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# Star-shaped conjugated compounds forming nematic discotic systems

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Abstract—Star-shaped compounds, having a benzene (9a,b) or a 1,3,5-triazine (11a,b) core and stilbenoid arms were prepared. Hexyloxy chains, attached in the middle of the arms, provide nematic discotic phases N<sub>D</sub>, which are unusual for such systems. The position of the sidechains prevents the micro-segregation, which is valid for star-shaped discs of columnar phases. The stilbenoid character of 9a,b and 11a,b guarantees a high light sensitivity. Apart from the statistical CC bond formation by irradiation in solution or in the LC phases, a topochemically controlled chemo-, regio- and stereoselective photocyclodimerization  $11a \rightarrow 12$  was found in the crystalline state. The structure determination of 12 is based on different two-dimensional NMR techniques (COSY, NOESY, HMQC, HMBC). © 2004 Elsevier Ltd. All rights reserved.

## 1. Introduction

Molecules with an arene or hetarene core and three or more conjugated arms, which consist of oligo(1,4-phenylenevinylene) arms (OPV) or oligo(1,4-phenyleneethynylene) arms (OPE), form (in the time average) planar discs and represent, therefore, suitable mesogens for discotic liquid crystals (LC). Most common are benzene cores<sup>1-17</sup> and 1,3,5-triazine or pyrazine cores<sup>18-23</sup> and long, flexible alkyl or alkoxy chains at the periphery. Such a molecular design provokes the formation of hexagonal or rectangular columnar LC phases having a micro-segregation between the region of the  $\pi$  electron systems and the region of the saturated chains. However, the attachment of alkoxy chains in the middle of the arms should prevent such an arrangement, so that nematic mesophases, formed by single discs or two or more weakly aggregated discs, can be expected. Moreover, we attached CN groups at the periphery of the arms in order to generate a donor-acceptor or an acceptor-donor-acceptor character of the arms. The multipolarity should increase the interaction between the discs. Thus, the molecular concept was based on benzene or 1,3,5-triazine cores with three corresponding stilbenoid arms—as shown for the compounds 9a,b and 11a,b in Scheme 1.

## 2. Results and discussion

## 2.1. Synthesis of star-shaped compounds

1,4-Dihexyloxybenzene (1) represents an electron-rich arene which enters a twofold electrophilic substitution by an uncatalyzed reaction with bromine.<sup>24-26</sup> The obtained 1,4-dibromo-2,5-dihexyloxybenzene (2) can be transformed by a Bouveault reaction to the monoaldehyde 3. Acetal formation with trimethoxymethane in the presence of Dowex furnishes high yields of the corresponding dimethyl acetal 4, which gives in a second Bouveault process the mono-protected terephthalaldehyde 5. The Wittig-Horner reaction of **5** and phosphonate  $6a^{27}$  or  $6b^{28}$  leads to the (*E*)stilbenes 7a and 7b, respectively. The protected aldehyde function is deprotected by acidic work-up (Scheme 1). After the purification of **7a**,**b** by column chromatopraphy, the amount of (Z)-isomer is below the limit of detection (3%) in the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The subsequent Wittig-Horner reaction of the triphosphonate  $8^{13,29}$  with 7a,b yields the target compounds 9a,b. In contrast to mesitylene, 2,4,6trimethyl-1,3,5-triazine (10) shows with the aldehydes 7a,b a smooth threefold condensation reaction, which yields the target compounds 11a,b. Particularly 7b, which contains an electron-withdrawing CN group, gives high yields of the star-shaped compound 11b.

#### 2.2. Spectroscopic characterization

Keywords: Condensation; Liquid crystals; Photoreactivity.

The compounds **9a** and **9b** generate yellow solutions in CH<sub>2</sub>Cl<sub>2</sub> with  $\lambda_{max}$ =405 nm ( $\varepsilon_{max}$ =1.24×10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) and  $\lambda_{max}$ =418 nm ( $\varepsilon_{max}$ =1.39×10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>),

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Scheme 1. Preparation of the star-shaped compounds 9a,b and 11a,b.

