Star-Shaped Compounds Having 1,3,5-Triazine Cores

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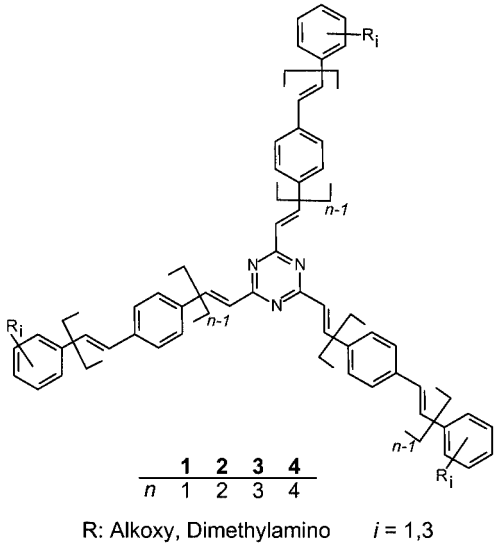
The 1,3,5-triazine derivatives **1**–**4** having styryl or higher oligo(phenylenevinylene) chains in the 2-, 4-, and 6-positions represent star-shaped push-pull compounds. Alkoxy or dimethylamino groups on the peripheral benzene rings, which act as electron donors, and the central 1,3,5-triazine ring, which acts as an electron acceptor, cause intramolecular charge transfer (ICT) to occur in the absorption $S_0 \rightarrow S_1$. Protonation of the 1,3,5-triazine core enhances the effect, as demonstrated by a bathochromic shift; a secondary protonation on the dimethylamino groups, however, leads to the breakdown of the ICT. Thus, the yellow compound **1d** first becomes violet and then colorless upon the addition of trifluoroacetic acid. In neutral solution, the long-wavelength absorption of the series **1f**, **2b**, **3**, and **4** converges to λ_∞ = 427 nm (with an effective conjugation length n_{ECL} = 7). The absorption of the corresponding protonated compounds approaches λ_∞ = 515 nm (n_{ECL} = 6).

Introduction

Conjugated oligomers are attracting increased attention because their optical, electrical, and optoelectronic properties lead to interesting applications in materials science; moreover, they are model compounds for their corresponding conjugated polymers.[1–20]

The building blocks of these oligomers, for example, 1,4-phenylenevinylene units, are in most cases linearly arranged, but instances of the use of cyclic,[21] dendritic,[22–29] and star-shaped structures[16,30] are also known. Recently, we found that a terminal donor–acceptor substitution in linear systems causes an unexpected behavior to occur in their optical properties.[31–39] This article focuses on the star-like systems **1**–**4**, which have an electron-deficient 1,3,5-triazine core and styryl or oligo(1,4-phenylenevinylene) (OPV) arms that feature terminal electron-releasing substituents. Scheme 1 displays the general formula of these compounds.



Scheme 1. Star-shaped compounds **1**–**4** having 1,3,5-triazine cores, which behave as electron acceptors, and OPV arms featuring terminal donor substituents

Results and Discussion

The high reactivity of 2,4,6-trimethyl-1,3,5-triazine (**5**) in alkaline condensation reactions with aldehydes is well known; however, the product of its reaction with benzaldehyde (**6a**), namely 2,4,6-tristyryl-1,3,5-triazine (**1a**), is mentioned sparingly in the literature.[34–36] We prepared the *para*-substituted derivatives **1b**–**e** by treating **5** with the aldehydes **6b**–**e** (Scheme 2). The reaction times at room temperature amounted to several days. The aldehyde **6d** reacts particularly slowly because of its low nucleophilicity. Thus, the twofold condensation product, 2,4-bis{(*E*)-2-[4-(dimethylamino)phenyl]ethenyl}-6-methyl-1,3,5-triazine (**1d′**), is still present after a reaction time of 7 d.

The push-pull effect in the three arms becomes evident by the polarization of the olefinic bridges, which is expressed by considerable differences in the chemical shifts observed in ^{13}C and ^{1}H NMR spectra. According to the trend of their increasing donor strengths, the $\Delta\delta$ (^{13}C) values of the two olefinic carbon atoms increase in the series

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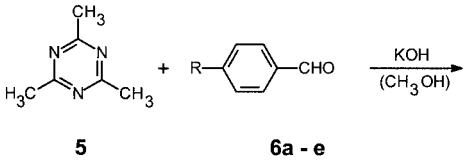
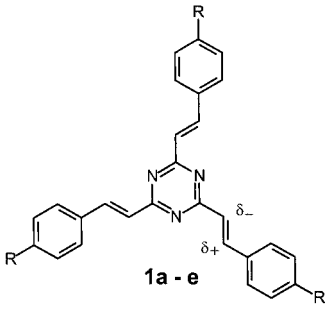
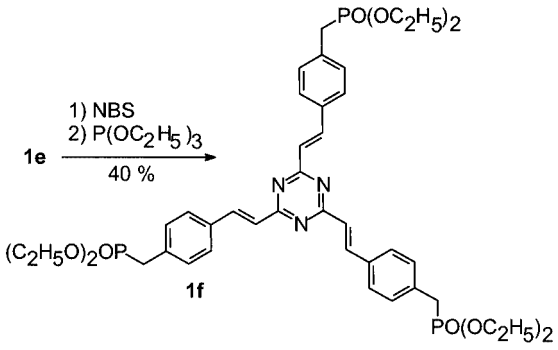
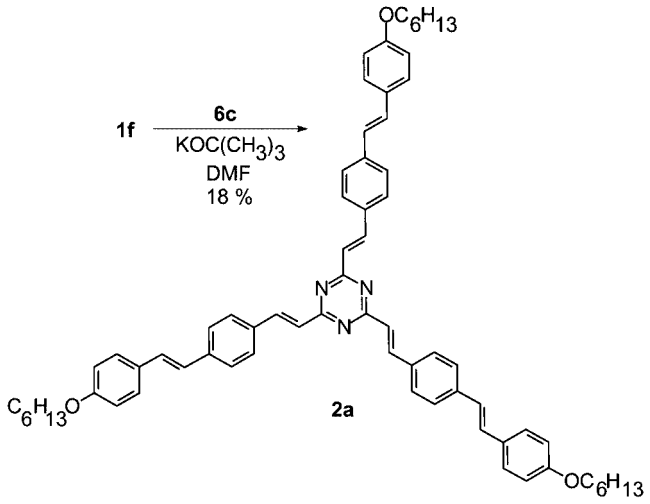




1,6	a	b	c	d	e
R	H	OCH_3	OC_6H_{13}	$N(CH_3)_2$	CH_3
Yield					
1 [%]	87	94	55	39	96

Scheme 2. Preparation of the (*E*,*E*,*E*)-2,4,6-tristyryl-1,3,5-triazines **1a**−**e**





Scheme 3. Preparation of 2,4,6-tris[(*E*)-2-(4-{(*E*)-2-[4-(hexyloxy)-phenyl]ethenyl}phenyl)ethenyl]-1,3,5-triazine (**2a**)

1a, **1e**, **1b**, **1c**, **1d** (15.4, 16.0, 16.7, 17.0, and 19.9 ppm, respectively), as do the values of $\Delta\delta$ (^{1}H) of the olefinic protons (1.11, 1.14, 1.20, 1.20, and 1.26 ppm, respectively). Table 1 summarizes the ^{1}H and ^{13}C NMR spectroscopic data of compounds **1a**−**e**.

