1 eq.) in dry toluene (30 mL) and 2,4,6-collidine (1 eq.) was stirred for 1 h at ambient temperature before cyanuric chloride (0.25 eq.) in toluene (2 mL) was added. The mixture was stirred for 1 day, additional cyanuric chloride (0.03 eq.) was added in 4 daily portions. The mixture was washed with hydrochloric acid (2 M), the organic layer was dried with MgSO₄, concentrated, and the residue purified by chromatography on a silica column with a head of basic alumina using toluene/ethyl acetate (70:1) as an eluent.

3,7,11-Tris(4-(4-*N,N*-didecylaminophenylazo)phenyl)tris([1,2,4]-triazolo)[4,3-*a*:4',3'-*c*:4'',3''-*e*][1,3,5]triazine (1): According to the general procedure, 213 mg (391 μmol) 5-[4-(4-*N,N*-didecylaminophenylazo)phenyl]tetrazole (**25**) gave 116 mg (213 μmol, 55 %) of a dark red solid with m.p. 132 °C. ¹H-NMR (300 MHz, CDCl₃): δ / ppm = 8.35 (d, ³J = 8.6 Hz, 2H, 2-H, 6-H (Ph)), 8.01 (d, ³J = 8.2 Hz, 2H, 3-H, 5-H (Ph)), 7.87 (d, ³J = 8.1 Hz, 2H, 2-H, 6-H (Ph')), 6.67 (d, ³J = 8.5 Hz, 2H, 3-H, 5-H (Ph')), 3.35 (t, ³J = 7.2 Hz, 4H, NCH₂), 1.66–1.61 (m, 4H, NCH₂CH₂), 1.32–1.28 (m, 28H, Alkyl), 1.16–0.55 (m, 6H, CH₃). ¹³C-NMR (75 MHz, CDCl₃): δ / ppm = 155.16 (C-4 (Ph)), 151.25 (C-4 (Ph')), 150.79 (C-5 (tria)), 143.03 (C-1 (Ph')), 140.71 (C-3 (tria)), 131.20 (C-2, C-6 (Ph)), 125.87 (C-2, C-6 (Ph')), 123.96 (C-1 (Ph)), 122.27 (C-3, C-5 (Ph)), 111.28 (C-3, C-5 (Ph')), 51.47 (NCH₂), 32.03, 29.79, 29.71, 29.62, 29.56, 29.47, 27.47, 27.25, 22.83 (CH₂), 14.27 (CH₃). **FD-MS:** *m/z* (%) = 813.6 (1), 814.2 (87), 814.8 (6), 815.6 (4) [M]²⁺, 1085.5 (4), 1086.5 (2) [M]₃²⁺, 1627.6 (68), 1628.5 (100), 1629.3 (23), 1630.6 (16), 1631.6 (2) [M]⁺. **IR** (ATR): ν / ν̄ = cm⁻¹ = 2921 s, 2852 m, 1592 ss, 1512 m, 1467 w, 1391 m, 1362 m, 1255 m, 1130 ss, 845 m, 822 m. **HRMS-ES(+):** [M + H]⁺ calcd. 1628.2369, found 1628.2408.