respectively. Due to the 1,3,5-trisubstitution at the central benzene ring, these values correspond to absorptions of 1,4distyrylbenzenes;<sup>30</sup> the effect of the cross-conjugation can be neglected. The 1,3,5-triazine systems **11a** and **11b** exhibit bathochromically shifted absorption maxima at 431 and 435 nm, respectively [ $\varepsilon_{max}$ =(1.23±0.1)×10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>]. Each arm of **11a** can be regarded as an acceptor–donor (A–D) system and of **11b** as an A–D–A system. The <sup>1</sup>H and <sup>13</sup>C NMR data of **2–5** and **9a**, **9b**, **11a**, **11b** are summarized in the Tables 1 and 2, respectively. The assignment of the signals to certain <sup>1</sup>H and <sup>13</sup>C nuclei is based on two-dimensional measurements (HMQC and HMBC).<sup>31</sup> The (*E*)-configurations of the CC double bonds are certified by coupling constants <sup>3</sup>J (H,H)=16.2\pm0.2 Hz for the olefinic AB spin systems. The IR and MS data of **2–5**, **9a**,**b** and **11a**,**b** as well as IR, NMR and MS data of the stilbenes **7a** and **7b** are listed in Section 4.

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR data of 2-5 (solvent: CDCl<sub>3</sub>, TMS as internal standard)

Compound	C-1	C-2	HC-3	C-4	C-5	HC-6	$\alpha\text{-}CH_2$	$\beta$ -CH <sub>2</sub>	$\gamma$ -CH <sub>2</sub>	$\delta$ -CH <sub>2</sub>	$\epsilon\text{-}CH_2$	$CH_3$	$R^{1}, R^{2}$
2			7.06			7.06	3.92	1.78	1.41	1.31	1.31	0.89	
-	111.2	150.1	118.5	111.2	150.1	118.5	70.4	29.1	25.6	31.5	22.5	14.0	10 20/100 0 (CHO)
3	124.3	155.6	118.5	121.0	149.9	110.7	3.98 69.5 69.9	1.78 29.0	1.41 25.6	31.5	1.31 22.6	0.88 14.0	10.38/188.9 (CHO)
4			7.07			7.05	3.93	1.76	1.45	1.31	1.31	0.88	3.36/54.2 (OCH <sub>3</sub> )
	126.8	151.0	117.4	112.6	149.6	112.6	69.4 70.1	29.2	25.7	31.5	22.6	14.0	5.54/99.3 (CH)
5			7.28			7.17	3.96 4.04	1.78	1.43	1.31	1.31	0.88	10.44/189.6 (CHO) 3.40/54.6 (OCH <sub>3</sub> )
	124.7	156.1	109.8	134.7	150.5	112.1	68.9 69.2	29.2	25.7	31.5	22.6	14.0	5.58/99.3 (CH)

Compound Positions (shown in Scheme 1) b d f h,h' i,i' j k а с e g 9a 7.26 7.37 7.54 7.15 7.51 7.15/7.16 7.55 127.1 138.1 111.0/111.2 151.3/151.3 127.1 127.2 128.6 126.6 129.0 123.7 124.3 9b 7.62 7.59 7.13 7.60 7.12/7.15 7.53 119.1 111.0/111.2 151.2/151.6 132.4 126.9 142.6 127.4 126.9 125.9 128.2 124.2 11a 7.27 7.36 7.55 7.18 7.49 7.16/7.23 8.60 127.6 126.5 137.7 129.9 123.3 129.2 110.0/111.3 150.9/152.3 125.1 128.6 1363 11b 7.63 7.56 7.17 7.58 7.13/7.23 8.59 119.1 151.2/152.2 132.5 126.8 142.2 127.8 127.3 127.9 110.9/111.8 126.1 136.2 γ-CH<sub>2</sub> δ-CH<sub>2</sub> CN 1 m  $\alpha$ -CH<sub>2</sub> β-CH<sub>2</sub> ε-CH<sub>2</sub> CH<sub>3</sub> n 7.21 7.59 4.06/4.10 0.88/0.93 9a 1.90 1.56 1.40 1.40 25.9/26.0 31.6/31.7 138.7 29 5/29 6 128.9 124.0 69.7/69.8 22.6 14.09b 7.22 7.56 4.07/4.08 1.89 1.55 1.38 1.38 0.87/0.92 129.5 138.6 69.6/69.8 119.1 124.2 29.5 26.031.6 22.6 14.0 0.85/0.92 11a 7.21 4.04/4.11 1.90 1.55 1.38 1.38 171.5 29.3/29.4 25.8/25.9 69 4/69 6 14.0126.7 31.6 22.6 9.84/0.91 11b 1.90 7.22 4.05/4.10 1.54 1.37 1.37 127.0 171.5 69.3/69.6 29.3 25.8/25.9 31.6 22.6 14.0 119.1

Table 2. <sup>1</sup>H and <sup>13</sup>C NMR data of the star-shaped compounds 9a, 9b, 11a and 11b (CDCl<sub>3</sub>, TMS an internal standard)

