Crown ethers in the OPV series

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DOI: http://dx.doi.org/10.3998/ark.5550190.p007.988

Abstract
The present paper deals with the synthesis of oligo(1,4-phenylenevinylene)s (trimers, tetramers and a nonamer), which contain 1–3 (E)-stilbene crowns. A classical reaction route led first to stilbene crown subunits. Wittig-Horner reactions of diphosphonates with mono- or dialdehydes or of dialdehydes with mono- or diphosphonates yielded then the desired all-trans configured OPVs, which were designed for the complexation of metal cations.

Keywords: Absorption, condensation reactions, conjugated oligomers, crown ethers, Wittig-Horner reactions

Introduction
Among the conjugated oligomers, 1,4-phenylenevinylene, OPVs (1) are prominent examples with various applications in materials science, such as light emitting diodes (LEDs), semiconductive or photoconductive devices, nonlinear optics, conversion of sunlight, formation of liquid crystals, etc. The OPV chains (Figure 1) can bear special functionalities, electrophores, chromophores, fluorophores and they can represent building blocks in star-shaped or dendritic compounds. See for example: Selected recently published work on OPV chains1-10 and reviews or monographs on this topic.11-25

Now we studied the preparation of OPVs 1 (m = 3, 4, 9), which contain crown ether segments of type 2 (n = 1, 3), which can be called stilbene crowns. To our best knowledge, until now only the parent system 2 (R=H) and some simply substituted systems are known,26-32 but no higher conjugated stilbenoid crown 2 (–R: –CH=CH–) and particularly no OPV crown.
OPVs, bearing stilbene crown units, are interesting in the context of sensor techniques, because their absorption and their fluorescence change by the complexation of metal cations. In comparison to stilbene, OPVs have some favourable properties, such as a bathochromically shifted, intense absorption and the corresponding fluorescence with an increased quantum yield. Moreover, OPVs do not show $E \rightarrow Z$ isomerization reactions on direct irradiation ($S_0 \rightarrow S_1$).

**Results and Discussion**

In order to get OPV crowns, we synthesized first the stilbene crowns $8a,b$ and $9a,b$ (Scheme 1), which bear substituents, that are suitable for the extension of the conjugated chain. The synthetic protocol for the parent stilbene crown was originally conceived by Gandour et al.\textsuperscript{26,27} and improved by Merz et al.\textsuperscript{28} We used a somewhat modified procedure: The methyl substituted salicylaldehyde $3^{34}$ was first reacted with the twofold methylsulfonic acid ester $4a^{35,36}$ or $4b^{35,37}$ in the presence of sodium ethoxide to yield $5a,b$. McMurry reactions led then to the tricyclic crowns $6a,b$. The formation of the CC double bond showed a slight selectivity in favour of the ($E$)-configuration. The separation of the stereoisomers was performed for $6a$ by column chromatography and for $6b$ by complexation with NaClO$_4$. ($Z$)-$6b$ formed a more stable Na$^+$ complex than ($E$)-$6b$ (see experimental part). However, it turned out that the $E/Z$-mixtures can be directly used for the next step, the Wohl-Ziegler bromination, in which a radical induced isomerization occurred. The thermal equilibrium was then perfectly on the side of the ($E$)-isomers $7a,b$, which were transformed by Arbusov reactions to the disphosphonates $8a,b$. Oxidation of $7a,b$ with 2-nitropropane in the presence of sodium ethoxide yielded the dialdehydes $9a,b$ (Scheme 1).
Scheme 1. Preparation of substituted stilbene crowns.

Twofold Wittig-Horner reactions of 8a,b and the substituted benzaldehydes 10, 11, 12, 13, 14, 15, 16 led to an extension of the conjugated chain in the all-trans configured 4,4'-distyrylstilbenes 17a,b–23a,b. Phase-transfer catalysis with Aliquat 336 in the presence of KOH gave yields between 48 and 66% (Methode a), Scheme 2.)
Scheme 2. Preparation of distyrylstilbene crowns.

The products 18a and 18b were also obtained by “inverse” Wittig-Horner processes of the dialdehydes 9a,b and the monophosphonate 24\textsuperscript{43,44} (Methode b), Scheme 2). The OPV trimers 17a,b–23a,b have all absorption maxima in the visible region (see experimental part), whereas for example the λ\textsubscript{max} values of (E)-6a,b and (Z)-6a,b are in the UV.

Acidic hydrolysis of the acetals 21a,b–23a,b yielded the dialdehydes 25a,b–27a,b (Scheme 3).
Scheme 3. Cleavage of acetals $21a,b \rightarrow 25a,b - 27a,b$.

All stilbene crowns $6a,b - 9a,b$, $17a,b - 23a,b$ and $25a,b - 27a,b$ with $(E)$-configurations in the macrocyclic ring show fast rotations of the single bonds adjacent to the olefinic double bond. Thus, inner and outer olefinic H atoms exchange and the $C_s$ symmetry becomes a de facto $C_{2v}$ symmetry. The resonance of the olefinic protons in the $(E)$-configured 13-membered ring systems $6a - 9a$, $17a - 23a$ and $25a - 27a$ is at much lower field ($\delta > 7.7$ ppm) than in the $(E)$-configured 19-membered crowns $6b - 9b$, $17b - 23b$ and $25b - 27b$ ($\delta < 7.5$ ppm). This cannot be a result of different planarity, since the resonance of the olefinic protons is at $\delta = 7.49$ ppm in $(E)$-2,2′-dimethoxy stilbene which is a planar model compound.\textsuperscript{46,47} We assume that the down-field shift in the 13-membered rings is owing to transannular steric interactions in this constrained ring systems.

OPVs have the principal problem of a low solubility. Alkyl or better alkoxy substituents improve the solubility. Therefore, we prepared additionally the diphosphonates $28$\textsuperscript{48} and $29$\textsuperscript{49} and reacted them with an excess amount of $9a,b$ (Scheme 4). The portion, which was soluble in CH$_2$Cl$_2$, consisted of the 1,4-phenylenevinylene tetramers $30a,b$ and $31a,b$ with formyl end groups. Phosphonate end groups could not be found. The insoluble major part consisted of higher OPVs.
Scheme 4. Synthesis of double stilbene crowns connected by a 1,4-divinylenephenylene unit.

The tricyclic crowns in 30a,b and 31a,b show the same molecular dynamics as the stilbene crowns discussed above. However, the $C_{2h}$ symmetry is not affected by this process. Each crown contains four ($n = 1$) or eight ($n = 2$) different OCH$_2$ groups — documented for example by the number of $^{13}$C NMR signals.

The compounds 8, 9, 19, 20 and 25–31 are bifunctional systems whose terminal functionalities can be used for condensation reactions: The dibromides 19 and 20 for Yamamoto or Heck coupling reactions, the dialdehydes 9, 25–27, 30 and 31 for iterative McMurry reactions or repeated Wittig-Horner reactions with the diphosphonates 8, 28 and 29. In the two latter cases 1,4-phenylenevinylenes of oligomer type 32 or 33 should result. Our first attempts in this direction led predominately to insoluble and intractable materials, which we did not study further. The Wittig-Horner reaction of dialdehyde 27a and diphosphonate 8a was in so far an exception as a small portion of an oligomer could be obtained which was the only soluble component in hot CHCl$_3$. It was essentially the 2:1 adduct of 27a and 8a and had the 1,4-phenylenevinylene nonamer structure 34 (Scheme 5). The FD-MS technique showed a distinct molecular ion of $m/z = 2160$ for C$_{140}$H$_{174}$O$_{19}$.
All monodisperse OPVs bearing crown ether units were characterized by their $^1$H and $^{13}$C NMR data and by MS spectra. Their electronic excitation resembles that of alkoxy substituted oligo(1,4-phenylenevinylene)s.\textsuperscript{16,50} The trimers 17–23 and 25–27 have in CH$_2$Cl$_2$ $\lambda_{\text{max}}$ values between 399 and 438 nm, the tetrarners 30 and 31 between 443 and 447 nm and the nonamer 34 has its absorption maximum at 457 nm. The change of the absorption and fluorescence spectra by complexation with alkali cations (Li, Na, K, Rb, Cs) is under investigation.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{Scheme5.png}
\caption{Higher OPVs containing (E)-stilbene crown ether structures.}
\end{scheme}

**Conclusions**

In conclusion, the preparation of special oligo(1,4-phenylenevinylene)s is described here. On the basis of Wittig-Horner reactions, the trimers 17–23 and 25–27, the tetrarners 30, 31 and a nonamer 34 were obtained. The conjugated chains contain one, two or three (E)-stilbene crown ether subunits, which were designed for the complexation of alkali cations.
Experimental Section

General. UV/Vis: Perkin-Elmer Lambda 15. \(^1\)H NMR and \(^{13}\)C NMR: Bruker AM 400, CDCl\(_3\) as solvent if not otherwise stated, TMS as internal standard. EI- and FD-MS: Varian MAT CH7A. The melting points were measured on a Büchi apparatus and are not corrected.