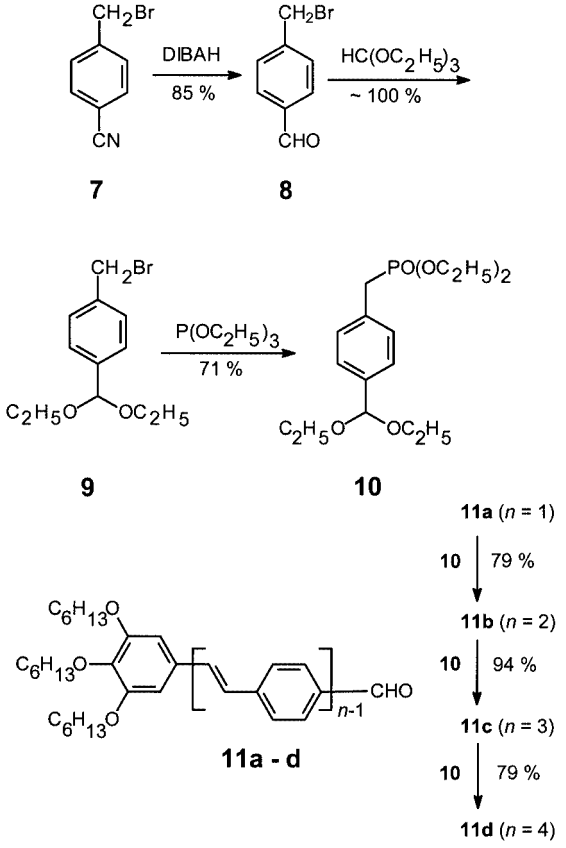
To extend the conjugated arms of the star-shaped compounds **1**, we transformed **1e** into the triphosphonate **1f** by a Wohl−Ziegler bromination with NBS and a subsequent Arbusov reaction with triethyl phosphite. The Wittig−Horner olefination of **1f** with 4-(hexyloxy)benzaldehyde (**6c**) gave the target compound **2a** (Scheme 3).

The push-pull effect in **2a** causes a polarization of the olefinic bonds, which is reduced relative to that of **1c**. The values of $\Delta\delta(^{13}C)$ and $\Delta\delta(^1H)$ for the inner double bond are 15.4 and 1.12 ppm, respectively, and for the outer double bond they are 3.8 and 0.16 ppm, respectively.[37]

Table 1. ^{1}H and ^{13}C NMR spectroscopic data of compounds **1a**−**e** (δ values in $CDCl_3$, relative to TMS as internal standard; coupling constants $^3J_{trans}$ in Hz)

	Triazine	Vinylene			Phenyl(ene)				Side chain	
	C_q	$HC_{i(nner)}$	$HC_{o(uter)}$	$^3J_{H,H}$	*i*-C	*o*-CH	*m*-CH	*p*-C(H)		
1a		7.17	8.28	16.0		7.69	7.41	7.41		
	171.3	126.3	141.7		135.5	128.2	128.9	129.7		
1b		7.01	8.21	15.8		7.62	6.94		3.85 (OCH_3)	
	171.4	124.3	141.0		128.5	129.7	114.4	161.1	55.4 (OCH_3)	
1c		7.00	8.20	15.7		7.61	6.92		3.99 (OCH_2)	1.79 (CH_2) 0.90(CH_3)
										1.46 (CH_2)
										1.34 ($2CH_2$)
	171.4	124.1	141.1		128.3	129.7	114.9	160.7	68.2 (OCH_2)	31.6 (CH_2) 14.0(CH_3)
										29.2 (CH_2)
										25.7 (CH_2)
										22.6 (CH_2)
1d		6.92	8.18	15.9		6.71	7.57		3.02 (NCH_3)	
	171.3	121.5	141.4		123.8	129.7	112.0	151.3	40.2 (NCH_3)	
1e		7.10	8.24	16.0		7.58	7.22		2.38 (CH_3)	
	171.4	125.5	141.5		132.9	128.1	129.6	140.1	21.4 (CH_3)	

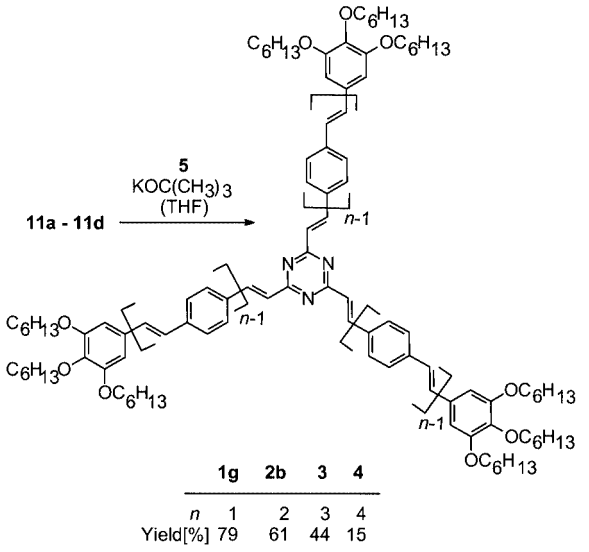
Because of the moderate yields of **2a**, we explored another route for the preparation of the star-shaped 1,3,5-triazines **2**−**4** having extended conjugated arms and terminal donor substituents. Starting with 3,4,5-tris(hexyloxy)benzaldehyde (**11a**), we prepared the OPV aldehydes **11b**, **11c**, and **11d**. The phosphonate **10**, which contains a protected formyl group, proved to be very valuable for this purpose. In the acidic workup of the Wittig−Horner reaction between **11a** and **10**, a deprotection occurred, such that aldehyde **11b** was obtained, which could be extended by the same procedure to **11c** and further to **11d** (Scheme 4). The purified aldehydes did not show any traces of *cis*-configured isomers when analyzed by ^{1}H and ^{13}C NMR spectroscopy (detection limit = 3%). The synthon **10**, which we have used earlier,[28,30,38] was prepared using a new route that resulted in much higher yields. 4-Bromomethylbenzonitrile (**7**) was first transformed into 4-bromomethylbenzaldehyde (**8**), whose quantitatively formed diethyl acetal (**9**) was subjected to an Arbusov reaction with triethyl phosphite (Scheme 4).