## 2.3. Formation of liquid crystalline phases

Star-shaped compounds, which consist of stilbenoid building blocks and long flexible chains in peripheral positions, can generate thermotropic mesophases. In contrast to earlier studied systems,<sup>23,32</sup> the compounds **9a**, **9b**, **11a** and **11b** bear hexyloxy chains in the middle of the three arms-and not at the periphery. Thus, the usual micro-segregation between the  $\pi$ -electron regions and the aliphatic regions cannot be realized. Consequently, nematic discotic phases can be expected instead of columnar phases. The differential scanning calorimetry (DSC) of 9a reveals in the second heating curve (rate  $10^{\circ}$  per min) a glass transition ( $T_g=8$  °C) to a first nematic discotic phase N<sub>D</sub>. A second mesophase  $N'_{D}$  is formed at 114 °C. The small endothermic peak for the latter transition corresponds to a low transition enthalpy of  $0.2 \text{ kJ mol}^{-1}$ . Finally, the isotropic molten phase is reached at 126 °C ( $\Delta H=0.4 \text{ kJ mol}^{-1}$ ). The first (and second) cooling curve exhibits only one nematic discotic phase, which is formed at 126 °C ( $\Delta H=0.4 \text{ kJ mol}^{-1}$ ) and disappears at  $T_g=2$  °C. The structural difference between the two nematic phases is not known. The polarized optical microscopy shows typical nematic 'Schlieren' textures<sup>33,34</sup> for both phases, which have a low viscosity. Moreover, at 114 °C a homeotropic reorganization becomes visible in the microscope. Possibly, the N<sub>D</sub> phase consists of molecular pairs (or higher aggregates), whereas the  $N'_D$  phase consists of single discs.

The introduction of cyano groups causes a push-pull character of the arms; the phase transition temperatures and the corresponding  $\Delta H$  values of **9b** are much higher. The second heating curve (heating rate 10° per min) reveals a transformation of the crystalline phase to a nematic discotic phase at 209 °C ( $\Delta H$ =40 kJ mol<sup>-1</sup>) and the formation of the isotropic phase at 232 °C ( $\Delta H$ =1 kJ mol<sup>-1</sup>). The cooling curve confirms this phase behavior; at 232 °C ( $\Delta H$ =-1 kJ mol<sup>-1</sup>) the nematic phase is found and at 201 °C ( $\Delta H$ =-37 kJ mol<sup>-1</sup>) the crystalline phase. Figure 1 shows the typical nematic textures of **9b** and **11a**. The 1,3,5-triazine **11a** exhibits in the second heating curve an N<sub>D</sub> phase ( $T_g$ =95 °C) before the isotropic melt is reached at

107 °C ( $\Delta H$ =35 kJ mol<sup>-1</sup>). The acceptor–donor–acceptor (A–D–A) character of **11b** leads to a strong increase of the phase transition temperatures. A nematic phase is obtained at  $T_g$ =210 °C and disappears at 236 °C ( $\Delta H$ =49.8 kJ mol<sup>-1</sup>). The cooling curve of **11b** shows the formation of the nematic phase at 213 °C; the undercooling effect for **11a** is so high and the rate of the phase transitions so low, that the DSC of **11a** does not exhibit an endothermic peak in the cooling curve. These observations and the high  $\Delta H$ 

Figure 1. Nematic 'Schlieren' textures obtained by polarization microscopy. Upper part: measurement of 11a at 99 °C; lower part: measurement of 9b at 224 °C.



values for the isotropization of **11a** and **11b** are an indication for  $N_{col}$  phases.<sup>35</sup>

## 2.4. Photochemistry

Stilbenoid compounds like **9a,b** and **11a,b** are lightsensitive.<sup>36</sup> The major irreversible process in solution as well as in the LC phases consists of CC bond formations between the original olefinic centers (Scheme 2). Monochromatic irradiation with  $\lambda$ =366 nm or even an extended absorption of daylight is sufficient for the break-down of the LC phases of **9a,b** and **11a,b**. Finally crosslinked oligomers and polymers are generated, in which four-membered rings and CC bonds in different directions are generated. The process can be used as imaging technique with liquid crystals.



**Scheme 2.** Photochemical CC bond formation between olefinic centers of stilbenoid compounds.

In contrast to the statistical CC bond formation, **11a** shows in the crystalline state a selective photodimerization. Daylight or monochromatic irradiation with  $\lambda$ =366 nm provokes a chemoselective  $[2\pi+2\pi]$  cycloaddition of the inner, more polar olefinic double bonds. The NMR studies reveal a regioselective head-to-tail dimerization with a stereoselective syn arrangement of head and tail and a preservation of the trans configuration, which is originally present at the olefinic CC bonds (Scheme 3). The chemo-, regio- and stereoselectivity can be explained by a topochemical control. Amorphous **11a** does not exhibit this photocyclodimerization.