2,2'-[Oxybis(2,1-ethanediyoxy)]bis(4-methylbenzaldehyde) (5a). Aldehyde 3\(^{27}\) (50.0 g, 0.37 mol), dissolved in 100 mL of ethanol, was slowly added to a solution of sodium ethoxide, obtained from sodium (10.35 g, 0.45 mol) and 300 mL of ethanol. After 12 h stirring at room temperature, the formed crystals were filtered off and washed several times with cold ethanol. The dried sodium phenolate was then added to the dimethylsulfonate 4a\(^{28,29}\) (41.97 g, 0.16 mol) in 500 mL of dry toluene. After 48 h of heating to reflux, the formed precipitate was filtered off and washed several times with toluene and then with 2% aqueous NaOH. The dried product 5a was recrystallized from diethylether. Yield: 40.4 g (72%), mp 79 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.34 (s, 6H, CH\(_3\)), 3.90-4.00 (m, 4H, OCH\(_2\)), 4.16-4.26 (m, 4H, OCH\(_2\)), 6.75 (s, 2H, H-3), 6.79 (d, \(^3J\) 7.8 Hz, 2H, H-5), 7.67 (d, \(^3J\) 7.8 Hz, 2H, H-6), 10.39 (s, 2H, CHO). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 22.3 (CH\(_3\)), 68.3, 69.9 (OCH\(_2\)), 113.4 (C-3), 122.1 (C-5), 122.9 (C-1), 128.4 (C-6), 147.4 (C-4), 161.2 (C-2), 189.3 (CHO). MS (FD), \(m/z\) (100) [M]+. Anal. Calcd for C\(_{20}\)H\(_{22}\)O\(_5\) (342.4): C, 70.16; H, 6.41. Found: C, 70.06; H, 6.51.

2,2'-[Oxybis(2,1-ethanediyoxy-2,1-ethanediyoxy)]bis(4-methylbenzaldehyde) (5b). The preparation was performed according to 5a. 45.4 g (0.29 mol) of the sodium phenolate and 34.2 g (0.13 mol) of the dimethylsulfonate 4b yielded after 48 h heating to reflux in 500 mL of toluene 25.6 g (58%) of 5b as a viscous oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 2.32 (s, 6H, CH\(_3\)), 3.60-3.70 (m, 8H, OCH\(_2\)), 3.79-3.89 (m, 4H, OCH\(_2\)), 4.11-4.21 (m, 4H, OCH\(_2\)), 6.72 (s, 2H, H-3), 6.76 (d, \(^3J\) 7.8 Hz, 2H, H-5), 7.65 (d, \(^3J\) 7.8 Hz, 2H, H-6), 10.38 (s, 2H, CHO). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 22.3 (CH\(_3\)), 68.1, 69.5, 70.7, 71.0 (OCH\(_2\)), 113.4 (C-3), 122.0 (C-5), 122.9 (C-1), 128.2 (C-6), 147.3 (C-4), 161.3 (C-2), 189.4 (CHO). MS (FD), \(m/z\) (%) 430 (100) [M]+. Anal. Calcd for C\(_{24}\)H\(_{30}\)O\(_7\) (430.5): C, 66.96; H, 7.02. Found: C, 66.60; H, 6.83.

3,13-Dimethyl-6,7,9,10-tetrahydro-5,8,11-trioxadiibenz[a,e]cyclocladecene (6a). A reaction vessel with a high dilution equipment was filled under Ar with 600 mL of dry THF. At 0 °C 89.6 g (0.47 mol) TiCl\(_4\) were added dropwise before a Zn/Cu couple (105.4 g, 0.94 mol) was added. The originally light yellow solution turned dark. After 30 min boiling (110 °C bath temperature), dialdehyde 5a (40.4 g, 0.12 mol), dissolved in 300 mL of dry THF, was dropped in 30 h through a high-precision funnel into the reflux of the solvent. The mixture was boiled for another hour before 800 mL of an aqueous 10% Na\(_2\)CO\(_3\) solution and 800 mL of diethylether were added. Filtration over Celit gave an organic phase which was dried over MgSO\(_4\) and evaporated. The solid residue (23.15 g, 63%) consisted of a 2:1 mixture of (E)- and (Z)-6a. MS (EI) (70 ev), \(m/z\)
The separation of the stereoisomers was possible by column chromatography (SiO$_2$, CH$_2$Cl$_2$), but the next step could be made with the $E/Z$ mixture as well.

(E)-6a: Colorless powder, mp 136 °C. $^1$H NMR (CDCl$_3$): $\delta$ 2.32 (s, 6H, CH$_3$), 3.85-3.94 (m, 4H, OCH$_2$), 4.09-4.19 (m, 4H, OCH$_2$), 6.80 (s, 2H, H-4, H-12), 6.83 (d, $^3$J 7.9 Hz, 2H, H-2, H-14), 7.36 (d, $^3$J 7.9 Hz, 2H, H-1, H-15), 7.73 (s, 2H, H-16, H-17). $^{13}$C NMR (CDCl$_3$): $\delta$ 21.3 (CH$_3$), 70.1, 70.7 (OCH$_2$), 118.1, 123.4, 125.4, 127.6 (aromat. and olefin. CH), 126.6, 137.9, 157.0 (aromat. C$_q$). UV (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) 328 nm (20100 M$^{-1}$cm$^{-1}$).

(Z)-6a: Oil. $^1$H NMR (CDCl$_3$): $\delta$ 2.25 (s, 6H, CH$_3$), 3.67-3.77 (m, 4H, OCH$_2$), 3.94-4.03 (m, 4H, OCH$_2$), 6.61-6.63 (m, 6H, H-2, H-4, H-12, H-14, H-16, H-17), 6.88 (d, $^3$J 7.6 Hz, 2H, H-1, H-15). $^{13}$C NMR (CDCl$_3$): $\delta$ 20.9 (CH$_3$), 69.7, 71.0 (OCH$_2$), 116.3, 122.2, 127.2, 130.1 (aromat. and olefin. CH), 126.6, 137.2, 155.8 (aromat. C$_q$). UV (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) 290 nm (6300 M$^{-1}$cm$^{-1}$).

3,19-Dimethyl-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (6b). Preparation according to 6a. The oily product (39.9 g, 88%) obtained from 89.5 g (0.46 mol) 5b was obtained as a 6:4 mixture of (E)- and (Z)-6b after a reaction time of 3 d. MS (FD), m/z (%) 398 (100) [M]$^+$: Anal. Calcd for C$_{24}$H$_{36}$O$_5$ (398.5): C, 72.34; H, 7.59. Found: C, 71.97; H, 7.39.

The product could be used directly for the next step. The separation of the stereoisomers was performed with the help of the complex formation with NaClO$_4$. The oil, dissolved in 300 mL of dry THF, was treated with NaClO$_4$ (13.0 g, 0.11 mol) in 200 mL of THF. After stirring at room temperature for 6 h, the formed precipitate was filtered off and dissolved in 300 mL of water. The aqueous solution was then continuously extracted with CH$_2$Cl$_2$. The organic phase was dried (Na$_2$SO$_4$) and the solvent evaporated. The residue consisted of 15.6 g (34%) of pure (Z)-isomer which formed the more stable Na$^+$ complex.

(Z)-6b: Viscous oil. $^1$H NMR (CDCl$_3$): $\delta$ 2.28 (s, 6H, CH$_3$), 3.56-3.76 (m, 12H, OCH$_2$), 3.94-4.04 (m, 4H, OCH$_2$), 6.60 (d, $^3$J 7.8 Hz, 2H, H-2), 6.65 (s, 2H, H-4, H-18), 6.71 (s, 2H, H-22, H-23), 7.09 (d, $^3$J 7.8 Hz, 2H, H-1, H-21). $^{13}$C NMR (CDCl$_3$): $\delta$ 21.5 (CH$_3$), 69.0, 69.5, 70.7, 71.1 (OCH$_2$), 113.9, 121.3, 124.8, 129.1 (aromat. and olefin. CH), 125.3, 138.0, 155.8 (aromat. C$_q$). UV (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) 302 nm (7400 M$^{-1}$cm$^{-1}$).

The filtered THF solution was evaporated and the residue dissolved in 300 mL of CH$_2$Cl$_2$. The solution was washed twice with the same amount of H$_2$O and the dried organic phase (Na$_2$SO$_4$) evaporated. The remaining solid was recrystallized from diethyl ether to which at the boiling point petroleum ether (bp 40-70 °C) was added, till the precipitation started.

(E)-6b (24.3 g, 54%) was obtained as a colorless solid, mp 121 °C. $^1$H NMR (CDCl$_3$): $\delta$ 2.32 (s, 6H, CH$_3$), 3.63-3.79 (m, 8H, OCH$_2$), 3.94-4.04 (m, 4H, OCH$_2$), 4.11-4.21 (m, 4H, OCH$_2$), 6.70 (s, 2H, H-4, H-18), 6.76 (d, $^3$J 7.8 Hz, 2H, H-2, H-20), 7.31 (d, $^3$J 7.8 Hz, 2H, H-1, H-21), 7.35 (s, 2H, H-22, H-23). $^{13}$C NMR (CDCl$_3$): $\delta$ 21.6 (CH$_3$), 67.7, 69.9, 71.2, 71.5 (OCH$_2$), 112.9,
121.5, 128.6, 126.4 (aromat. and olefin. CH), 125.0, 138.0, 156.4 (aromat. C_q). UV (CH_2Cl_2): λ_max (ε) 328 nm (9800 M⁻¹cm⁻¹).