Scheme 4. Extension of the conjugated OPV chain in the series of the aldehydes **11a**−**d**

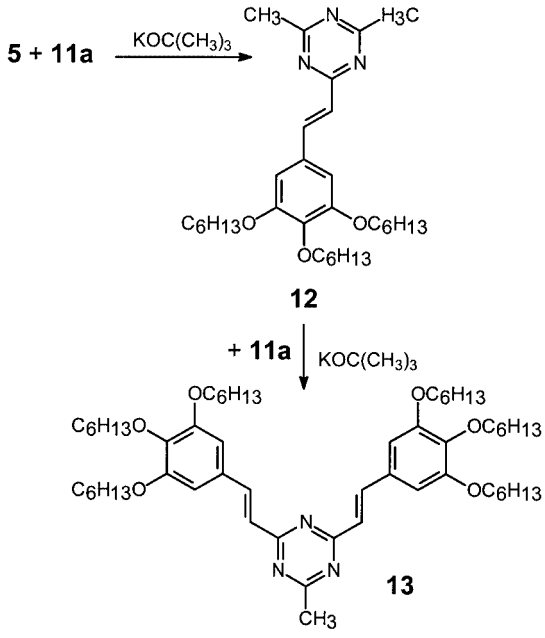
The convergent synthesis of **1**−**4** was then accomplished by the alkaline condensation of 2,4,6-trimethyl-1,3,5-triazine (**5**) with the aldehydes **11a**−**d**. The yields decrease within this series from 79 to 15% (Scheme 5).

When the condensation reaction between **5** and **11a** was performed with less than 3 mol-equiv. of **11a**, we obtained



Scheme 5. Preparation of the 1,3,5-triazines **1g**, **2b**, **3**, and **4** having conjugated OPV arms and threefold terminal hexyloxy substitution

the monostyryl compound **12** and the distyryl system **13** as the major products (Scheme 6).



Scheme 6. Stepwise condensation of **5** and **11a** to yield **12** and **13**

The ^{1}H and ^{13}C NMR spectroscopic data of the olefinic units in **1g**, **2b**, **3**, and **4** are summarized in Table 2. The polarization of the inner double bond α,α′ is strong and slightly reduced by the extension of the conjugation; the polarization of the other double bonds is low and also changes slightly with the length of the OPV chain.

The length of the conjugated chain has, of course, a strong influence on the UV/Vis spectra. Because of cross-conjugation on the central triazine ring, the long-wavelength maxima do not depend significantly on the number

Table 2. ^{1}H and ^{13}C NMR spectroscopic data of the polarized vinylene bridges in the OPV arms of **1g**, **2b**, **3**, and **4** (δ values in $CDCl_3$, relative to TMS as internal standard; coupling constants $^3J_{trans}$ in Hz; the symbols α to δ′ correspond to the olefinic positions from the core to the periphery)[37]

	Olefinic double bonds											
	α-HC	α′-HC	^3J	β-HC	β′-HC	^3J	γ-HC	γ′-HC	^3J	δ-HC	δ′-HC	^3J
1g	7.00	8.15	15.7									
	125.1	141.8										
2b	7.15	8.25	15.9	6.97	7.08	16.2						
	125.9	141.1		126.9	130.1							
3	7.13	8.23	15.6	7.10	7.16	16.4	6.95	7.02	16.0			
	126.0	141.0		127.6	129.4		127.1	129.0				
4	7.11	8.22	15.7	7.08	7.14	16.0	7.08	7.08	[a]	6.94	7.00	16.0
	126.0	140.6		127.7	129.1		127.9	128.2		127.1	128.9	

[a] AB spin pattern collapsed to a singlet.

of arms present in **12**, **13**, and **1g**. The absorption intensities increase regularly, however, on proceeding from **12** to **13** and further to **1g** (Figure 1). The push-pull effect causes an intramolecular charge transfer (ICT), which results in a bathochromic shift of the lowest-energy electron transition: the parent system **1a** has an absorption maximum at λ = 327 nm, the methoxy derivative **1b** at λ = 356 nm and the *p*-dimethylamino compound **1d** at λ = 425 nm (measurements in CH_2Cl_2). Extension of the conjugation in the series **1g**, **2b**, **3**, and **4** leads to a systematic bathochromic and hyperchromic effect (Figure 2). The convergence limit, calculated on the basis of exponential functions[39] is predicted as $\lambda_\infty = 427 \pm 3$ nm (Figure 3). Interestingly, the effective conjugation length $n_{ECL} = 7$ is smaller than that in the open-chained OPV series, where $n_{ECL} = 11$ was established.[19]

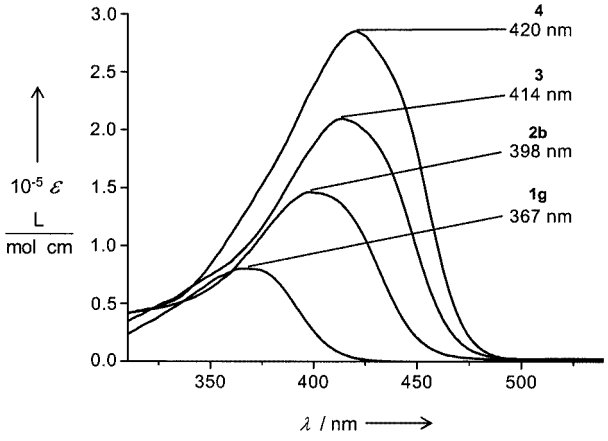


Figure 2. UV/Vis spectra of the series **1g**, **2b**, **3**, and **4** in CH_2Cl_2

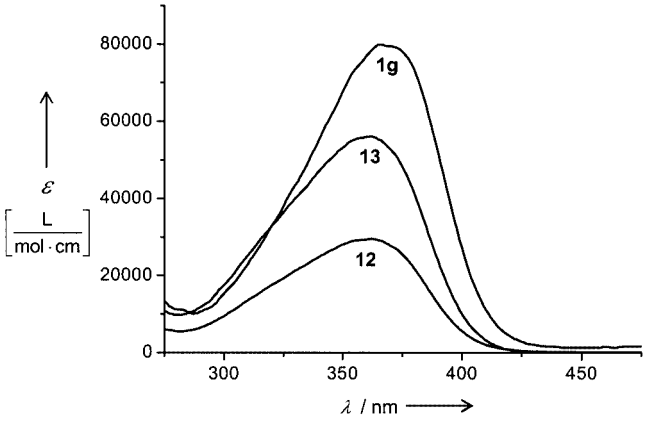


Figure 1. UV/Vis spectra of the mono-, di-, and tristyryl-substituted 1,3,5-triazines **12**, **13**, and **1g**, respectively (measured in CH_2Cl_2)