The structure elucidation of **12** is based on one- and twodimensional NMR techniques (COSY, NOESY, HMQC and HMBC).<sup>31</sup> The integration of the <sup>1</sup>H NMR signals proves that only one four-membered ring is formed. The symmetry of the dimer is manifested in the number of <sup>1</sup>H and <sup>13</sup>C NMR signals. The chemoselective reaction of the inner CC double bonds in **11b** becomes obvious (HMBC) by the couplings of 1-H ( $\delta$ =4.87) and 2-H ( $\delta$ =5.27) with the quaternary carbon atom OC<sub>q</sub> ( $\delta$ =151.2) of the adjacent benzene ring and the carbon atom NC<sub>q</sub> ( $\delta$ =178.2) of the 1,3,5-triazine ring. The *syn* head-to-tail cycloaddition is revealed by the through-space interactions (NOESY) of the substituents on C-1 and C-4 of **12**.

The protons on the four-membered ring constitute an AA'MM' spin system. Figure 2 shows the measured and





Figure 2. <sup>1</sup>H NMR signals of the protons at the four-membered ring of 12, representing an AA'MM' spin pattern. Upper part: measured signals in CDCl<sub>3</sub>; lower part: calculated spectrum<sup>38</sup> ( ${}^{3}J_{AM}={}^{3}J_{A'M}=10.7$  Hz,  ${}^{3}J_{AM'}={}^{3}J_{A'M}=7.2$  Hz,  $|{}^{4}J_{AA'}|=0.5$  Hz,  $|{}^{4}J_{MM'}|=0.8$  Hz).

the calculated signal pattern. A head-to-tail addition with *anti* orientation would lead to an  $A_2M_2$  spin system with a completely different pattern.<sup>37</sup>

#### 3. Conclusion

The star-shaped compounds **9a**,**b** having a benzene core and **11a,b** having a 1,3,5-triazine core could be obtained by Wittig-Horner reactions and alkaline condensation reactions, respectively. Due to the attachment of hexyloxy chains in the middle of the arms, nematic LC phases are formed-and no columnar phases, which require extended micro-segregations. The stilbenoid character of the arms provokes a high photoreactivity. The LC phases are transformed isothermally by irradiation to isotropic melts by statistical photochemical CC bond formations. This irreversible process provides an imaging technique with liquid crystals. A chemo-, regio- and stereoselective photocyclodimerization was found for 11a in the crystalline state. The topochemically controlled reaction works already in the daylight; amorphous particles of 11a do not show this process.

#### 4. Experimental

## 4.1. General remarks

Melting points were measured on a Büchi melting point apparatus and are uncorrected. The phase transitions of **9a,b** and **11a,b** were studied with a Perkin Elmer DSC 7. The polarization microscopy was performed with a Zeiss Jenapol equipped with a Linkam TMS 93 and a digital camera CC12, Soft Imaging System. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with the Bruker spectrometers AMX 400, ARX 400 and Avance 600. The UV/Vis spectra were obtained with a Zeiss MCS 320/340. A Perkin Elmer GX was used for the measurement of the IR spectra in transmission, whereas a Nicolet 5 SXB with a LOT-Oriel Golden-Gate ATR unit served for the measurements in reflection. The mass spectra were obtained on a Finnigan MAT 95 spectrometer with the field desorption (FD) technique. The elemental analyses were determined in the Microanalytical Laboratory of the Chemistry Department of the University of Mainz.

**4.1.1. 1,4-Dibromo-2,5-dihexyloxybenzene** (2). Preparation according to the literature.<sup>24-26</sup>

4.1.2. 4-Bromo-2,5-dihexyloxybenzaldehyde (3). To 80.0 g (0.18 mol) 2, dissolved in 300 mL dry diethylether, 71.9 mL (0.20 mol) of a 2.7 M solution of n-BuLi in *n*-heptane were slowly added under argon at -20 °C. After 1 h stirring at this temperature, the reaction mixture was brought to room temperature and treated tropwise with dry DMF till the reaction came to the end. After stirring for another hour, 30 mL 6 M HCl was added. The organic layer was separated, washed two times with the equivalent amount of water, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified by column filtration  $(10 \times 15 \text{ cm SiO}_2,$  $CCl_4$ ; 31.1 g (44%) aldehyde **3** could be obtained as a colorless solid, which melted at 58 °C. (Apart from the main fraction 3.0 g (5%) of 2,5-dihexyloxyterephthaldialdehyde could be isolated). **3**: IR (KBr):  $\tilde{\nu}$  (cm<sup>-1</sup>)=2970, 2850, 1670, 1590, 1490, 1470, 1380, 1260, 1200, 1020, 990, 970, 880, 750; FD MS: *m/z* (%)=385 (100) [M+H<sup>+</sup>], Br isotope pattern. Anal. Calcd for C19H29O3Br (385.3): C, 59.22; H, 7.59; Br 20.74. Found: C, 59.51; H, 7.41; Br, 20.35.