(E)-3,13-Bisbromomethyl-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclooctadecene (7a). N-Bromosuccinimide (11.5 g, 64.4 mmol), 6a (10.0 g, 32.2 mmol) and azobisisobutyronitrile (AIBN) (1.00 g, 6.0 mmol) were heated in 100 mL of dry CCl_4 to reflux. After 2 h the formed succinimide was filtered off and the solvent evaporated. The residue was recrystallized from CHCl_3. Yellow crystals. Yield: 7.38 g (49%). mp 186 °C. ¹H NMR (CDCl_3): δ 3.85-3.94 (m, 4H, OCH_2), 4.10-4.20 (m, 4H, OCH_2), 4.45 (s, 4H, CH_2Br), 7.00 (s, 2H, H-4, H-12), 7.03 (d, ³J 7.9 Hz, 2H, H-2, H-14), 7.42 (d, ³J 7.9 Hz, 2H, H-1, H-15), 7.71 (s, 2H, H-16, H-17). ¹³C NMR (CDCl_3): δ 33.6 (CH_2Br), 70.1, 70.9 (OCH_2), 118.0, 123.4, 126.6, 128.3 (aromat. and olefin. CH), 129.5, 137.7, 157.3 (aromat. C_q). MS (FD), m/z (%) 466, 468, 470 (100) [M⁺]; Br₂ pattern. Anal. Calcd for C_20H_20Br_2O_3 (468.2): C, 51.31; H, 4.31; Br, 34.31. Found: C, 51.39; H, 4.21; Br, 33.97.

(E)-3,19-Bisbromomethyl-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-dibenzo[a,e]cyclononadecene (7b). Preparation according to 7a. The heating was extended to 5 h. Recrystallization from diethylether/CHCl_3 2:1 gave a yellow solid, which melted at 145 °C. Yield: 2.61 g (45%) from 4.18 g (10.5 mmol) 6a. ¹H NMR (CDCl_3): δ 3.65-3.75 (m, 8H, OCH_2), 3.93-4.03 (m, 4H, OCH_2), 4.15-4.25 (m, 4H, OCH_2), 4.47 (s, 4H, CH_2Br), 6.90 (s, 2H, H-4, H-18), 6.95 (d, ³J 7.7 Hz, 2H, H-2, H-20), 7.35 (d, ³J 7.7 Hz, 2H, H-1, H-21), 7.37 (s, 2H, H-16, H-23). ¹³C NMR (CDCl_3): δ 33.9 (CH_2Br), 67.9, 69.8, 71.3, 71.5 (OCH_2), 112.7, 121.6, 127.5, 129.2 (aromat. and olefin. CH), 127.9, 137.8, 156.7 (aromat. C_q). MS (FD), m/z (%) 554, 556, 558 (100) [M⁺]; Br₂ pattern. Anal. Calcd for C_24H_28Br_2O_5 (556.3): C, 51.82; H, 5.07; Br, 28.73. Found: C, 51.44; H, 4.92; Br, 29.13.

[(E)-13-(Diethoxyphosphorylmethyl)-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclooctadecene-3-ylmethyl]-phosphonic acid diethyl ester (8a). Dibromide 7a (3.0 g, 6.4 mmol) and triethylphosphite (2.919 g, 16.0 mmol) were heated to 160 °C, so that the formed bromoethane was evaporated. After 6 h the excess triethylphosphite was distilled off at 1.0 kPa. The residue was purified by column chromatography (4 × 40 cm SiO₂, ethyl acetate/methanol 10:1). Yield: 2.70 g (73%). Colorless solid, mp 88 °C. ¹H NMR (CDCl_3): δ 1.24 (t, ³J 7.3 Hz, 12H, CH_3), 3.09 (d, ²J (P,H) 21.5 Hz, 4H, CH_2P), 3.87-4.04 (m, 12H, POCH_2 and OCH_2), 4.06-4.17 (m, 4H, OCH_2), 6.85-6.96 (m, 4H, H-2, H-4, H-12, H-14), 7.38 (d, ³J 8.1 Hz, 2H, H-1, H-15), 7.74 (s, 2H, H-16, H-17). ¹³C NMR (CDCl_3): δ 16.3 (CH_3), 33.7 (d, ¹J (P,C) 137.2 Hz, CH_2P), 62.2 (POCH_2), 70.2, 70.8 (OCH_2), 118.7, 124.1, 126.0, 127.9 (aromat. and olefin. CH), 128.0, 131.5, 157.2 (aromat. C_q). MS (FD), m/z (%) 582 (100) [M⁺]. Anal. Calcd for C_28H_40O_8P_2 (582.6): C, 57.73; H, 6.92. Found: C, 57.63; H, 7.15.
\[(E)-19-(Diethoxy-phosphorylmethyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-penta-
\text{oxa-dibenzo}[a,e]\text{cyclononadecene-3,13-ylmethyl]-phosphonic acid diethyl ester (8b)\].

Preparation according to 8a. Yield: 3.15 g (52%) obtained from 5.00 g (8.99 mmol) of 7b,
colorless solid, mp 122 °C. \(^1\)H NMR (CDCl\(_3\)): δ 1.22 (t, \(3J 7.3\) Hz, 12H, CH\(_3\)), 3.10 (d, \(2J (P,H) 21.5\) Hz, 4H, CH\(_2\)P), 3.62-3.72 (m, 8H, OCH\(_2\)), 3.90-4.07 (m, 12H, POCH\(_2\) and OCH\(_2\)), 4.11-
4.21 (m, 4H, OCH\(_2\)), 6.78-6.88 (m, 4H, H-2, H-4, H-16, H-20), 7.31 (d, 2H, \(3J 7.3\) Hz, 2H, H-1,
H-21), 7.33 (s, 2H, H-22, H-23). \(^13\)C NMR (CDCl\(_3\)): δ 16.3 (CH\(_3\)), 33.8 (d, \(1J (P,C) 137.3\) Hz,
CH\(_2\)P), 62.2 (POCH\(_2\)), 67.8, 69.8, 71.2, 71.5 (OCH\(_2\)), 113.5, 122.3, 126.9, 128.9 (aromat. and
olefin. CH), 126.3, 131.6, 156.4 (aromat. C\(_6\)). MS (FD), \(m/z\) (%) 670 (100) [M]\(^+\). Anal. Calcd for:
C\(_{32}\)H\(_{48}\)O\(_{11}\)P\(_2\) (670.6): C, 57.31; H, 7.21. Found: C, 57.66; H, 7.06.

\((E)-6,7,9,10\text{-Tetrahydro-5,8,11-trioxa-dibenzo}[a,e]\text{cyclo tridecene-3,13-dicarbaldehyde (9a)}\).

Na (450 mg, 19.17 mmol) was dissolved in 50 mL of dry methanol before 2-nitropropane (1.80
g, 19.17 mmol) was slowly added. After a reaction time of 30 min dibromide 7a (3.00 g, 6.39
mmol), suspended in 10 mL of dry methanol, was added in small portions. The mixture was
stirred at room temperature in the dark for 48 h. Then 1–2 mL of water was added in order to
quench the process. The formed precipitate was filtered off and recrystallized from ethyl acetate.
Yield: 1.17 g (54%). Yellowish powder, mp 165 °C. \(^1\)H NMR (CDCl\(_3\)): δ 3.89-4.00 (m, 4H,
OCH\(_2\)), 4.20-4.29 (m, 4H, OCH\(_2\)), 7.49 (s, 2H, H-4, H-12), 7.53 (d, \(3J 8.5\) Hz, 2H, H-2, H-14),
7.65 (d, \(3J 8.5\) Hz, 2H, H-1, H-6), 8.01 (s, 2H, H-16, H-17), 9.93 (s, 2H, CHO). \(^13\)C NMR (CDCl\(_3\)): δ 69.8,
70.8 (OCH\(_2\)), 116.3, 125.3, 128.7, 128.9 (aromat. and olefin. CH), 135.0, 136.4, 157.8 (aromat. C\(_6\)),
191.3 (CHO). MS (FD), \(m/z\) (%) 338 (100) [M]\(^+\). Anal. Calcd for C\(_{20}\)H\(_{18}\)O\(_5\) (338.4): C, 71.00; H, 5.36. Found: C, 70.65; H, 5.60.

