Crown ethers in the OPV series

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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-phenylenevinylenes, 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→Z isomerization reactions on direct irradiation (S₀→S₁).

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. and improved by Merz et al. We used a somewhat modified procedure: The methyl substituted salicylaldehyde 3 was first reacted with the twofold methylsulfonic acid ester 4a or 4b 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 NaClO₄. (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 \(10^{38}, 11^{39}, 12^{40}, 13^{41}, 14^{42}, 15^{40}, 16^{41}\) led to an extension of the conjugated chain in the all-\textit{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 \( ^{13,44} \) (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 \( \lambda_{\text{max}} \) 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 $21a,b$-$23a,b\rightarrow 25a,b$-$27a,b$.

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.
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-phenylenevinylene of oligomer type 32 or 33 should result. Our first attempts in this direction led predominantly 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 tetramers 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{center}
\begin{tikzpicture}
\node at (0,0) {32 (n = 1, 3)};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {33 (n = 1, 3; R = OC$_3$H$_7$, R = OC$_6$H$_{13}$)};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {34};
\end{tikzpicture}
\end{center}

\textbf{Scheme 5.} Higher OPVs containing (E)-stilbene crown ether structures.

\section*{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 tetramers 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-ethanediylxlo)]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, $^3$J 7.8 Hz, 2H, H-5), 7.67 (d, $^3$J 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), $m/z$ (%) 342 (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-ethanediylxlo)-2,1-ethanediylxlo)]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 dimethyl sulfonate 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, $^3$J 7.8 Hz, 2H, H-5), 7.65 (d, $^3$J 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-trioxo-dibenzo[a,e]cyclooctadecene (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 (SiO₂, CH₂Cl₂), but the next step could be made with the E/Z mixture as well.

(E)-6a: Colorless powder, mp 136 °C. ¹H NMR (CDCl₃): δ 2.32 (s, 6H, CH₃), 3.85-3.94 (m, 4H, OCH₂), 4.09-4.19 (m, 4H, OCH₂), 6.80 (s, 2H, H-4, H-12), 6.83 (d, 3J 7.9 Hz, 2H, H-2, H-14), 7.36 (d, 3J 7.9 Hz, 2H, H-1, H-15), 7.73 (s, 2H, H-16, H-17). ¹³C NMR (CDCl₃): δ 21.3 (CH₃), 70.1, 70.7 (OCH₂), 118.1, 123.4, 125.4, 127.6 (aromat. and olefin. CH), 126.6, 137.9, 157.0 (aromat. Cq). UV (CH₂Cl₂): λmax (ε) 328 nm (20100 M⁻¹cm⁻¹).

(Z)-6a: Oil. ¹H NMR (CDCl₃): δ 2.25 (s, 6H, CH₃), 3.67-3.77 (m, 4H, OCH₂), 3.94-4.03 (m, 4H, OCH₂), 6.61-6.63 (m, 6H, H-2, H-4, H-12, H-14, H-16, H-17), 6.88 (d, 3J 7.6 Hz, 2H, H-1, H-15). ¹³C NMR (CDCl₃): δ 20.9 (CH₃), 69.7, 71.0 (OCH₂), 116.3, 122.2, 127.2, 130.1 (aromat. and olefin. CH), 126.6, 137.2, 155.8 (aromat. Cq). UV (CH₂Cl₂): λmax (ε) 290 nm (6300 M⁻¹cm⁻¹).

3,19-Dimethyl-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclonona-decene (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 C₂₄H₃₀O₅ (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 NaClO₄. The oil, dissolved in 300 mL of dry THF, was treated with NaClO₄ (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 CH₂Cl₂. The organic phase was dried (Na₂SO₄) 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. ¹H NMR (CDCl₃): δ 2.28 (s, 6H, CH₃), 3.56-3.76 (m, 12H, OCH₂), 3.94-4.04 (m, 4H, OCH₂), 6.60 (d, 3J 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, 3J 7.8 Hz, 2H, H-1, H-21). ¹³C NMR (CDCl₃): δ 21.5 (CH₃), 69.0, 69.5, 70.7, 71.1 (OCH₂), 113.9, 121.3, 124.8, 129.1 (aromat. and olefin. CH), 125.3, 138.0, 155.8 (aromat. Cq). UV (CH₂Cl₂): λmax (ε) 302 nm (7400 M⁻¹cm⁻¹).