**4.1.3. 4-Bromo-2,5-dihexyloxybenzaldehyde dimethyl acetal** (**4**). Aldehyde **3** (24.0 g, 62.3 mmol), trimethoxymethane (19.83 g, 190 mmol) and 3.0 g Dowex 50 W-X8 were refluxed for 10 h. After stirring for 10 min with 2.5 g (23.6 mmol) Na<sub>2</sub>CO<sub>3</sub> at room temperature, the reaction mixture was filtered and evaporated. The residue was boiled with 50 mL dry *n*-hexane for 10 min and immediately filtered. After removal of the volatile parts, 24.13 g (90%) of an oil was obtained. IR (film):  $\tilde{\nu}$  (cm<sup>-1</sup>)=2930, 2850, 1490, 1460, 1370, 1200, 1090, 1050, 980, 880, 750; FD MS: *m/z* (%)=430 (100) [M<sup>+</sup>]. Anal. Calcd for C<sub>21</sub>H<sub>35</sub>O<sub>4</sub>Br (431.4): C, 58.47; H, 8.18; Br, 18.52. Found: C, 58.80; H, 7.95; Br, 18.02.

**4.1.4. 2,5-Dihexyloxy-4-dimethoxymethylbenzaldehyde (5).** To 23.13 g (53.36 mmol) **4** in 300 mL dry diethylether,

23.80 mL (64.40 mmol) of a 2.7 M solution of *n*-BuLi were dropped at -25 °C. After 2 h dry DMF was dropwise added at room temperature till the reaction stopped. Water (50 mL) was added, the organic layer was separated and the water phase several times extracted with diethylether. The combined organic phases were dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. Column filtration (15×10 cm SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>-triethylamine 99:1) yielded 18.40 g (90%) of a yellow oil. IR (film):  $\tilde{\nu}$  (cm<sup>-1</sup>)=2950, 2840, 1670, 1600, 1480, 1460, 1410, 1380, 1200, 1150, 1070, 980, 950, 880; FD MS: *m/z* (%)=380 (100) [M<sup>+</sup>]. Anal. Calcd for C<sub>22</sub>H<sub>36</sub>O<sub>5</sub> (380.5): C, 69.44; H, 9.54. Found: C, 69.10; H, 9.84.

4.1.5. (E)-2,5-Dihexyloxy-4-(2-phenylethenyl)benzaldehyde (7a). Diethyl benzylphosphonate  $(6a)^{27}$  (1.23 g, 5.4 mmol) and 5 (2.00 g, 5.3 mmol) were dissolved in 20 mL dry THF and dropped under Ar at 0 °C to 0.30 g (12.5 mmol) NaH in 40 mL dry THF. After 24 h 0.20 g (8.33 mmol) NaH in 30 mL dry THF was added and the stirring continued at room temperature for further 24 h. The mixture was cooled to 0 °C before 50 mL H<sub>2</sub>O were slowly added. The product was extracted with 100 mL CHCl<sub>3</sub> and the solution vigorously stirred with 20 mL 2 M HCl for 2 h. The organic layer was separated, washed with 50 mL saturated NaHCO<sub>3</sub> and 50 mL H<sub>2</sub>O. The organic phase was dried with MgSO<sub>4</sub> and evaporated. Column chromatography [20×10 cm SiO<sub>2</sub>, petroleum (bp 40-70 °C)/ethylacetate 25:1] yielded 1.80 g (84%) of a yellow oil. IR (film):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3050, 3020, 2940, 2920, 2860, 1655, 1595, 1205, 970, 750, 690; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ =0.90 (m, 6 H, CH<sub>3</sub>), 1.24-1.56 (m, 12H, CH<sub>2</sub>), 1.83 (m, 4H, CH<sub>2</sub>), 4.01 (t, 2H, OCH<sub>2</sub>), 4.10 (t, 2H, OCH<sub>2</sub>), 7.16 (s, 1H, 3-H), 7.31 (s, 1H, 6-H), 7.22/7.46 (AB,  ${}^{3}J=16.6$  Hz, 2H, olefin. H), 7.29 (m, 1H, p-H, phenyl), 7.36 (m, 2H, m-H, phenyl), 7.53 (m, 2H, *o*-H, phenyl), 10.43 (s, 1H, CHO); <sup>13</sup>C NMR (CDCl<sub>3</sub>);  $\delta = 13.9 (CH_3), 22.5 - 31.5 (CH_2, partly superimposed), 69.2,$ 69.4 (OCH<sub>2</sub>), 110.3, 110.8, 123.7, 126.9, 128.2, 128.7, 132.3 (aromat. and olefin. CH), 124.5, 134.4, 137.3 (aromat.  $C_q$ ), 150.9, 156.3 ( $C_q$ O), 189.0 (CHO); FD MS: m/z(%)=408 (100) [M<sup>+</sup>]. Anal. Calcd for C<sub>27</sub>H<sub>36</sub>O<sub>3</sub> (408.6): C, 79,37;H, 8.88. Found: C, 79.40;H, 8.74.