\((E)-6,7,9,10,12,13,15,16\text{-Octahydro-5,8,11,14,17-penta-oxa-dibenzo}[a,e]\text{cyclononadecene-
3,19-dicarbaldehyde (9b)}\). Preparation according to 9a. Yield: 2.70 g (71%) obtained from 5.00
g (8.99 mmol) 7b. Yellowish crystals, mp 155 °C. \(^1\)H NMR (CDCl\(_3\)): δ 3.69 (s, 8H, OCH\(_2\)),
4.00-4.09 (m, 4H, OCH\(_2\)), 4.22-4.32 (m, 4H, OCH\(_2\)), 7.38 (s, 2H, H-4, H-10), 7.44 (d, \(3J 7.6\) Hz,
2H, H-2, H-20), 7.57 (s, 2H, H-22, H-23), 7.58 (d, \(3J 7.6\) Hz, 2H, H-1, H-21), 9.93 (s, 2H,
CHO). \(^13\)C NMR (CDCl\(_3\)): δ 68.0, 69.5, 71.1, 71.5 (OCH\(_2\)), 110.4, 124.2, 129.5, 129.5 (aromat.
and olefin. CH), 133.3, 136.4, 157.1 (aromat. C\(_6\)), 191.5 (CHO). MS (FD), \(m/z\) (%) = 426 (100)

General procedures for the preparation of the phenylenevinylene trimers with a stilbene
crown (17a,b–23a,b). a) Diphosphonate 8a or 8b (2.0 mmol), aldehyde 10-16 (6.0 mmol), 550
mg Aliquat 336 and 1.0 g (15 mmol) 85% KOH powder (15% H\(_2\)O) were heated in 100 mL of
benzene/5 mL H\(_2\)O to reflux for 24 h. After cooling to ambient temperature, 30 mL of H\(_2\)O were
added. The organic phase was dried (Na\(_2\)SO\(_4\)) and the volatile parts evaporated. The residue was
dissolved in CH\(_2\)Cl\(_2\) or CHCl\(_3\) and the solution dropped into \(n\)-hexane. Yellow crystals
precipitated, which were analytically pure or could be recrystallized from diethylether.
b) Dialdehyde 9a or 9b (1.0 mmol), phosphonate 2443.44 (1950 mg, 2.5 mmol), 500 mg Aliquot 336 and 500 mg (7.5 mmol) 85% KOH were heated in 200 mL of benzene/1 mL of H2O to reflux for 24 h. After cooling to ambient temperature the reaction mixture was treated with 50 mL of H2O. The organic phase was dried (Na2SO4) and evaporated. Column chromatography (40×3 cm SiO2, diethylether/petroleum ether 1:2) yielded yellow crystals.

\[(E,E,E)-6,7,9,10\text{-Tetrahydro-3,13-bis[2-(4-methoxy-phenyl)vinyl]-5,8,11-trioxa-dibenzo-[a,e]cyclotridecene (17a)}\]. Method a), yield: 536 mg (49%), mp 254 °C. 1H NMR (CDCl3): δ 3.81 (s, 6H, OCHO), 3.93-3.96 (m, 4H, OCHO2), 4.21-4.25 (m, 4H, OCHO2), 6.88/7.43 (AA′BB′, 4H, aromat. H), 6.91/7.04 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.11 (s, 2H, H-4, H-12), 7.16 (d, 3J 8.3 Hz, 2H, H-2, H-14), 7.46 (d, 3J 8.3 Hz, 2H, H-1, H-15). 13C NMR (CDCl3): δ 55.5 (OCHO3), 70.6, 71.4 (OCHO2), 114.6, 115.2, 121.3, 126.3, 126.5, 128.2, 128.5, 128.6 (aromat. and olefin. CH), 128.9, 130.4, 138.7, 158.1, 159.8 (aromat. C). MS (FD), m/z (%) = 546 (100) [M]+ . UV/Vis (CH2Cl2): λmax (ε) = 401 nm (56700 M⁻¹cm⁻¹). Anal. Calcd for C36H34O3 (546.7): C, 79.10; H, 6.27. Found: C, 79.20; H, 6.28.

\[(E,E,E)-6,7,9,10,12,13,15,16\text{-Octahydro-3,19-bis[2-(4-methoxy-phenyl)vinyl]-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (17b)}\]. Method a), yield: 837 mg (66%), mp 226–233 °C. 1H NMR (CDCl3): δ 3.68-3.72 (m, 8H, OCHO), 3.82 (s, 6H, OCHO3), 4.02-4.09 (m, 4H, OCHO2), 4.22-4.30 (m, 4H, OCHO2), 6.88/7.44 (AA′BB′, 4H, aromat. H), 6.91/7.05 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.01 (s, 2H, H-4, H-18), 7.08 (d, 3J 7.3 Hz, 2H, H-2, H-20), 7.38–7.43 (m, 2H, H-1, H-21), 7.42 (s, 2H, H-22, H-23). 13C NMR (CDCl3): δ 55.3 (OCHO3), 68.0, 70.0, 71.2, 71.7, (OCHO2), 109.9, 114.2, 119.3, 126.5, 126.7, 127.7, 128.1, 128.8 (aromat. and olefin. CH), 127.1, 130.2, 137.8, 156.9, 159.4 (aromat. C). MS (FD), m/z (%) = 634 (100) [M]+ . UV/Vis (CH2Cl2): λmax (ε) = 401 nm (54800 M⁻¹cm⁻¹). Anal. Calcd for C40H42O7 (634.8): C, 75.69; H, 6.67. Found: C, 74.91; H, 6.22 (incomplete combustion).

\[(E,E,E)-6,7,9,10\text{-Tetrahydro-3,13-bis[2-(3,5-tridodecyloxyphenyl-phenyl)vinyl]-5,8,11-trioxa-dibenzo[a,e]cyclotridecene (18a)}\]. Method a), yield: 1620 mg (51%); method b), yield: 1003 mg (63%); mp 91 °C. 1H NMR (CDCl3): δ 0.84-0.90 (m, 18H, CH3), 1.20-1.38 (m, 96H, CH2), 1.40-1.50 (m, 12H, CH2), 1.68-1.75 (m, 4H, CH2), 1.75-1.84 (m, 8H, CH2), 3.93-3.98 (m, 8H, OCHO2), 3.98-4.03 (m, 8H, OCHO2), 4.20-4.24 (m, 4H, OCHO2), 6.69 (s, 4H, aromat. H), 6.91/6.98 (AB, 3J 16.2 Hz, 4H, olefin. H), 7.11 (s, 2H, H-4, H-12), 7.16 (d, 3J 8.1 Hz, 2H, H-2, H-14), 7.46 (d, 3J 8.1 Hz, 2H, H-1, H-15), 7.82 (s, 2H, H-16, H-17). 13C NMR (CDCl3): δ 14.0 (CH3), 22.6, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.8 (CH2, partly superimposed), 69.3, 70.3, 70.9, 73.5 (OCHO2), 105.6, 115.0, 121.1, 126.2, 127.3, 128.8, 128.9 (aromat. and olefin. CH), 128.1, 132.5, 137.5, 138.7, 153.4, 157.6 (aromat. C). MS (FD), m/z (%) = 1592 (100) [M]+ . UV/Vis (CH2Cl2): λmax (ε) = 406 nm (55400 M⁻¹cm⁻¹). Anal. Calcd for C106H174O9 (1592.5): C, 79.95; H, 11.01. Found: C, 79.77; H, 10.88.
(E,E,E)-6,7,9,10,12,13,15,16-Octahydro-3,19-bis[2-(3,4,5-tridodecyloxyphenyl)vinyl]-5,8,11,14,17-pentaaxa-dibenzo[a,e]cyclononadecene (18b). Method a), yield: 1850 mg (55%); method b), yield: 825 mg (49%); mp 87 °C. \( ^1 \text{H} \) NMR (CDCl\(_3\)): \( \delta \) 0.84-0.91 (m, 18H, CH\(_3\)), 1.20-1.39 (m, 96H, CH\(_2\)), 1.42-1.51 (m, 12H, CH\(_2\)), 1.69-1.76 (m, 4H, CH\(_2\)), 1.76-1.85 (m, 8H, CH\(_2\)), 3.69-3.73 (m, 4H, OCH\(_2\)), 3.74-3.78 (m, 4H, OCH\(_2\)), 3.93-3.98 (m, 4H, OCH\(_2\)), 3.98-4.04 (m, 8H, OCH\(_2\)), 4.0-4.08 (m, 4H, OCH\(_2\)), 4.23-4.28 (m, 4H, OCH\(_2\)), 6.70 (s, 4H, aromat. H), 6.92/6.98 (AB, \( ^3 \)J 16.3 Hz, 4H, olefin. H), 7.01 (s, 2H, H-4, H-18), 7.08 (d, \( ^3 \)J 7.8 Hz, 2H, H-2, H-20), 7.40 (d, \( ^3 \)J 7.8 Hz, 2H, H-1, H-21), 7.44 (s, 2H, H-22, H-23). \( ^13 \)C NMR (CDCl\(_3\)): \( \delta \) 14.0 (CH\(_3\)), 22.6, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.3, 31.9 (CH\(_2\), partly superimposed), 67.9, 69.3, 70.0, 71.2, 71.7, 73.5 (OCH\(_2\)), 105.5, 109.9, 119.5, 126.8, 127.5, 128.8, 129.0 (aromat. and olefin. CH), 127.2, 132.5, 137.5, 138.7, 153.4, 156.8 (aromat. C\(_q\)). MS (FD), \( m/z \) (%) = 1680 (100) [M]\(^+\). UV/Vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 406 nm (59500 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{110}\)H\(_{182}\)O\(_{11}\) (1680.7): C, 78.61; H, 10.92. Found: C, 78.70; H, 10.53.