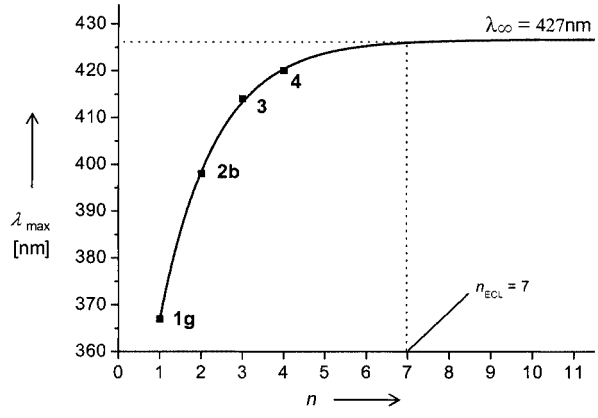


Figure 3. Long-wavelength absorption maxima of **1g**, **2b**, **3**, and **4** in CH_2Cl_2; dependence on the number of repeat units *n* and the convergence to λ_∞ ($n \rightarrow \infty$)

All of the spectroscopic results discussed so far refer to neutral solutions in tri- or dichloromethane. What effects occur when trifluoroacetic acid (TFA) is added? We observed that the yellow solution of **1d** in chloroform first turned violet upon the initial addition of TFA and then became colorless with further addition. We studied the acidochromic behavior by UV/Vis, ^{1}H NMR, and ^{13}C NMR spectroscopy.

Figure 4 depicts the change in the long-wavelength absorption A of **1d** in $CHCl_3$ that is caused by protonation with TFA. The corresponding ^{1}H NMR spectra in $CDCl_3$ reveal an increasing low-field shift and broadening of all of the signals, as a result of proton exchange processes, upon increasing the concentration of TFA. The ^{13}C NMR measurements are even more instructive. A two-dimensional shift correlation (HMBC) experiment using the violet solu-

tion reveals intense high-field shifts for the quaternary carbon atoms in the 1,3,5-triazine ring and their adjacent olefinic carbon atoms ($\Delta\delta = -5.3$ and -7.5 ppm, respectively); the other olefinic carbon atoms undergo low-field shifts ($\Delta\delta = 6.6$ ppm). This behavior is typical of the protonation of an aromatic N-heterocycle.[40] The ^{13}C NMR signals begin to broaden, particularly those that are shifted to high field; further addition of TFA causes these signals to disappear into the noise. Obviously, the protonation of **1d** occurs on the 1,3,5-triazine ring first and then on the dimethylamino groups. To support this explanation is the observation that the signal of the methyl group is almost unaffected in the violet solution but it is shifted to lower field [$\Delta\delta(^1H) = 0.42$ ppm] in the colorless solution. Scheme 7 illustrates the protonation process, which leads first to an increase in the degree of intramolecular charge transfer (ICT) and then to the disappearance of the push-pull effect that causes the ICT. The complete disappearance of the band having a maximum at 549 nm implies that protonation of the dimethylamino groups occurs in all three arms; otherwise, an unprotonated arm would still be expected to exhibit an ICT.

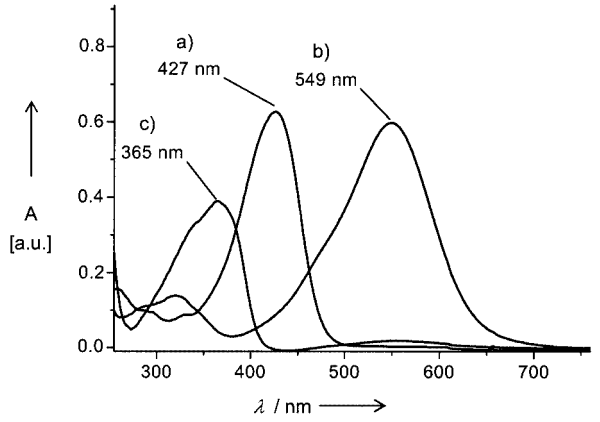
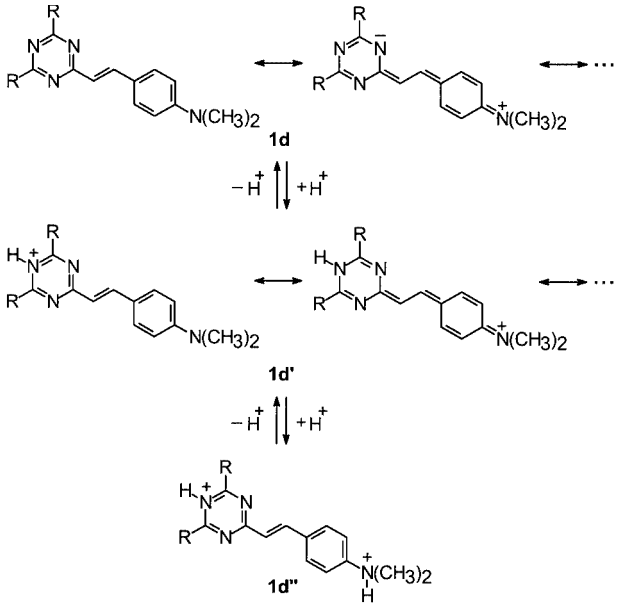


Figure 4. Protonation of **1d** in $CHCl_3/CF_3COOH$: a) yellow, neutral, $5.068 \cdot 10^{-6}$ M solution of **1d** in $CHCl_3$; b) violet solution of **1d′** (4-fold excess of TFA); and c) colorless solution of **1d′′** (20-fold excess of TFA)



Scheme 7. Protonation of **1d** in $CDCl_3/CF_3COOH$ yields the violet species **1d′** and the colorless form **1d′′** (R represents the three equal arms of **1d**, **1d′**, and **1′′**)

All six nitrogen atoms are involved in the proton exchange mechanisms, which are fast on the NMR time scale. Thus, the protonated forms of compound **1d** never appear to lose their threefold symmetry (point group: D_{3h}).

The protonation of the alkoxy-substituted compounds **1g**, **2b**, **3**, and **4** with TFA takes place solely at the central 1,3,5-triazine ring. The bathochromic shifts amount to 82, 92, 93, and 91 nm, respectively, and then remain constant upon further addition of TFA to the solutions in CH_2Cl_2. The convergence for $n \rightarrow \infty$ in the protonated series leads to $\lambda_\infty = 515$ nm; this limiting value is reached at an effective conjugation length of $n_{ECL} = 6$.

Finally, we note that compounds **1**−**4**, which have altogether nine long, flexible, alkoxy chains, form liquid crystals (columnar mesophases, whose helical arrangements are now under investigation). The clearing points of these phases are described in the Exp. Sect.