4.1.6. (E)-4-[2-(4-Formyl-2,5-dihexyloxyphenyl)**ethenyl]benzonitrile (7b).** 137 g (5.4 mmol) diethyl 4-cyanobenzylphosphonate (**6b**),<sup>28</sup> 2.00 g (5.3 mmol) **5** and 0.60 g (25.0 mmol) NaH in 40 mL dry THF were reacted as described for 7a. The corresponding work-up and the column chromatography [petroleum (bp 40-70 °C)/ ethyl-acetate 15:1] yielded 2.00 g (88%) of a yellow oil which was used without further purification for the following reaction step. Spectroscopic characterization. IR (film):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3040, 2940, 2920, 2840, 1665, 1600, 1415, 1205, 970, 865; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ=0.88 (m, 6H, CH<sub>3</sub>), 1.23–1.51 (m, 12H, CH<sub>2</sub>), 1.83 (m, 4H, CH<sub>2</sub>), 4.01 (t, 2H, OCH<sub>2</sub>), 4.08 (t, 2H, OCH<sub>2</sub>), 7.14 (s, 1H, aromat. H), 7.31 (s, 1H, aromat. H), 7.20/7.55 (AB,  ${}^{3}J=16.6$  Hz, 2H, olefin. H), 7.58/7.63 (AA'BB', 4H, aromat. H), 10.43 (CHO); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ=14.0 (CH<sub>3</sub>), 22.5-31.5 (CH<sub>2</sub>, partly superimposed), 69.1, 69.3 (OCH<sub>2</sub>), 110.3/ 111.1 (aromat. CH and C-1), 127.1, 126.7, 130.1, 132.5 (aromat. and olefin. CH), 118.9 (CN), 125.0, 132.8, 141.7 (aromat. C<sub>q</sub>), 151.0, 156.0 (aromat. C<sub>q</sub>O), 189.0 (CHO); FD MS: m/z (%)=433 (100) [M<sup>+</sup>].

4.1.7. all-(E)-1,3,5-Tris{2-[2,5-dihexyloxy-4-(2-phenylethenyl)phenyl]ethenyl}benzene (9a). Tri-phosphonate  $8^{13}$  (0.42 g, 0.79 mmol) and aldehyde 7a (1.00 g, 2.45 mmol) were dissolved in 10 mL dry THF and dropped at 0 °C under Ar to 0.25 g (6.3 mmol) NaH (60% in paraffin) suspended in 40 mL dry THF. The reaction mixture was warmed to room temperature and stirred for 2H, before it was poured on 50 g crushed ice; 50 mL 2 M HCl was added. The precipitate was filtered off, dried and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Portionwise addition of ethanol yielded 0.36 g (35%) of a yellow solid with the clearing point  $T_{\rm cl}=126$  °C. IR (KBr):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3030, 2950, 2920, 2860, 1590, 1570, 1200, 970, 755, 695; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}} = 405 \text{ nm}, \ \varepsilon = 1.24 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}; \text{ FD MS: } m/z$ (%)=1293 (100) [M+H<sup>+</sup>]. Anal. Calcd for C<sub>90</sub>H<sub>114</sub>O<sub>6</sub> (1291.9): C, 83.68;H, 8.89. Found: C, 83.47;H, 8.82.