(E,E,E)-3,13-Bis[2-(4-bromo-2,5-dipropoxyphenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11,13,16-trioxao-dibenzo[a,e]cyclopentadecene (19a). Method a), yield: 1120 mg (64%); mp 188 °C. \( ^1 \text{H} \) NMR (CDCl\(_3\)): \( \delta \) 1.04-1.12 (m, 12H, CH\(_3\)), 1.80-1.90 (m, 8H, CH\(_2\)), 3.90-3.94 (m, 4H, OCH\(_2\)), 3.94-3.96 (m, 4H, OCH\(_2\)), 3.97-4.01 (m, 4H, OCH\(_2\)), 4.20-4.25 (m, 4H, OCH\(_2\)), 7.05/7.36 (AB, \( ^3 \)J 16.4 Hz, 4H, olefin. H), 7.07 (s, 2H, aromat. H), 7.10 (s, 2H, aromat. H), 7.12 (s, 2H, H-4, H-12), 7.19 (d, \( ^3 \)J 8.2 Hz, 2H, H-2, H-14), 7.47 (d, \( ^3 \)J 8.2 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H-16, H-17). \( ^13 \)C NMR (CDCl\(_3\)): \( \delta \) 10.5, 10.5 (CH\(_3\)), 22.6, 22.6 (CH\(_2\)), 70.2, 70.9, 71.2, 71.8 (OCH\(_2\)), 111.9, 115.1, 118.1, 121.1, 123.0, 126.2, 128.1, 128.9 (aromat. and olefin. CH), 112.0, 126.6, 137.7, 149.9, 151.1, 156.8 (aromat. C\(_q\), partly superimposed). MS (FD), \( m/z \) (%) = 878, 876, 874 (100) [M]\(^+\), Br\(_2\) isotope pattern. UV/Vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 412 nm (58300 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{46}\)H\(_{52}\)O\(_3\)Br\(_2\) (876.7): C, 63.02; H, 5.98; Br, 18.23. Found: C, 62.84; H, 5.90; Br, 18.05.

(E,E,E)-3,19-Bis[2-(4-bromo-2,5-dipropoxyphenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaaxa-dibenzo[a,e]cyclononadecene (19b). Method a), yield: 1100 mg (57%). \( ^1 \text{H} \) NMR (CDCl\(_3\)): \( \delta \) 1.05-1.11 (m, 12H, CH\(_3\)), 1.80-1.90 (m, 8H, CH\(_2\)), 3.69-3.73 (m, 4H, OCH\(_2\)), 3.73-3.77 (m, 4H, OCH\(_2\)), 3.90-3.94 (m, 4H, OCH\(_2\)), 3.94-4.01 (m, 4H, OCH\(_2\)), 4.20-4.25 (m, 4H, OCH\(_2\)), 7.07 (s, 2H, aromat. H), 7.11 (s, 2H, H-4, H-18), 7.12 (d, \( ^3 \)J 7.9 Hz, H-2, H-20), 7.42 (d, \( ^3 \)J 7.9 Hz, 2H, H-1, H-21), 7.45 (s, 2H, H-22, H-23). \( ^13 \)C NMR (CDCl\(_3\)): \( \delta \) 10.6, 10.6 (CH\(_3\)), 22.7, 22.7 (CH\(_2\)), 68.0, 70.0, 71.2, 71.3, 71.6, 71.9 (OCH\(_2\)), 110.2, 111.9, 118.2, 119.5, 123.0, 126.9, 129.0, 129.3 (aromat. and olefin. CH), 112.0, 126.8, 127.4, 137.8, 150.0, 151.2, 156.9 (aromat. C\(_q\)). MS (FD), \( m/z \) (%) = 966, 964, 962 (100) [M]\(^+\), Br\(_2\) isotope pattern. UV/Vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 412 nm (69900 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{50}\)H\(_{56}\)O\(_3\)Br\(_2\) (964.8): C, 62.24; H, 6.27; Br, 16.56. Found: C, 61.96; H, 5.89; Br, 16.42.
(E,E,E)-3,13-Bis[2-(4-bromo-2,5-dihexyloxyphenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxadibenzo[a,e]cyclooctadecene (20a). Method a), yield: 1023 mg (49%). 1H NMR (CDCl3): δ 0.87-0.93 (m, 12H, CH3), 1.25-1.40 (m, 16H, CH2), 1.46-1.55 (m, 8H, CH2), 1.78-1.86 (m, 8H, CH2), 3.92-3.97 (m, 8H, OCH2), 3.99-4.03 (m, 4H, OCH2), 4.20-4.23 (m, 4H, OCH2), 7.05/7.35 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.06 (s, 2H, aromat. H), 7.09 (s, 2H, aromat. H), 7.12 (s, 2H, H-4, H-12), 7.19 (d, 3J 8.0 Hz, 2H, H-2, H-14), 7.47 (d, 3J 8.0 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H-16, H-17). 13C NMR (CDCl3): δ 13.9, 13.9 (CH3), 22.5, 22.6, 25.6, 25.8, 29.5, 29.5, 31.5, 31.5 (CH2), 69.6, 70.2, 70.3, 70.8 (OCH2), 111.8, 115.1, 117.9, 121.2, 123.0, 126.2, 128.4 (aromat. and olefin. CH). Anal. Calcd for C38H76O7Br2 (1045.1): C, 66.66; H, 7.33; Br, 15.29. Found: C, 66.27; H, 7.08; Br, 15.1.

(E,E,E)-3,19-Bis[2-(4-diethoxymethylphenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxadibenzo[a,e]cyclotridecane (21a). Method a), yield: 770 mg (56%), mp 204 °C. 1H NMR (CDCl3): δ 1.23 (t, 3J 7.4 Hz, 12H, CH3), 3.49-3.66 (m, 8H, OCH2CH3), 3.91-3.98 (m, 4H, OCH2), 4.20-4.25 (m, 4H, OCH2), 5.50 (s, 2H, CH(OCH2CH3)2), 7.05/7.09 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.13 (s, 2H, H-4, H-12), 7.18 (d, 3J 8.2 Hz, 2H, H-2, H-14), 7.44/7.48 (AA’BB’, 8H, aromat. H), 7.48 (d, 3J 8.2 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H-16, H-17). 13C NMR (CDCl3): δ 15.2 (CH3), 61.1 (OCH2CH3), 70.3, 71.0 (OCH2), 101.4 (CH(OCH2CH3)2), 115.2, 121.3, 126.3, 126.4, 127.3, 128.2, 128.4, 128.6 (aromat. and olefin. CH). Anal. Calcd for C44H60O7 (690.9): C, 76.49; H, 7.29. Found: C, 76.19; H, 7.01.

(E,E,E)-3,19-Bis[2-(4-diethoxymethylphenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (21b). Method a), yield: 970 mg (62%), mp 209
°C. $^1$H NMR (CDCl$_3$): δ 1.24 (t, $^3$J 7.4 Hz, 12H, CH$_3$), 3.46-3.67 (m, 8H, OCH$_2$CH$_3$), 3.67-3.79 (m, 8H, OCH$_3$), 4.01-4.10 (m, 4H, OCH$_2$), 4.22-4.30 (m, 4H, OCH$_2$), 5.50 (s, 2H, CH$(\text{OC}_3\text{H}_5)_{2}$), 7.03 (s, 2H, H-4, H-18), 7.08 (s, 4H, olefin. H), 7.11 (d, $^3$J 8.2 Hz, 2H, H-2, H-20), 7.42 (d, $^3$J 8.2 Hz, 2H, H-1, H-21), 7.44 (s, 2H, H-22, H-23), 7.45/7.50 (AA’BB’, 8H, aromat. H). $^{13}$C NMR (CDCl$_3$): δ 15.2 (CH$_3$), 61.0 (OCH$_2$CH$_3$), 68.1, 70.0, 71.3, 71.7 (OCH$_2$), 101.4 (CH$(\text{OC}_3\text{H}_5)_{2}$), 110.2, 119.7, 126.3, 127.0, 127.1, 128.3, 128.8, 129.0 (aromat. and olefin. CH), 127.5, 137.4, 137.5, 138.7, 156.9 (aromat. C$_{6}$). MS (FD), m/z (%) = 778 (100) [M]$^+$ $. UV (\text{CH}_2\text{Cl}_2): \lambda_{\text{max}} (\varepsilon) = 399 \text{ nm (71400 M}^{-1}\text{cm}^{-1})$. Anal. Calcd for C$_{48}$H$_{58}$O$_9$ (779.0): C, 74.01; H, 7.50. Found: C, 74.22; H, 7.39.