Summary and Conclusion

The 1,3,5-triazine derivatives **1**−**4** having styryl or OPV arms on C-2, C-4, and C-6 can be prepared readily by condensation reactions between 2,4,6-trimethyl-1,3,5-triazine (**5**) and the corresponding aldehydes **6**. The push-pull character of compounds **1**−**4** having terminal donor substituents is evidenced by the polarization of the olefinic bridges observed in the ^1H and ^{13}C NMR spectroscopic data and, particularly, in the UV/Vis spectra that prove the existence of intramolecular charge transfer (ICT). Extending the conjugation in the three arms leads to a relatively fast convergence of the absorption to $\lambda_\infty = 427$ nm. We predict the effective conjugation length (n_{ECL}) to be 7 repeat units. Initial protonation on the central 1,3,5-triazine ring increases the ICT (evidenced by the corresponding bathochromic shift); further protonation on the dimethylamino groups of **1d** leads to the disappearance of the push-pull character and, hence, to a hypsochromic effect. The acidochromic behavior of **1d** is expressed by its color change from yellow to violet and then to colorless. The compounds **1**−**4**, which have nine hexyloxy chains, form thermotropic columnar mesophases. Moreover, these star-shaped compounds should exhibit interesting non-linear optical (NLO) properties.[16,41]

Experimental Section

General Remarks: UV/Vis: Zeiss MCS 320/340; $CHCl_3$ or CH_2Cl_2 as solvents. ^1H and ^{13}C NMR: Bruker Avance 600, ARX 400, AMX 400 and AC 300; $CDCl_3$/TMS as internal standard. IR: Nicolet 5SXB, LOT-Oriel ATR unit or Perkin−Elmer GX. MS: Finnigan MAT 95 (FD; accelerating voltage 5 kV) and Varian MAT

CH7A (EI; 70 eV). Elemental analyses: Microanalytical Laboratory of the Institute of Organic Chemistry, University of Mainz. DSC: Perkin−Elmer DSC 7 (clearing points, T_{cl}, measured on second heating curve). Melting points: Stuart Scientific SMP/3; uncorrected.

General Procedure for the Preparation of the 2,4,6-Tristyryl-1,3,5-triazines 1a−e: Aldehyde **6a**, **6b**, **6d**, **6e** (commercially available), or **6c**[43] in methanol (25 mL) was added to 2,4,6-trimethyltriazine (**5**)[42] (310 mg, 2.52 mmol) dissolved in 20% methanolic KOH (25 mL, 7.56−10.08 mmol). The reaction mixture was stirred under reflux until TLC (SiO_2; toluene) indicated the complete consumption of **5** (3−6 d). After cooling to 5 °C, the precipitate that formed was filtered off and carefully washed with cold methanol. Further purification was achieved by column chromatography (4 × 40 cm of SiO_2; toluene or diethyl ether) and/or recrystallization.

2,4,6-Tris[(*E*)-2-phenylethenyl]-1,3,5-triazine (1a): Colorless powder, yield 87%, m.p. 229 °C (ref.[34] 224−226 °C). Identification was made by comparison with an authentic sample.[21,22] UV/Vis (CH_2Cl_2): λ_{max} = 327 nm; log ε = 5.04.

2,4,6-Tris[(*E*)-2-(4-methoxyphenyl)ethenyl]-1,3,5-triazine (1b): Yellowish needles, yield 94%, m.p. 228 °C. IR (TR): $\tilde{\nu}$ = 3034, 3004, 2964, 2934, 2840, 1633, 1601, 1572, 1496, 1441, 1420, 1371, 1315, 1304, 1288, 1246, 1167, 1111, 1028, 972, 872, 836, 797, 767 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 356 nm; log ε = 5.04. FD MS: *m/z* (%) = 477 (100) [M^+]. $C_{30}H_{27}N_3O_3$ (477.6): calcd. C 75.45, H 5.70, N 8.80; found C 75.31, H 5.88, N 8.72.

2,4,6-Tris{(*E*)-2-[4-(hexyloxy)phenyl]ethenyl}-1,3,5-triazine (1c): Yellow powder, yield 55%, m.p. 94 °C. IR (TR): $\tilde{\nu}$ = 2955, 2941, 2921, 2868, 2854, 1628, 1605, 1573, 1501, 1474, 1423, 1407, 1380, 1307, 1295, 1246, 1171, 1119, 1059, 1030, 979, 876, 833, 791, 724 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 361 nm; log ε = 5.02. FD MS: *m/z* (%) = 688 (100) [M + H^+]. $C_{45}H_{57}N_3O_3$ (687.9): calcd. C 78.56, H 8.35, N 6.11; found C 78.23, H 8.61, N 5.88.

2,4,6-Tris{(*E*)-2-[(4-dimethylamino)phenyl]ethenyl}-1,3,5-triazine (1d): Violet crystals, yield 39%, m.p. 252 °C. IR (TR): $\tilde{\nu}$ = 2885, 2852, 2800, 1623, 1596, 1553, 1526, 1484, 1443, 1431, 1413, 1380, 1354, 1279, 1258, 1234, 1214, 1165, 1123, 1067, 1047, 977, 967, 947, 873, 860, 818, 792 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 425; log ε = 5.10. FD MS: *m/z* (%) = 517 (100) [M^+]. $C_{33}H_{36}N_6$ (516.7): calcd. C 76.71, H 7.02, N 16.27; found C 76.64, H 7.06, N 16.30. After a reaction time of 7 d, the raw material provided a second fraction (chromatography on 4 × 25 cm of SiO_2; CH_2Cl_2/EtOAc, 19:1) — the twofold condensation product **1d′** — which became the major product (52%) when the molar ratio **5/6c** was 1:2.

2,4-Bis{(*E*)-2-[(4-dimethylamino)phenyl]ethenyl}-6-methyl-1,3,5-triazine (1d′): Red solid, m.p. 169 °C. IR (TR): $\tilde{\nu}$ = 2889, 2852, 2800, 1624, 1598, 1553, 1494, 1429, 1385, 1345, 1290, 1269, 1253, 1178, 1165, 1122, 1062, 975, 945, 869, 817, 793 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 421 nm; log ε = 4.93. ^{1}H NMR ($CDCl_3$): δ = 2.61 (s, 3 H, 6-CH_3), 3.02 (s, 12 H, NCH_3), 6.69, 7.54 (AA′BB′, 8 H, aromat. H), 6.87, 8.17 (AB, ^3J = 16.0 Hz, olefinic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 25.8 (6-CH_3), 40.2 (NCH_3), 111.9, 129.8 (aromat. CH), 120.8, 142.0 (olefinic CH), 123.6, 151.5 (aromat. C_q), 171.4 (C-2, C-4), 175.4 (C-6) ppm. FD MS: *m/z* (%) = 385 (100) [M^+]. $C_{24}H_{27}N_5$ (385.5): calcd. C 74.77, H 7.06, N 18.17; found C 74.68, H 6.95, N 18.37.