4.1.8. all-(E)-1,3,5-Tris(2-{4-[2-(4-cyanophenyl)ethenyl]-2,5-dihexloxyphenyl}ethenyl)benzene (9b) or all-(E)-4-[2-(4-{2-[3,5-bis(2-{4-[2-(4-cyanophenyl)ethenyl]-2,5dihexyloxyphenyl}ethenyl)phenyl]ethenyl}-2,5-dihexyloxyphenyl)ethenyl]benzonitrile (9b). According to the preparation of 9a, 0.26 g (25%) of pure 9b was obtained from 1.00 g (2.3 mmol) **7b**, 0.40 g (0.8 mmol) **8** and 0.25 g (6.3 mmol) NaH. The raw product (about 1.0 g) was first purified on a column  $[10 \times 15 \text{ cm SiO}_2, \text{ toluene-ethyl}]$ acetate 2:1] before it was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/ C<sub>2</sub>H<sub>5</sub>OH as described for 9a. The yellow solid 9b has a clearing point  $T_{cl}$ =232 °C. IR (KBr):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3020, 2940, 2910, 2850, 2220, 1615, 1580, 1200, 960, 855, 815; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ =418 nm,  $\epsilon$ =1.39×10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>; FD MS: m/z (%)=1368 (100) [M+H<sup>+</sup>]. Anal. Calcd for C<sub>93</sub>H<sub>111</sub>N<sub>3</sub>O<sub>6</sub> (1366.9): C, 81.72;H, 8.18; N, 3.07. Found: C, 81.34;H, 7.90; N, 2.91.

**4.1.9.** *all*-(*E*)-2,4,6-Tris{2-[2,5-dihexyloxy-4-(2-phenylethenyl)phenyl]ethenyl}-1,3,5-triazine (11a). Aldehyde 7a (0.5 g, 1.22 mmol), dissolved in 7 mL dry THF, was added to 45.2 mg (0.37 mmol) 10 and 180 mg (1.60 mmol) KOC(CH<sub>3</sub>)<sub>3</sub> in 7 mL dry THF. After stirring for 5 d at ambient temperature, the raw product was precipitated by the addition of methanol. Column chromatography (4×40 cm SiO<sub>2</sub>, toluene) yielded 153 mg (32%) of a yellow solid;  $T_{cl}$ =107.5 °C. IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3081, 3057, 3025, 2953, 2928, 2869, 2857, 1623, 1601, 1504, 1467, 1422, 1376, 1288, 1251, 1207, 1030, 986, 964, 873, 852, 753, 692; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ =431 nm, log  $\varepsilon$ =5.0; FD MS: *m/z* (%)=1296 (100) [M+H<sup>+</sup>]. Anal. Calcd for C<sub>87</sub>H<sub>111</sub>N<sub>3</sub>O<sub>6</sub> (1294.9): C, 80.70;H, 8.64; N, 3.25. Found: C, 80.48;H, 8.84; N, 3.21.

4.1.10. *all*-(*E*)-2,4,6-Tris(2-{4-[2-(4-cyanophenyl)ethenyl]-2,5-dihexyloxyphenyl}ethenyl)-1,3,5-triazine (11b) or *all*-(*E*)-4[2-(4-{2-[4,6-bis(2-{4-[2-(4-cyanophenyl)ethenyl]-2,5-dihexyloxyphenyl}ethenyl)-1,3,5triazin-2-yl]ethenyl}-2,5-dihexyloxyphenyl)ethenyl]benzonitrile (11b). According to the preparation of 11a, 257 mg (94%) of 11b was obtained from 286 mg (0.66 mmol) 7b, 24.5 mg (0.20 mmol) 10 and 67.5 mg (0.60 mmol) KOC(CH<sub>3</sub>)<sub>3</sub> in 15 mL dry THF. After refluxing for 2 d, the purification was performed by column chromatography [4×40 cm SiO<sub>2</sub>, petroleum (bp 40–70 °C/ ethyl-acetate 7:1] and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/

CH<sub>3</sub>OH. The orange solid has a clearing point at  $T_{\rm cl}$ =235.8 °C. IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>)=3060, 2926, 2856, 2222, 1679, 1623, 1601, 1483, 1467, 1423, 1374, 1337, 1320, 1285, 1253, 1204, 1173, 1029, 987, 968, 855, 817, 726, 666; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$ =435, log  $\varepsilon$ =5.09; FD MS: m/z (%)=1371 (100) [M+H<sup>+</sup>]. Anal. Calcd for C<sub>90</sub>H<sub>108</sub>N<sub>6</sub>O<sub>6</sub> (1369.9): C, 78.91;H, 7.95; N, 6.13. Found: C, 78.74;H, 8.13; N, 6.09.