*(E,E,E)*-3,13-Bis[2-(4-dimethoxymethyl-2,5-dipropoxyphenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclooctadecene (22a). Method a), yield: 830 mg (48%) yellow crystals, mp 112 °C. $^1$H NMR (CDCl$_3$): δ 1.04-1.07 (m, 12H, CH$_3$), 1.80-1.85 (m, 8H, CH$_2$), 3.39 (s, 12H, OCH$_3$), 3.95-3.99 (m, 12H, OCH$_2$), 4.20-4.22 (m, 4H, OCH$_2$), 5.62 (s, 2H, CH$(\text{OC}_3\text{H}_5)_{2}$), 7.06/7.44 (AB, 16.3 Hz, 4H, olefin. H), 7.07 (s, 4H, aromat. H), 7.13 (s, 2H, H-4, H-12), 7.20 (d, $^3$J 8.1 Hz, 2H, H-2, H-14), 7.47 (d, $^3$J 8.0 Hz, 2H, H-1, H-15), 7.83 (s, 2H, H-16, H-17). $^{13}$C NMR (CDCl$_3$): δ 10.7 (CH$_3$), 22.8 (CH$_2$), 54.1 (OCH$_3$), 70.3, 70.9, 70.9, 71.1 (OCH$_2$), 99.6 (CH$(\text{OC}_3\text{H}_5)_{2}$), 110.4, 112.1, 115.2, 121.3, 123.7, 126.3, 128.1, 128.8 (aromat. and olefin. CH), 127.3, 127.5, 128.9, 138.0, 150.9, 150.9, 157.6 (aromat. C$_{6}$). MS (FD), m/z (%) = 866 (100) [M]$^+$ $. UV/Vis (\text{CH}_2\text{Cl}_2): \lambda_{\text{max}} (\varepsilon) = 411 \text{ nm (67000 M}^{-1}\text{cm}^{-1})$. Anal. Calcd for C$_{52}$H$_{66}$O$_{11}$ (867.1): C, 72.03; H, 7.67. Found: C, 71.63; H, 7.33.

*(E,E,E)*-3,19-Bis[2-(4-dimethoxymethyl-2,5-dipropoxyphenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (22b). Method a), yield: 920 mg (48%) yellow crystals, mp 251–265 °C. $^1$H NMR (CDCl$_3$): δ 1.04-1.07 (m, 12H, CH$_3$), 1.82-1.87 (m, 8H, CH$_2$), 3.39 (s, 12H, OCH$_3$), 3.70-3.77 (m, 8H, OCH$_2$), 3.95-4.00 (m, 8H, OCH$_2$), 4.02-4.07 (m, 4H, OCH$_2$), 4.23-4.27 (m, 4H, OCH$_2$), 5.62 (s, 2H, CH$(\text{OC}_3\text{H}_5)_{2}$), 7.03 (s, 2H, H-4, H-18), 7.07/7.43 (AB, $^3$J 16.4 Hz, 4H, olefin. H), 7.08, 7.08 (2 s, 4H, aromat. H), 7.12 (d, $^3$J 8.1 Hz, 2H, H-2, H-20), 7.41 (d, $^3$J 8.1 Hz, 2H, H-1, H-21), 7.44 (s, 2H, H-22, H-23). $^{13}$C NMR (CDCl$_3$): δ 10.7 (CH$_3$), 22.9 (CH$_2$), 54.2 (OCH$_3$), 68.0, 70.0, 71.0, 71.2, 71.3, 71.7 (OCH$_2$), 99.7 (CH$(\text{OC}_3\text{H}_5)_{2}$), 110.3, 110.5, 112.2, 119.6, 123.7, 126.9, 129.0, 129.1 (aromat. and olefin. CH), 127.2, 127.3, 127.5, 138.1, 150.9, 151.0, 156.9 (aromat. C$_{6}$). MS (FD), m/z (%) = 955 (100) [M]$^+$ $. UV/Vis (\text{CH}_2\text{Cl}_2): \lambda_{\text{max}} (\varepsilon) = 412 \text{ nm (69900 M}^{-1}\text{cm}^{-1})$. Anal. Calcd for C$_{56}$H$_{74}$O$_{13}$ (955.2): C, 70.42; H, 7.81. Found: C, 69.97; H, 7.60.

*(E,E,E)*-3,13-Bis[2-(2,5-dihexyloxy-4-dimethoxymethyl-phenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclooctadecene (23a). Method a), yield: 1160 mg (56%) yellow crystals, mp 93–96 °C. $^1$H NMR (CDCl$_3$): δ 0.87-0.92 (m, 12H, CH$_3$), 1.25-1.38 (m, 16H, CH$_2$), 1.43-1.55 (m, 8H, CH$_2$), 1.76-1.86 (m, 8H, CH$_2$), 3.39 (s, 12H, OCH$_3$), 3.93-3.97 (m, 4H, OCH$_2$), 3.96-4.04 (m, 8H, OCH$_2$), 4.19-4.23 (m, 4H, OCH$_2$), 5.60 (s, 2H, CH$(\text{OC}_3\text{H}_5)_{2}$),
7.05/7.43 (AB, $^3J$ 16.2 Hz, 4H, olefin, H), 7.07 (s, 4H, aromat. H), 7.13 (s, 2H, H-4, H-12), 7.19 (d, $^3J$ 8.2 Hz, 2H, H-2, H-14), 7.47 (d, $^3J$ 8.2 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H-16, H-17). $^{13}$C NMR (CDCl$_3$): δ 14.0 (CH$_3$), 22.6, 25.8, 29.4, 31.6 (CH$_2$), 54.2 (OCH$_3$), 69.4, 69.5, 70.3, 70.9 (OCH$_2$), 99.7 (CH(OCH$_3$)$_2$), 110.4, 111.9, 115.1, 121.3, 123.7, 126.3, 128.1, 128.8 (aromat. and olefin. CH), 127.3, 127.4, 128.9, 138.0, 150.9, 150.9, 157.6 (aromat. C$_q$). MS (FD), $m/z$ (%) = 1035 (100) [M]$^+$.

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 411 nm (67100 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{64}$H$_{90}$O$_{11}$ (1035.4): C, 74.24; H, 8.76. Found: C, 73.94; H, 8.99.

(E,E,E)-3,19-Bis[2-(2,5-dihexyloxy-4-dimethoxymethyl-phenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (23b). Method a), yield: 1416 mg (63%) yellow crystals, mp 128 °C. $^1$H NMR (CDCl$_3$): δ 0.87-0.94 (m, 12H, CH$_3$), 1.31-1.39 (m, 16H, CH$_2$), 1.43-1.54 (m, 8H, CH$_2$), 1.76-1.85 (m, 8H, CH$_2$), 3.39 (s, 12H, OCH$_3$), 3.69-3.77 (m, 8H, OCH$_2$), 3.97-4.06 (m, 8H, OCH$_2$), 4.22-4.27 (m, 4H, OCH$_2$), 5.61 (s, 2H, CH(OCH$_3$)$_2$), 7.02 (s, 2H, H-4, H-18), 7.07, 7.08 (2s, 4H, aromat. H), 7.07/7.43 (AB, $^3J$ 16.1 Hz, 4H, olefin. H), 7.13 (d, $^3J$ 8.0 Hz, 2H, H-2, H-20), 7.41 (d, $^3J$ 8.0 Hz, 2H, H-1, H-21), 7.45 (s, 2H, H-22, H-23). $^{13}$C NMR (CDCl$_3$): δ 14.0 (CH$_3$), 22.6, 25.8, 25.9, 29.5, 31.6 (CH$_2$, partly superimposed), 54.2 (OCH$_3$), 68.0, 69.4, 69.6, 70.0, 71.3, 71.7 (OCH$_2$), 99.7 (CH(OCH$_3$)$_2$), 110.3, 110.5, 112.0, 119.6, 125.7, 126.9, 129.0, 129.1 (aromat. and olefin. CH), 127.2, 127.3, 127.5, 138.1, 150.9, 151.0, 156.9 (aromat. C$_q$). MS (FD), $m/z$ (%) = 1123 (100) [M]$^+$.

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 411 nm (62000 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{68}$H$_{98}$O$_{13}$ (1123.5): C, 72.70; H, 8.79. Found: C, 72.33; H, 8.39.

Preparation of the Dialdehydes 25a,b–27a,b. The acetals 21a,b–23a,b (0.2 mmol), dissolved in 50 mL of CHCl$_3$, were vigorously stirred with 30 mL of 10% HCl for 2 h. The organic phase was dried (Na$_2$SO$_4$) and evaporated. A saturated solution of the residue in CH$_2$Cl$_2$ was then slowly dropped into a mixture of petroleum ether (bp 40-70 °C) and diethyl ether (10:1) or into n-hexane. The formed precipitate is analytically pure.

(E,E,E)-3,13-Bis[2-(4-formyl-phenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxo-dibenzo[a,e]-cyclotridecene (25a). Yellow-orange powder; yield: 93 g (86%); mp > 300 °C. $^1$H NMR (CDCl$_3$): δ 3.94-4.02 (m, 4H, OCH$_2$), 4.20-4.28 (m, 4H, OCH$_2$), 7.12/7.20 (AB, $^3J$ 16.2 Hz, 4H, olefin. H), 7.16 (s, 2H, H-4, H-12), 7.21 (d, $^3J$ 8.2 Hz, 2H, H-14), 7.50 (d, $^3J$ 8.2 Hz, H-2, H-1, H-15), 7.64/7.86 (AA'BB', 8H, aromat. H), 7.87 (s, 2H, olefin. H), 9.95 (s, 2H, CHO). Owing to the very low solubility, a $^{13}$C NMR spectrum was not measured. MS (FD), $m/z$ (%) = 542 (100) [M]$^+$.

UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 421 nm (69300 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{36}$H$_{36}$O$_5$ (542.6): C, 79.69; H, 5.57. Found: C, 79.31; H, 5.17.