3,7,11-Tris(4-(2,4-didecyloxyphenylazo)phenyl)tris([1,2,4]-triazolo)[4,3-*a*:4',3'-*c*:4'',3''-*e*][1,3,5]triazin (2): According to the general procedure, 200 mg (355 μmol, 1 eq.) 5-[4-(2,4-didecyloxyphenylazo)phenyl]tetrazole (**26**) gave 87 mg (155 μmol, 44 %) of an orange-red solid with m.p. 111 °C. ¹H-NMR (300 MHz, CDCl₃): δ / ppm = 8.35 (d, ³J = 8.3 Hz, 2H, 2-H, 6-H (Ph)), 8.06 (d, ³J = 8.3 Hz, 2H, 3-H, 5-H (Ph)), 7.79 (d, ³J = 8.9 Hz, 1H, 6-H (Ph')), 6.57 (d, ⁴J = 2.4 Hz, 1H, 3-H (Ph')), 6.53 (dd, ³J = 9.0, ⁴J = 2.5 Hz, 1H, 5-H (Ph')), 4.17 (t, ³J = 6.7 Hz, 2H, OCH₂), 4.02 (t, ³J = 6.5 Hz, 2H, OCH₂), 2.09–1.87 (m, 2H, OCH₂CH₂), 1.87–1.72 (m, 2H, OCH₂CH₂), 1.70–1.06 (m, 28H, Alkyl), 1.08–0.68 (m, 6H, CH₃). ¹³C-NMR (101 MHz, CDCl₃): δ / ppm = 164.19, 159.35 (C-4, C-2 (Ph')), 155.06 (C-4 (Ph)), 150.76 (C-5 (tria)), 140.79 (C3 (tria)), 137.12 (C-1 (Ph')), 131.23 (C-2, C-6 (Ph)), 124.73 (C-1 (Ph)), 122.85 (C-3, C-5 (Ph)), 118.27 (C-6 (Ph')), 106.77 (C-5 (Ph')), 100.93 (C-3 (Ph')), 70.05 (OCH₂), 68.62 (OCH₂), 32.05, 29.77, 29.72, 29.66, 29.54, 29.48, 29.45, 29.34, 26.16, 22.82, 22.78 (CH₂), 14.27 (CH₃). **IR** (ATR): ν / ν̄ = cm⁻¹ = 2923 s, 2853 m, 1591 ss, 1465 m, 1286 s, 1247 s, 1181 s, 1109 m, 1018 m, 753 s. **FD-MS:** *m/z* (%) = 839.1 (5), 839.7 (10), 840.5 (2) [M]²⁺, 1678.3 (46), 1679.0 (100), 1679.7 (14), 1680.1 (7), 1681.3 (7), 1682.3 (2) [M]⁺.

3,7,11-Tris(4-(3,4-didecyloxyphenylazo)phenyl)tris([1,2,4]-triazolo)[4,3-*a*:4',3'-*c*:4'',3''-*e*][1,3,5]triazine (3): According to the general procedure, 200 mg (355 μmol) 5-[4-(3,4-didecyloxyphenylazo)phenyl]tetrazole (**27**) gave 79 mg (140 μmol, 32 %) of an or-

ange-red solid with m.p. 56 °C clearing point 145 °C. Eluent: toluene/ethyl acetate, 40:1. ¹H-NMR (300 MHz, CDCl₃): δ / ppm = 8.37 (d, ³J = 8.3 Hz, 2H, 2-H, 6-H (Ph)), 8.02 (d, ³J = 8.3 Hz, 2H, 3-H, 5-H (Ph)), 7.55 (dd, ³J = 8.3, ⁴J = 2.1 Hz, 1H, 6-H (Ph')), 7.44 (d, ⁴J = 2.2 Hz, 1H, 2-H (Ph')), 6.90 (d, ³J = 8.6 Hz, 1H, 5-H (Ph')), 4.04 (m, 4H, OCH₂), 1.94–1.70 (m, 4H, OCH₂CH₂), 1.55–1.13 (m, 28H, Alkyl), 0.98–0.78 (m, 6H, CH₃). ¹³C-NMR (101 MHz, CDCl₃): δ / ppm = 154.51 (C-4 (Ph)), 152.74 (C-4 (Ph')), 150.53 (C-5 (tria)), 149.63 (C-3 (Ph')), 146.85 (C-1 (Ph')), 140.63 (C-3 (tria)), 131.25 (C-2, C-6 (Ph)), 125.04 (C-1 (Ph)), 122.69 (C-3, C-5 (Ph)), 121.58 (C-6 (Ph')), 111.94 (C-5 (Ph')), 103.66 (C-2 (Ph')), 69.30 (OCH₂), 69.21 (OCH₂), 32.07, 29.80, 29.80, 29.78, 29.75, 29.66, 29.60, 29.58, 29.51, 29.27, 29.24, 26.19, 26.13, 22.84, 22.83, 22.82 (CH₂), 14.27 (CH₃). **IR** (ATR): ν / ν̄ = cm⁻¹ = 2923 s, 2853 m, 1589 s, 1503 m, 1465 m, 1258 ss, 1112 s, 1012 m, 908 m, 851 m, 807 w, 730 ss. **FD-MS:** *m/z* (%) = 838.3 (1), 839.4 (49), 840.1 (10), 840.7 (3) [M]²⁺, 1676.7 (1), 1678.5 (94), 1679.2 (100), 1679.8 (4), 1680.3 (31), 1681.6 (8), 1682.2 (1) [M]⁺. **EA:** C₁₀₂H₁₄₇N₁₅O₆ (1679.36) calcd. 72.95 % C, 8.82 % H, 12.51 % N, found: 72.13 % C, 8.58 % H, 12.41 % N.