2,4,6-Tris[(*E*)-2-(4-methylphenyl)ethenyl]-1,3,5-triazine (1e): Colorless powder, yield 96%, m.p. 231 °C. IR (KBr): $\tilde{\nu}$ = 3050, 3023, 2919, 2858, 1634, 1609, 1589, 1514, 1412, 1400, 1377, 1321, 1289, 1273, 1255, 1212, 1179, 1114, 1045, 1019, 980, 879, 829, 788, 666, 652, 504 cm^{-1}. FD MS: *m/z* (%) = 430 (100) [M^+]. $C_{30}H_{27}N_3$ (429.6): calcd. C 83.88, H 6.34, N 9.78; found C 84.12, H 6.19, N 9.74.

2,4,6-Tris[(*E*)-2-{4-[(diethoxyphosphoryl)methyl]phenyl}ethenyl]-1,3,5-triazine (1f): A mixture of NBS (623 mg, 3.5 mmol), **1e** (450 mg, 1.0 mmol) and repeatedly added small portions of AIBN was heated under reflux in dry CCl_4 (50 mL). When the reaction reached completion, as indicated by the amount of succinimide appearing at the surface, the mixture was filtered, the volatile parts were evaporated, and the residue was treated with triethyl phosphite (10 mL, 9.69 g, 58.3 mmol). After heating at 150 °C for 5 h with continuous distillation of the bromoethane that formed, the excess triethyl phosphite was removed and the residue purified by column chromatography (7 × 50 cm of SiO_2; EtOAc/EtOH, 7:1) to yield a highly viscous colorless oil; yield: 300 mg (40%). IR (TR): $\tilde{\nu}$ = 2982, 2908, 1680, 1631, 1607, 1568, 1503, 1443, 1421, 1375, 1292, 1231, 1182, 1163, 1097, 1048, 1018, 962, 854 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.24 (t, 18 H, CH_3), 3.18 [d, ^2J(H,P) = 21.9 Hz, 6 H, CH_2P], 4.02 (m, 12 H, OCH_2), 7.13 (d, ^3J = 16.0 Hz, 3 H, inner olefinic H), 7.35, 7.63 (AA′BB′, 12 H, aromat. H), 8.24 (d, ^3J = 16.0 Hz, 3 H, outer olefinic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3 [d, ^3J(C,P) = 6.1 Hz, CH_3], 33.8 [d, ^1J(C,P) = 138.1 Hz, CH_2P], 62.2 [d, ^2J(C,P) = 6.9 Hz, OCH_2], 126.2 (inner olefinic CH), 128.3, 130.3 [d, ^3J(C,P) = 6.1 Hz, aromat. CH], 133.7 [d, ^2J(C,P) = 9.9 Hz), 134.2 [d, ^5J(C,P) = 3.8 Hz, aromat. C_q], 141.5 (outer olefinic CH), 171.3 (C-2) ppm. FD MS: *m/z* (%) = 838 (100) [M^+]. $C_{42}H_{54}N_3O_9P_3$ (837.8): calcd. C 60.21, H 6.50, N 5.02; found C 59.87, H 6.81, N 4.93.

2,4,6-Tris[(*E*)-2-(4-{(*E*)-2-[4-(hexyloxy)phenyl]ethenyl}phenyl)-ethenyl]-1,3,5-triazine (2a): A mixture of triphosphonate **1f** (160 mg, 0.214 mmol) and aldehyde **6c** (288 mg, 1.4 mmol), dissolved in dry DMF (10 mL), was added slowly at room temperature to a suspension of $KOC(CH_3)_3$ (170 mg, 1.5 mmol) in dry DMF (10 mL). The stirred reaction mixture turned blue and then, somewhat later, green. After 2 h, the temperature was raised to 50 °C and kept for 30 min before methanol (80 mL) was added. A yellow precipitate was formed that was recrystallized from CH_2Cl_2/MeOH (1:1). The product **2a** is a brilliant yellow powder (34 mg, 18%), m.p. 197 °C. IR (TR): $\tilde{\nu}$ = 3023, 2924, 2854, 1625, 1606, 1594, 1574, 1556, 1499, 1470, 1416, 1402, 1372, 1302, 1292, 1271, 1247, 1218, 1172, 1109, 1028, 960, 937, 879, 863, 833, 726 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 400 nm; log ε = 5.41. ^{1}H NMR ($CDCl_3$):[37] δ = 0.90 (t, 9 H, CH_3), 1.34 (m, 12 H, CH_2), 1.46 (m, 6 H, CH_2), 1.78 (m, 6 H, CH_2), 3.97 (t, 6 H, OCH_2), 6.88, 7.44 (AA′BB′, 12 H, outer aromat. H), 6.96, 7.12 (AB, ^3J = 16.2 Hz, 6 H, outer olefinic H), 7.13, 8.25 (AB, ^3J = 15.8 Hz, 12 H, inner olefinic H), 7.52, 7.65 (AA′BB′, 12 H, inner aromat. H) ppm. ^{13}C NMR ($CDCl_3$):[37] δ = 14.0 (CH_3), 22.6, 25.7, 29.2, 31.6 (CH_2), 68.1 (OCH_2), 114.7, 127.9 (outer aromat. CH), 125.7, 129.5 (outer olefinic CH), 125.7, 141.1 (inner olefinic CH), 126.6, 128.6 (inner aromat. CH), 129.6, 134.3, 139.3 (aromat. C_q), 159.2 (C_qO), 171.2 (C-2) ppm. FD MS: *m/z* (%) = 995 (100) [M + H^+], 498 (20) [M^{2+}]. $C_{69}H_{75}N_3O_3$ (994.4): calcd. C 83.34, H 7.60, N 4.23; found C 83.11, H 7.89, N 4.17.

4-(Bromomethyl)benzaldehyde (8): Prepared and identified according to the literature by reaction of 4-bromobenzonitrile (**7**) with DIBAH.[44]

1-(Bromomethyl)-4-(diethoxymethyl)benzene (9): A mixture of triethoxymethane (9 mL, 8.02 g, 54.1 mmol), **8** (1.05 g, 5.3 mmol) and Dowex 50WX 8 (1.0 g) was stirred in dry EtOH (30 mL) for 3 h at

room temperature. Half of the solvent was removed, Na_2CO_3 (1.0 g) was added, and the mixture then stirred for a further 10 min. The volatile parts of the filtered solution were then removed. The raw product (1.29 g, 100%), a colorless oil, was used for the next step without further purification.