(E,E,E)-3,19-Bis[2-(4-formyl-phenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (25b). Yellow-orange powder; yield: 109 mg (86%); mp 219 °C. $^1$H NMR (CD$_2$Cl$_2$): δ 3.68-3.72 (m, 4H, OCH$_2$), 3.72-3.76 (m, 4H, OCH$_2$), 4.03-4.07 (m, 4H, OCH$_2$), 4.25-4.29 (m, 4H, OCH$_2$), 7.12 (s, 2H, H-4, H-18), 7.19/7.28 (AB, $^3J$ 16.4
Hz, 4H, olefin. H), 7.20 (d, 3J 8.1 Hz, 2H, H-2, H-20), 7.48 (d, 3J 8.1 Hz, 2H, H-1, H-21), 7.49 (s, 2H, H-22, H-23), 7.69/7.87 (AA’BB’, 8H, aromat. H), 9.98 (s, 2H, CHO). 13C NMR (CD2Cl2): δ 68.6, 70.3, 71.6, 72.2 (OCH2), 110.8, 120.5, 127.4, 127.6, 127.8, 129.6, 130.6, 132.3 (aromat. and olefin. CH), 128.5, 136.1, 137.4, 143.9, 157.5 (aromat. Cq), 191.8 (CHO). MS (FD), m/z (%): 630 (100) [M]+. UV/Vis (CH2Cl2): λmax (ε) = 421 nm (55000 M⁻¹cm⁻¹). Anal. Caled for C40H38O7 (630.5): C, 76.17; H, 6.07. Found: C, 76.53; H, 5.71.

(E,E,E)-3,13-Bis[2-(4-formyl-2,5-dipropoxy-phenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxadiibenzo[a,e]cyclotridecene (26a). Orange crystals; yield: 129 g (83%); mp 168-176 °C. 1H NMR (CDCl3): δ 1.07 (t, 3J = 7.2 Hz, 12H, CH3), 1.82-1.92 (m, 8H, CH2), 3.93-3.96 (m, 4H, OCH2), 3.96 (t, 3J = 7.3 Hz, 4H, OCH2), 4.06 (t, 3J = 7.3 Hz, 4H, OCH2), 4.20-4.24 (m, 4H, OCH2), 7.14-7.17 (m, 4H, H-4, H-12, aromat. H), 7.19/7.45 (AB, 3J = 16.4 Hz, 4H, olefin. H), 7.22 (d, 3J = 8.2 Hz, 2H, H-2, H-14), 7.31 (s, 2H, aromat. H), 7.50 (d, 3J = 8.2 Hz, 2H, H-1, H-15), 7.86 (s, 2H, olefin. H), 10.44 (s, 2H, CHO). 13C NMR (CDCl3): δ 10.6 (CH3), 22.6, 22.7 (CH2), 70.3, 70.8, 70.9, 71.0 (OCH2), 110.5, 110.8, 115.5, 121.7, 123.1, 126.6, 128.3, 131.9 (aromat. and olefin. CH), 124.5, 129.6, 134.3, 137.4, 150.9, 156.3, 157.7 (aromat. Cq), 189.0 (CHO). MS (FD), m/z (%) = 774 (100) [M]+. UV/Vis (CH2Cl2): λmax (ε) = 438 nm (58100 M⁻¹cm⁻¹). Anal. Caled for C48H34O9 (775.0): C, 74.40; H, 7.02. Found: C, 74.02; H, 6.73.

(E,E,E)-3,19-Bis[2-(4-formyl-2,5-dipropoxy-phenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (26b). Orange powder; yield: 154 mg (89%); mp 92-102 °C. 1H NMR (CDCl3): δ 1.08 (t, 3J = 7.2 Hz, 12H, CH3), 1.75-1.95 (m, 8H, CH2), 3.65-3.78 (m, 8H, OCH2), 3.93-4.10 (m, 12H, OCH2), 4.20-4.22 (m, 4H, OCH2), 7.05 (s, 2H, H-4, H-18), 7.12-7.19 (m, 4H, H-2, H-20, aromat. H), 7.21/7.45 (AB, 3J = 16.2 Hz, 4H, olefin. H), 7.31 (s, 2H, aromat. H), 7.39-7.51 (m, 2H, H-1, H-21), 7.47 (s, 2H, H-22, H-23). 13C NMR (CDCl3): δ 10.6, 10.5 (CH3), 22.6 (CH2), 68.0, 70.0, 70.7, 70.9, 71.2, 71.7 (OCH2), 110.5, 110.8, 119.9, 122.9, 127.2, 127.9, 129.1 (aromat. and olefin. CH), 124.5, 132.1, 134.3, 137.4, 150.9, 156.3, 157.7 (aromat. Cq), 189.0 (CHO). MS (FD), m/z (%) = 862 (100) [M]+. UV/Vis: λmax (ε) = 438 nm (70000 M⁻¹cm⁻¹). Anal. Caled for C52H62O11 (863.1): C, 72.37; H, 7.24. Found: C, 72.54; H, 7.32.

(E,E,E)-3,13-Bis[2-(4-formyl-2,5-dihexyloxy-phenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxadiibenzo[a,e]cyclotridecene (27a). Orange crystals; yield: 170 mg (90%); mp 99 °C. 1H NMR (CDCl3): δ 0.88-0.95 (m, 12H, CH3), 130-1.40 (m, 16H, CH2), 1.45-1.55 (m, 8H, CH2), 1.80-1.88 (m, 8H, CH2), 3.93-3.98 (m, 4H, OCH2), 3.98-4.04 (m, 4H, OCH2), 4.06-4.12 (m, 4H, OCH2), 4.20-4.25 (m, 4H, CH2), 7.14-7.18 (m, 4H, H-4, H-12, aromat. H), 7.19/7.44 (AB, 3J = 16.4 Hz, 4H, olefin. H), 7.20-7.25 (m, 2H, H-2, H-14), 7.31 (s, 2H, aromat. H), 7.50 (3J = 7.9 Hz, 2H, H-1, H-15), 7.87 (s, 2H, olefin. H), 10.43 (s, 2H, CHO). 13C NMR (CDCl3): δ 14.0 (CH3), 22.6, 22.6, 25.8, 25.9, 29.2, 29.2, 31.5, 31.6 (CH2), 69.3, 69.4, 70.3, 70.9 (OCH2), 110.4, 110.8, 115.4, 121.7, 123.1, 126.6, 128.3, 131.8 (aromat. and olefin. CH), 124.5, 129.6, 134.3, 137.4,
150.9, 156.3, 157.7 (aromat. C₄), 189.0 (CHO). MS (FD), m/z (%) = 943 (100) [M]⁺. UV/Vis: λmax (ε) = 438 nm (66400 M⁻¹·cm⁻¹). Anal. Caled for C₆₀H₇₈O₉ (943.7) : C, 76.40; H, 8.33. Found: C, 76.11; H, 8.51.

**(E,E,E)-3,19-Bis[2-(4-formyl-2,5-dihexyloxy-phenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (27b)**. Orange powder, yield: 192 mg (93%), mp 95 °C. ¹H NMR (CDCl₃): δ 0.81-0.95 (m, 12H, CH₂), 1.25-1.40 (m, 16H, CH₂), 1.40-1.60 (m, 8H, CH₂), 1.75-1.95 (m, 8H, CH₂), 3.66-3.77 (m, 8H, OCH₂), 3.95-4.15 (m, 12H, OCH₂), 4.20-4.30 (m, 4H, OCH₂), 7.05 (s, 2H, H-4, H-18), 7.12-7.19 (m, 4H, H-2, H-20, aromat. H), 7.21/7.44 (AB, ³J 16.2 Hz, 4H, olefin. H), 7.31 (s, 2H, aromat. H), 7.39-7.50 (m, 4H, H-1, H-21, H-22, H-23), 10.43 (s, 2H, CHO). ¹³C NMR (CDCl₃): δ 13.9, 14.0 (CH₃), 22.5, 22.6, 25.7, 25.9, 29.2, 29.2, 31.5, 31.5 (CH₂), 68.0, 69.2, 69.4, 69.9, 71.2, 71.7 (OCH₂), 110.4, 110.5, 110.8, 119.9, 123.0, 127.2, 129.1, 132.1 (aromat. and olefin. CH), 124.4, 127.9, 134.3, 137.4, 150.8, 156.2, 156.9 (aromat. C₉), 189.0 (CHO). MS (FD), m/z (%) = 1031 (100) [M]⁺. UV/Vis: λmax (ε) = 438 nm (73900 M⁻¹·cm⁻¹). Anal. Caled for C₆₀H₇₈O₁₁ (1031.4) : C, 74.53; H, 8.40. Found: C, 74.23; H, 8.11.

1,4-Phenylenevinylene tetramers with two stilbene crowns 30a,b and 31a,b. Dialdehyde 9a or 9b (0.6 mmol), diphenosphate 28 or 29, (10.2 mmol), 85% KOH (50 m, 0.76 mmol), 0.50 g Aliquat 336, 0.5 mL of H₂O and 100 mL of benzene were heated to reflux for 24 h. H₂O (10 mL) was added and the organic phase separated and evaporated. The residue was treated with 5-10 mL of CH₂Cl₂. The filtered solution was slowly dropped in petroleum ether (bp 40-70 °C), where the product as red solid precipitated. (The major, insoluble part in CH₂Cl₂ contained higher oligomers).