3,7,11-Tris(4-(3,4-didodecyloxyphenylazo)phenyl)tris([1,2,4]triazolo)[4,3-*a*:4',3'-*c*:4'',3''-*e*][1,3,5]triazine (4): According to the general procedure, 280 mg (452 μmol) 5-[4-(3,4-didodecyloxyphenylazo)phenyl]tetrazole (**28**) gave 93 mg (50 μmol, 34 %) of an orange-red solid with clearing point 172 °C. Eluent: toluene/ethyl acetate, 80:1. ¹H-NMR (300 MHz, CDCl₃): δ / ppm = 8.37 (d, ³J = 8.2 Hz, 2H, 2-H, 6-H (Ph)), 8.06 (d, ³J = 8.2 Hz, 2H, 3-H, 5-H (Ph)), 7.60 (d, ³J = 8.5 Hz, 1H, 6'-H (Ph)), 7.50 (s, 1H, 2'-H (Ph)), 6.96 (d, ³J = 8.6 Hz, 1H, 2'-H), 4.08 (m, 4H, OCH₂), 2.00–1.69 (m, 4H, OCH₂CH₂), 1.66–1.08 (m, 36H, Alkyl), 0.88 (m, 6H, CH₃). ¹³C-NMR (75 MHz, CDCl₃): δ / ppm = 154.46 (C-4 (Ph)), 152.99 (C-4 (Ph')), 150.64 (C-5 (tria)), 149.72 (C-3 (Ph')), 146.83 (C-1 (Ph')), 140.74 (C-3 (tria)), 131.34 (C-2, C-6 (Ph)), 125.05 (C-1 (Ph)), 122.75 (C-3, C-5 (Ph)), 122.01 (C-6 (Ph')), 112.06 (C-5 (Ph')), 103.83 (C-2 (Ph')), 69.36 (OCH₂), 69.27 (OCH₂), 32.08, 29.87, 29.82, 29.79, 29.61, 29.57, 29.52, 29.28, 29.24, 26.21, 26.14, 22.85 (CH₂), 14.28 (CH₃). **IR** (ATR): ν / ν̄ = cm⁻¹ = 2923 s, 2853 m, 1590 s, 1504 m, 1468 m, 1258 ss, 1113 m, 1016 w, 907 s, 848 w, 729 ss. **FD-MS:** *m/z* (%) = 923.3 (23), 923.7 (65), 924.6 (47), 925.2 (3) [M]²⁺, 1844.4 (3), 1845.5 (1), 1846.5 (16), 1847.0 (100), 1847.7 (76), 1848.6 (27), 1849.3 (6), 1849.8 (3), 1850.6 (3), 1852.1 (1) [M]⁺. **EA:** C₁₁₄H₁₇₁N₁₅O₆ (1847.67) calcd. 74.11 % C, 9.33 % H, 11.37 % N, found: 73.75 % C, 8.77 % H, 11.24 % N.

Acknowledgments

The authors are grateful to Maria Müller for measuring DSC thermograms, the DFG for generous funding (De 515/9-1), and to the reviewers for important advice.

Keywords: Acidochromic Dyes · Discotic liquid crystals · Azobenzene · Differential scanning calorimetry · Polarizing optical microscopy

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Received: May 7, 2019