Diethyl [4-(Diethoxymethyl)benzyl]phosphonate (10): A mixture of triethyl phosphite (2.0 mL, 1.94 g, 11.6 mmol) and **9** (1.25 g, 5.1 mmol) was heated at 160 °C. The generated bromoethane was distilled off, as was the excess triethyl phosphite after a reaction time of 1 h, and the residue was purified by column chromatography (16 × 5 cm of basic Al_2O_3; EtOAc). Yield: 1.20 g (71%) of a colorless oil. Identification by comparison with an authentic sample.[30,38] Preparation of the aldehydes **11a**−**d** was performed according to the literature: **11a**,[45,46] **11b**−**d**.[30]

General Procedure for the Preparation of the 1,3,5-Triazine Derivatives 1g, 2b, 3, and 4: A solution of **5** (61.5 mg, 0.50 mmol), aldehyde **11a**−**d** (1.50−2.00 mmol) and $KOC(CH_3)_3$ (168 mg, 1.50 mmol) in dry THF (10−20 mL) was heated under reflux (monitored by TLC: SiO_2; CH_2Cl_2). The mixture was cooled to 0 °C and treated with MeOH until precipitation of the product was complete. Column chromatography (4 × 40 cm of SiO_2; CH_2Cl_2) yielded the pure target compounds.

2,4,6-Tris{(*E*)-2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-1,3,5-triazine (1g): Yield: 79%, brilliant yellow wax with clearing point T_{cl} = 109.5 °C. IR (TR): $\tilde{\nu}$ = 2954, 2927, 2858, 1633, 1579, 1496, 1467, 1431, 1379, 1327, 1291, 1241, 1111, 972, 926, 876, 835, 725 cm^{-1}. UV-Vis (CH_2Cl_2): λ_{max} = 366 nm; log ε = 4.90. ^1H NMR ($CDCl_3$):[37] δ = 0.90 (2 t, 27 H, CH_3), 1.33 (m, 36 H, CH_2), 1.49 (m, 18 H, CH_2), 1.74 (m, 6 H, CH_2), 1.82 (m, 12 H, CH_2), 3.99 (t, 6 H, OCH_2), 4.01 (t, 12 H, OCH_2), 6.88 (s, 6 H, aromat. CH), 7.00 (d, ^3J = 15.7 Hz, 3 H, inner olefinic H), 8.15 (d, ^3J = 15.7 Hz, 3 H, outer olefinic H) ppm. ^{13}C NMR ($CDCl_3$):[37] δ = 14.0, 14.1 (CH_3), 22.6, 22.7, 25.7, 25.8, 29.3, 30.3, 31.6, 31.7 (CH_2), 69.2, 73.6 (OCH_2), 106.7 (aromat. CH), 125.1 (inner olefinic CH), 130.5 (aromat. C_q), 140.2, 153.3 (C_qO), 141.8 (outer olefinic CH), 171.2 (C-1) ppm. FD MS: *m*/*z* (%) = 1289 (100) [M + H^+]. $C_{81}H_{129}N_3O_9$ (1288.9): calcd. C 75.48, H 10.09, N 3.26; found C 75.51, H 10.16, N 3.21.

2,4,6-Tris[(*E*)-2-(4-{(*E*)-2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-phenyl)ethenyl]-1,3,5-triazine (2b): Yield: 61%, waxy yellow solid, T_{cl} = 96.0 °C. IR (TR): $\tilde{\nu}$ = 2952, 2926, 2856, 1627, 1599, 1578, 1558, 1499, 1467, 1430, 1375, 1342, 1317, 1243, 1176, 1111, 977, 956, 833 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 398 nm; log ε = 5.165. ^1H NMR ($CDCl_3$):[37] δ = 0.90 (2 t, 27 H, CH_3), 1.34 (m, 36 H, CH_2), 1.49 (m, 18 H, CH_2), 1.75 (m, 6 H, CH_2), 1.82 (m, 12 H, CH_2), 3.97 (t, 6 H, OCH_2), 4.02 (t, 12 H, OCH_2), 6.72 (s, 6 H, aromat. CH), 6.97, 7.08 (AB, ^3J = 16.2 Hz, 6 H, outer olefinic H), 7.15, 8.25 (AB, ^3J = 15.9 Hz, 6 H, inner olefinic H), 7.61, 7.84 (AA′BB′, 12 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$):[37] δ = 14.0, 14.1 (CH_3), 22.6, 22.7, 25.8, 25.8, 29.4, 30.3, 31.6, 31.8 (CH_2), 69.2, 73.5 (OCH_2), 105.3, 126.8, 128.6 (aromat. CH), 125.9, 141.1 (inner olefinic CH), 126.9, 130.1 (outer olefinic CH), 132.2, 134.5, 139.1 (aromat. C_q), 138.6, 153.3 (C_qO), 171.2 (C-1) ppm. FD MS: *m*/*z* (%) = 1596 (100) [M + H^+], 789 (41) [M^{2+}]. $C_{105}H_{147}N_3O_9$ (1595.3): calcd. C 79.05, H 9.29, N 2.63; found C 78.91, H 9.46, N 2.51.

2,4,6-Tris[(*E*)-2-{4-[(*E*)-2-(4-{(*E*)-2-[3,4,5-tris(hexyloxy)phenyl]-ethenyl}phenyl)ethenyl]phenyl}ethenyl]-1,3,5-triazine (3): Yield: 44%, orange solid, T_{cl} = 233.3 °C. IR (TR): $\tilde{\nu}$ = 3024, 2924, 2855, 1627, 1593, 1577, 1499, 1468, 1429, 1374, 1341, 1225, 1175, 1109, 954, 832 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 414; log ε = 5.35. ^1H NMR ($CDCl_3$):[37] δ = 0.90 (2 t, 27 H, CH_3), 1.34 (m, 36 H, CH_2), 1.48 (m, 18 H, CH_2), 1.75 (m, 6 H, CH_2), 1.81 (m, 12 H, CH_2), 3.97 (t, 6 H, OCH_2), 4.01 (t, 12 H, OCH_2), 6.70 (s, 6 H, aromat. H), 6.95, 7.02 (AB, ^3J = 16.0 Hz, 6 H, outer olefinic H), 7.10, 7.16 (AB, ^3J = 16.4 Hz, 6 H, middle olefinic H), 7.13, 8.23 (AB, ^3J = 15.6 Hz, 6 H, inner olefinic H), 7.48 ("s", 12 H, aromat. H, middle benzene ring), 7.54, 7.65 (AA′BB′, 12 H, aromat. H, inner benzene ring) ppm. ^{13}C NMR ($CDCl_3$):[37] δ = 14.0, 14.1 (CH_3), 22.6, 22.7, 25.8, 25.8, 29.4, 30.3, 31.6, 31.8 (CH_2), 69.1, 73.5 (OCH_2), 105.1, 126.7, 126.9, 127.0, 128.6 (aromat. CH), 126.0, 141.0 (inner olefinic CH), 127.1, 129.0 (outer olefinic CH), 127.6, 129.4 (middle olefinic CH), 132.4, 134.7, 136.2, 137.1, 138.9 (aromat. C_q), 138.3, 153.3 (C_qO), 171.2 (C-1) ppm. FD MS: *m*/*z* (%) = 1901 (100) [M^+], 951 (77) [M^{2+}]. $C_{129}H_{165}N_3O_9$ (1901.7): calcd. C 81.47, H 8.75, N 2.21; found C 81.51, H 8.66, N 2.15.