**(E,E,E,E)-PV-Tetramer 30a**. Yield: 21 mg (11%) red solid, mp 275-280 °C. ¹H NMR (CD₂Cl₂): δ 1.14 (t, ³J = 7.6 Hz, 6H, CH₃), 1.87-1.95 (m, 4H, CH₂), 3.92-4.10 (m, 12H, OCH₂), 4.18-4.29 (m, 8H, OCH₂), 7.13-7.25 (m, 6H, aromat. and olefin. H), 7.25-7.33 (d, ³J 8.2 Hz, 2H, aromat. H), 7.49 (s, 2H, aromat. H), 7.53 (d, ³J 16.2 Hz, 2H, olefin. H), 7.54 (d, ³J 7.9 Hz, 2H, aromat. H), 7.57 (d, ³J 7.9 Hz, 2H, aromat. H), 7.65 (d, ³J 7.9 Hz, 2H, aromat. H), 7.79 (d, ³J 16.7 Hz, 2H, olefin. H), 8.13 (d, ³J 16.7 Hz, 2H, olefin. H), 9.93 (s, 2H, CHO). ¹³C NMR (CDCl₃): δ 11.0 (CH₃), 23.3 (CH₂), 70.4, 70.7, 71.1, 71.6, 71.8 (OCH₂), 111.1, 116.0, 116.3, 121.8, 124.4, 125.3, 125.5, 128.5, 128.7, 129.0, 130.4 (aromat. and olefin. CH), 127.4, 128.7, 136.0, 136.4, 139.5, 151.7, 158.1, 158.5 (aromat. C₁₉), 191.5 (CHO). MS (FD), m/z (%) = 946 (100) [M]⁺. UV/Vis (CH₂Cl₂): λmax (ε) = 447 nm (104300 M⁻¹·cm⁻¹). Anal. Caled for C₆₀H₆₆O₁₀ (946.6): C, 76.09; H, 7.02. Found: C, 75.73; H, 7.37.

**(E,E,E,E)-PV-Tetramer 30b**. Yield: 72 mg (35%), red solid, mp 234 °C. ¹H NMR (CDCl₃): δ 1.12 (t, ³J = 7.6 Hz, 6H, CH₃), 1.82-2.00 (m, 4H, CH₂), 3.63-3.79 (m, 16H, OCH₂), 3.95-4.10 (m, 12H, OCH₂), 4.20-4.32 (m, 8H, OCH₂), 7.05 (s, 2H, aromat. H), 7.08-7.18 (m, 6H, aromat.
and olefin. H), 7.37-7.52 (m, 10H, aromat. and olefin. H), 7.54-7.64 (m, 4H, aromat. and olefin. H), 9.93 (s, 2H, CHO). $^{13}$C NMR (CDCl$_3$): δ 10.7 (CH$_3$), 22.9 (CH$_2$), 67.9, 68.1, 69.7, 69.8, 71.1, 71.2, 71.5, 71.7 (OCH$_2$), 110.2, 110.6, 111.0, 119.5, 124.0, 124.3, 125.9, 128.4, 128.6, 129.9, 130.5 (aromat. and olefin. CH), 126.3, 127.0, 134.6, 136.0, 139.0, 151.3, 156.9, 157.2 (aromat. C$_q$), 191.4 (CHO). MS (FD), $m/z$ (%) = 1039 (100) [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 443 nm (111500 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{62}$H$_{70}$O$_{14}$ (1039.2): C, 71.66; H, 6.79. Found: C, 71.42; H, 6.59.

$(E,E,E,E)$-PV-Tetramer 31a. Yield: 32 mg (17%), red powder, mp 230 °C. $^1$H NMR (CDCl$_3$): δ 0.89-0.95 (m, 6H, CH$_3$), 1.33-1.43 (m, 8H, CH$_2$), 1.52-1.60 (m, 4H, CH$_2$), 1.83-1.92 (m, 4H, CH$_2$), 3.92-4.00 (m, 8H, OCH$_2$), 4.05 (t, $^3$J = 6.4 Hz, 4H, OCH$_2$), 4.20-4.27 (m, 8H, OCH$_2$), 7.10/7.32 (AB, $^3$J = 16.4 Hz, 4H, olefin. H), 7.10 (s, 2H, aromat. H), 7.18 (s, 2H, aromat. H), 7.62-7.27 (m, 2H, aromat. H), 7.46 (s, 2H, aromat. H), 7.50 (d, $^3$J = 8.8 Hz, 2H, aromat. H), 7.53 (d, $^3$J = 8.2 Hz, 2H, aromat. H), 7.60 (d, $^3$J = 7.9 Hz, 2H, aromat. H), 7.72/8.16 (AB, $^3$J = 16.7 Hz, 4H, olefin. H), 9.94 (s, 2H, CHO). $^{13}$C NMR (CDCl$_3$): δ 14.0 (CH$_3$), 22.6, 26.0, 29.6, 31.6 (CH$_2$), 69.6, 70.1, 70.3, 70.4, 71.4 (OCH$_2$), 110.9, 115.5, 115.7, 121.5, 124.1, 125.0, 125.2, 128.0, 128.3, 128.7, 130.2 (aromat. and olefin. CH), 127.0, 135.7, 135.7, 139.1, 151.3, 157.6, 157.9 (aromat. C$_q$, partly superimposed), 191.2 (CHO). MS (FD), $m/z$ (%) = 946 (100) [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 447 nm (100900 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{66}$H$_{78}$O$_{10}$ (947.2): C, 76.09; H, 7.02. Found: C, 75.89; H, 7.30.

$(E,E,E,E)$-PV-Tetramer 31b. Yield: 25 mg (11%), red crystals, mp 196 °C. $^1$H NMR (CDCl$_3$): δ 0.89-0.95 (m, 6H, CH$_3$), 1.33-1.43 (m, 8H, CH$_2$), 1.52-1.60 (m, 4H, CH$_2$), 1.83-1.92 (m, 4H, CH$_2$), 3.68-3.77 (m, 16H, OCH$_2$), 4.00-4.04 (t, $^3$J = 5.0 Hz, 4H, OCH$_2$), 4.04-4.09 (m, 8H, OCH$_2$), 4.24-4.30 (m, 8H, OCH$_2$), 7.04 (s, 2H, aromat. H), 7.11/7.43 (AB, $^3$J = 16.4 Hz, 4H, olefin. H), 7.11 (s, 2H, aromat. H), 7.15 (d, $^3$J = 8.2 Hz, 2H, aromat. H), 7.38 (s, 2H, aromat. H), 7.40 (d, $^3$J = 8.2 Hz, 2H, aromat. H), 7.42-7.46 (m, 2H, aromat. H), 7.48/7.57 (AB, $^3$J = 16.4 Hz, 4H, olefin. H), 7.60 (d, $^3$J = 7.8 Hz, 2H, aromat. H), 9.92 (s, 2H, CHO). $^{13}$C NMR (CDCl$_3$): δ 14.0 (CH$_3$), 22.6, 26.0, 29.5, 31.6 (CH$_2$), 67.9, 68.1, 69.6, 69.7, 69.9, 71.2, 71.3, 71.5, 71.7 (OCH$_2$), 110.2, 110.6, 110.9, 119.5, 124.1, 124.3, 125.9, 128.4, 128.6, 129.9, 130.5 (aromat. and olefin. CH), 126.3, 127.0, 134.6, 136.0, 139.0, 151.3, 156.9, 157.2 (aromat. C$_q$), 191.4 (CHO). MS (FD), $m/z$ (%) = 1122 (100) [M]$^+$. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) = 443 nm (108200 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{68}$H$_{82}$O$_{14}$ (1123.3): C, 72.70; H, 7.36. Found: C, 72.70; H, 7.06 (incomplete combustion).

all-(E)-Nonamer 34. Dialdehyde 27a (114 mg, 0.12 mmol), diphasonate 8a (35 mg, 0.06 mmol), KOH (85%, 20 mg, 0.42 mmol) and Aliquat 336 (10 mg) were heated to reflux in 300 mL of benzene/0.5 mL H$_2$O for 3 d. After the addition of 50 mL of H$_2$O, the mixture was stirred at r. t. and the precipitate filtered off, dried and extracted with hot CHCl$_3$. The soluble part consisted of the red solid 34 (16 mg, 12%) which melted at 245 °C. $^1$H NMR (CD$_2$Cl$_2$): δ 0.89-0.95 (m, 24H, CH$_3$), 1.30-1.75 (m, 48H, CH$_2$), 1.80-1.90 (m, 16H, CH$_2$), 3.80-4.30 (m, 40H,
OCH2), 7.00-7.60 (m, 38H, aromat. and olefin. H), 7.80-7.90 (m, 6H, olefin. H in crown), 9.74 (s, 2H, CHO). MS (FD), m/z (%) = 2160 (20) [M]+, 671 (100). UV/Vis (CH2Cl2): λmax (ε) = 457 nm (very low solubility, ε not determined). Anal. Calcd for C140H174O19 (2160.9): C, 77.82; H, 8.12. Found: C, 77.54; H, 8.31.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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