The filtered THF solution was evaporated and the residue dissolved in 300 mL of CH₂Cl₂. The solution was washed twice with the same amount of H₂O and the dried organic phase (Na₂SO₄) evaporated. The remaining solid was recrystallized from diethylether 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. ¹H NMR (CDCl₃): δ 2.32 (s, 6H, CH₃), 3.63-3.79 (m, 8H, OCH₂), 3.94-4.04 (m, 4H, OCH₂), 4.11-4.21 (m, 4H, OCH₂), 6.70 (s, 2H, H-4, H-18), 6.76 (d, 3J 7.8 Hz, 2H, H-2, H-20), 7.31 (d, 3J 7.8 Hz, 2H, H-1, H-21), 7.35 (s, 2H, H-22, H-23). ¹³C NMR (CDCl₃): δ 21.6 (CH₃), 67.7, 69.9, 71.2, 71.5 (OCH₂), 112.9,
121.5, 128.6, 126.4 (aromat. and olefin. CH), 125.0, 138.0, 156.4 (aromat. Cq).

UV (CH2Cl2): λmax (ε) 328 nm (9800 M⁻¹cm⁻¹).

(E)-3,13-Bisbromomethyl-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclotridecenc (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 CHCl3 to reflux. After 2 h the formed succinimide was filtered off and the solvent evaporated. The residue was recrystallized from CHCl3. Yellow crystals. Yield: 7.38 g (49%), mp 186 °C. ³¹H NMR (CDCl₃): δ 3.85-3.94 (m, 4H, OCH₂), 4.10-4.20 (m, 4H, OCH₂), 4.45 (s, 4H, CH₂Br), 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 (CDCl₃): δ 33.6 (CH₂Br), 70.1, 70.9 (OCH₂), 118.0, 123.4, 126.6, 128.3 (aromat. and olefin. CH), 129.5, 137.7, 157.3 (aromat. Cq). MS (FD), m/z (%) 466, 468, 470 (100) [M]+; Br₂ pattern. Anal. Calcd for C₂₀H₂₀Br₂O₃ (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-dibenz[a,e]cyclononadecene (7b). Preparation according to 7a. The heating was extended to 5 h. Recrystallization from diethylene/CHCl₃ 2:1 gave a yellow solid, which melted at 145 °C. Yield: 2.61 g (45%) from 4.18 g (10.5 mmol) 6a. ¹³H NMR (CDCl₃): δ 3.65-3.75 (m, 8H, OCH₂), 3.93-4.03 (m, 4H, OCH₂), 4.15-4.25 (m, 4H, OCH₂), 4.47 (s, 4H, CH₂Br), 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-17). ¹³C NMR (CDCl₃): δ 33.9 (CH₂Br), 67.9, 69.8, 71.3, 71.5 (OCH₂), 112.7, 121.6, 127.5, 129.2 (aromat. and olefin. CH), 127.9, 137.8, 156.7 (aromat. Cq). MS (FD), m/z (%) 554, 556, 558 (100) [M]+; Br₂ pattern. Anal. Calcd for C₂₄H₂₈Br₂O₅ (556.3): C, 51.82; H, 5.07; Br, 28.73. Found: C, 51.44; H, 4.92; Br, 29.13.