4.1.11. all-(E)-1r,3t-Bis(4,6-bis{2-[2,5-dihexyloxy-4-(2phenylethenyl)phenyl]ethenyl}-1,3,5-triazin-2-yl)-2c,4tbis[2,5-dihexvloxy-4-(2-phenvlethenvl)phenvl]cvclobutan (12). A saturated solution of 129 mg (0.1 mmol) 11a in CHCl<sub>3</sub> was spread on a glass surface; the solvent was slowly vaporized and crystallization of 11a started. Irradiation of the ready thin crystalline layer with monochromatic light ( $\lambda$ =366 nm) or with day light led to the dimerization, which was followed by TLC control (SiO<sub>2</sub>, toluene).Column chromatography ( $20 \times 3$  cm SiO<sub>2</sub>, toluene) yielded up to 84 mg (65%) of 12, which melted at 160 °C. IR (ATR):  $\tilde{\nu}$  (cm<sup>-1</sup>)=2954, 2932, 2870, 2858, 1624, 1600, 1518, 1467, 1424, 1378, 1288, 1251, 1207, 1030, 991, 962, 753, 691; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ=0.77 (t, 6H, CH<sub>3</sub>), 0.79 (t, 6H, CH<sub>3</sub>), 0.80 (t, 12H, CH<sub>3</sub>), 0.90 (t, 12H, CH<sub>3</sub>), 1.14–1.58 (m, 72H, CH<sub>2</sub>), 1.84 (m, 24H, CH<sub>2</sub>), 3.70 (m, 2H, OCH<sub>2</sub>), 3.78 (m, 2H, OCH<sub>2</sub>), 3.88 (m, 4H, OCH<sub>2</sub>), 4.01 (t, 8H, OCH2), 4.05 (t, 8H, OCH2), 4.87 (AA' of AA'MM', 2H, 1-H, 3-H), 5.27 (MM', 2H, 2-H, 4-H), 6.86 (s, 2H, aromat. H), 6.91/7.31 (AM, <sup>3</sup>J=16.4 Hz, 4H, olefin. H), 7.03 (s, 2H, aromat. H), 7.08/8.47 (AX,  ${}^{3}J=16.2$  Hz, 8H, olefin. H), 7.11 (s, 4H, aromat. H), 7.16/7.48 (AM, <sup>3</sup>J=16.2 Hz, 8H, olefin. H), 7.16 (s, 4H, aromat. H), 7.25 (m, 6H, aromat. H), 7.37 (m, 12H, aromat. H), 7.53 (m, 12H, aromat. H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ =14.0 (12 CH<sub>3</sub>), 22.6 (12 CH<sub>2</sub>), 25.7-25.9 (12 CH<sub>2</sub>), 29.2-29.4 (12 CH<sub>2</sub>), 31.5-31.9 (12 CH<sub>2</sub>), 40.5 (C-1, C-3), 49.5 (C-2, C-4), 69.4 (4 OCH<sub>2</sub>), 69.5 (4 OCH<sub>2</sub>), 70.1 (2 OCH<sub>2</sub>), 109.0 (2 aromat. CH), 110.5 (4 aromat. CH), 111.8 (4 aromat. CH), 114.4 (2 aromat. CH), 123.4 (4 olefin. CH), 123.9 (2 olefin. CH), 124.9 (2 aromat. Cq,) 125.0 (4 aromat. Cq), 126.3 (4 aromat. CH), 126.5 (4 olefin. CH), 126.6 (8 aromat. CH), 126.9 (2 aromat. CH), 127.6 (2 olefin. CH), 127.6 (4 aromat. CH), 128.5 (4 aromat. CH), 128.7 (8 aromat. CH), 129.1 (4 aromat. C<sub>q</sub>), 129.7 (4 olefin. CH), 130.6 (2 aromat.  $C_q$ ), 136.1 (4 olefin. CH), 137.8 (4 aromat. C<sub>q</sub>), 138.2 (2 aromat. C<sub>q</sub>), 150.6 (2 aromat.  $C_qO$ ), 150.9 (4 aromat.  $C_qO$ ), 151.2 (2 aromat.  $C_qO$ ), 152.3 (4 aromat.  $C_qO$ ), 170.9 (4  $C_qN$ ), 178.2 (2  $C_qN$ ); FD MS: m/z (%)=1295 (100) [M<sup>2+</sup>], 2590 (88) [M<sup>+</sup>]. Anal. Calcd for C<sub>174</sub>H<sub>222</sub>N<sub>6</sub>O<sub>12</sub> (2589.7): C, 80.70;H, 8.64; N, 3.25. Found: C, 80.57;H, 8.91; N, 3.32.

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