2,4,6-Tris[(*E*)-2-{4-[(*E*)-2-{4-[(*E*)-2-(4-{(*E*)-2-[3,4,5-tris(hexyloxy)-phenyl]ethenyl}phenyl)ethenyl]phenyl}ethenyl]phenyl}ethenyl]-1,3,5-triazine (4): Yield: 15%, intensely yellow powder that does not give an isotropic melt below 300 °C. IR (KBr): $\tilde{\nu}$ = 3025, 2955, 2929, 2858, 1629, 1591, 1577, 1505, 1468, 1431, 1378, 1342, 1233, 1175, 1119, 959, 836, 625, 547 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} = 420 nm; log ε = 5.46. ^1H NMR ($CDCl_3$):[37] δ = 0.90 (2 t, 27 H, CH_3), 1.33 (m, 36 H, CH_2), 1.47 (m, 18 H, CH_2), 1.74 (m, 6 H, CH_2), 1.80 (m, 12 H, CH_2), 3.95 (t, 6 H, OCH_2), 4.00 (t, 12 H, OCH_2), 6.69 (s, 6 H, aromat. H), 6.94, 7.00 (AB, ^3J = 16.0 Hz, 6 H, outer olefinic H), 7.08, 7.14 (AB, ^3J = 16.0 Hz, 6 H, second inner olefinic H), 7.11, 8.22 (AB, ^3J = 15.7 Hz, 6 H, inner olefinic H), 7.08 ("s", 6 H, second outer olefinic H), 7.46 ("s", 12 H, aromat. H), 7.48 ("s", 12 H, aromat. H), 7.53, 7.64 (AA′BB′, 12 H, aromat. H, inner benzene ring) ppm. ^{13}C NMR ($CDCl_3$):[37] δ = 14.1, 14.1 (CH_3), 22.6, 22.7, 25.8, 25.8, 29.5, 29.7, 30.4, 31.7, 31.8 (CH_2), 69.1, 73.5 (OCH_2), 105.1, 126.8, 127.0, 127.1, 128.6 (aromat. CH, partly superimposed), 126.0, 140.6 (inner olefinic CH), 127.1, 128.9 (outer olefinic CH), 127.7, 129.1 (second inner olefinic CH), 127.8, 128.2 (second outer olefinic CH), 132.4, 134.6, 136.2, 136.3, 136.7, 136.7, 138.6 (aromat. C_q), 138.4, 153.3 (C_qO), 170.8 (C-1) ppm. FD MS: *m*/*z* (%) = 2208 (100) [M^+], 1104 (59) [M^{2+}]. $C_{153}H_{183}N_3O_9$ (2208.2): calcd. C 83.22, H 8.35, N 1.90; found C 83.10, H 8.53, N 1.81.

2,4-Dimethyl-6-{(*E*)-2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-1,3,5-triazine (12): A solution of **11a** (406 mg, 1.0 mmol) in MeOH (4 mL) was added slowly at 0 °C to a solution of $KOC(CH_3)_3$ (168 mg, 1.5 mmol) and **5** (123.2 mg, 1.0 mmol) in dry MeOH (10 mL). After vigorous stirring for 30 min, the reaction mixture was kept at room temperature overnight. The volatile parts were removed and the residue was purified by column chromatography (5 × 20 cm of SiO_2; CH_2Cl_2/EtOAc, 10:1). After the first fractions eluted with small amounts of unchanged **11a**, **13**, and **1g**, the title compound **12** was obtained as a yellow-green viscous oil. Yield: 200 mg (39%). UV/Vis (CH_2Cl_2): λ_{max} = 362 nm; log ε = 4.47. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 0.88 (t, 3 H, CH_3), 1.31 (m, 12 H, CH_2), 1.45 (m, 6 H, CH_2), 1.72 (m, 2 H, CH_2), 1.79 (m, 4 H, CH_2), 2.60 (s, 6 H, CH_3), 3.97 (t, 6 H, OCH_2), 6.82 (s, 2 H, aromat. H), 6.91, 8.06 (AB, ^3J = 15.9 Hz, 2 H, olefinic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0, 14.1 (CH_3), 22.6, 22.6, 25.6, 25.7, 29.2, 30.2, 31.5, 31.6 (CH_2), 25.6 (2-CH_3), 69.0, 73.5 (OCH_2), 106.5 (aromat. CH), 124.3, 142.5 (olefinic CH), 130.2 (aromat. C_q), 140.1, 153.2 (C_qO), 171.0 (C-6), 175.9 (C-2) ppm. FD MS: *m*/*z* (%) = 512 (100) [M + H^+]. $C_{31}H_{49}N_3O_3$ (511.7): calcd. C 72.76, H 9.65, N 8.21; found C 72.58, H 9.84, N 8.05.

2-Methyl-4,6-bis{(*E*)-2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-1,3,5-triazine (13): The procedure described for the preparation of **12**

was modified by using **5** (123.2 mg, 1.0 mmol) and **11c** (812 mg, 2.0 mmol). An analogous workup yielded a yellow-green viscous oil (150 mg, 32%). UV/Vis (CH_2Cl_2): λ_{max} = 362 nm; log ε = 4.75. ^{1}H NMR ($CDCl_3$): δ = 0.89 (2 t, 18 H, CH_3), 1.32 (m, 24 H, CH_2), 1.46 (m, 12 H, CH_2), 1.73 (m, 4 H, CH_2), 1.80 (m, 8 H, CH_2), 2.63 (s, 3 H, 2-CH_3), 3.98 (t, 12 H, OCH_2), 6.84 (s, 4 H, aromat. H), 6.95, 8.10 (AB, ^3J = 15.7 Hz, 4 H, olefinic H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0, 14.1 (CH_3), 22.6, 22.6, 25.7, 25.7, 29.3, 30.2, 31.5, 31.7 (CH_2), 25.8 (2-CH_3), 69.0, 73.5 (OCH_2), 106.5 (aromat. CH), 124.7, 142.0 (olefinic CH), 130.3 (aromat. C_q), 140.1, 153.2 (C_qO), 171.0 (C-4), 175.4 (C-2) ppm. FD MS: *m*/*z* (%) = 900 (100) [M^+]. $C_{56}H_{89}N_3O_6$ (900.3): calcd. C 74.71, H 9.96, N 4.67; found C 74.47, H 10.23, N 4.58.

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