[(E)-13-(Diethoxy-phosphorylmethyl)-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclotridecenc-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 triethylphosphate 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. ¹³H NMR (CDCl₃): δ 1.24 (t, ³J 7.3 Hz, 12H, CH₃), 3.09 (d, ³J (P,H) 21.5 Hz, 4H, CH₂P), 3.87-4.04 (m, 12H, POCH₂ and OCH₂), 4.06-4.17 (m, 4H, OCH₂), 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 (CDCl₃): δ 16.3 (CH₃), 33.7 (d, ¹J (P,C) 137.2 Hz, CH₂P), 62.2 (POCH₂), 70.2, 70.8 (OCH₂), 118.7, 124.1, 126.0, 127.9 (aromat. and olefin. CH), 128.0, 131.5, 157.2 (aromat. Cq). MS (FD), m/z (%) 582 (100) [M]+. Anal. Calcd for C₂₈H₄₀O₈P₂ (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-oxa-dibenzo[a,e]cyclononadecene-3,3-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. 1H NMR (CDCl3): δ 1.22 (t, 3J 7.3 Hz, 12H, CH3), 3.10 (d, 2J (P,H) 21.5 Hz, 4H, CH2P), 3.62-3.72 (m, 8H, OCH2), 3.90-4.07 (m, 12H, POCH2 and OCH2), 4.11-4.21 (m, 4H, OCH2), 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). 13C NMR (CDCl3): δ 16.3 (CH3), 33.8 (d, 1J (P,C) 137.3 Hz, CH2P), 62.2 (POCH2), 67.8, 69.8, 71.2, 71.5 (OCH2), 113.5, 122.3, 126.9, 128.9 (aromat. and olefin. CH), 126.3, 131.6, 156.4 (aromat. C3). MS (FD), m/z (%) 670 (100) [M]+. Anal. Calcd for: C32H48O11P2 (670.6): C, 57.31; H, 7.21. Found: C, 57.66; H, 7.06.

(E)-6,7,9,10-Tetrahydro-5,8,11-trioxa-dibenzo[a,e]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. 1H NMR (CDCl3): δ 3.89-4.00 (m, 4H, OCH2), 4.20-4.29 (m, 4H, OCH2), 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). 13C NMR (CDCl3): δ 69.8, 70.8 (OCH2), 116.3, 125.3, 128.7, 128.9 (aromat. and olefin. CH), 135.0, 136.4, 157.8 (aromat. C3), 191.3 (CHO). MS (FD), m/z (%) 338 (100) [M]+. Anal. Calcd for C20H18O5 (338.4): C, 71.00; H, 5.36. Found: C, 70.65; H, 5.60.

(E)-6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxa-dibenzo[a,e]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. 1H NMR (CDCl3): δ 3.69 (s, 8H, OCH2), 400-4.09 (m, 4H, OCH2), 4.22-4.32 (m, 4H, OCH2), 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). 13C NMR (CDCl3): δ 68.0, 69.5, 71.1, 71.5 (OCH2), 110.4, 124.2, 129.5, 129.5 (aromat. and olefin. CH), 133.3, 136.4, 157.1 (aromat. C4), 191.5 (CHO). MS (FD), m/z (%) = 426 (100) [M]+. Anal. Calcd for C24H20O7 (426.4): C, 67.59; H, 6.15. Found: C, 67.47; H, 6.03.

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% H2O) were heated in 100 mL of benzene/5 mL H2O to reflux for 24 h. After cooling to ambient temperature, 30 mL of H2O were added. The organic phase was dried (Na2SO4) and the volatile parts evaporated. The residue was dissolved in CH2Cl2 or CHCl3 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 24\(^{43,44}\) (1950 mg, 2.5 mmol), 500 mg Aliquat 336 and 500 mg (7.5 mmol) 85% KOH were heated in 200 mL of benzene/1 mL of \(\text{H}_2\text{O}\) to reflux for 24 h. After cooling to ambient temperature the reaction mixture was treated with 50 mL of \(\text{H}_2\text{O}\). The organic phase was dried (Na\(_2\text{SO}_4\)) and evaporated. Column chromatography (40×3 cm SiO\(_2\), diethylether/petroleum ether 1:2) yielded yellow crystals.

\(\text{(E,E,E)-6,7,9,10-Tetrahydro-3,13-bis[2-(4-methoxy-phenyl)vinyl]-5,8,11-trioxa-dibenzo-[a,e]cyclooctadecene (17a)}\). Method a), yield: 536 mg (49%), mp 254 °C. \(^1\text{H NMR (CDCl}_3\):} \delta 3.81 (s, 6H, \(\text{OCH}_3\)), 3.93-3.96 (m, 4H, \(\text{OCH}_2\)), 4.21-4.25 (m, 4H, \(\text{OCH}_2\)), 6.88/7.43 (AA‘BB‘, 4H, aromat. H), 6.91/7.04 (AB, \(^3\text{J} 16.4\) Hz, 4H, olefin. H), 7.11 (s, 2H, H-4, H-12), 7.16 (d, \(^3\text{J} 8.3\) Hz, 2H, H-2, H-14), 7.46 (d, \(^3\text{J} 8.3\) Hz, 2H, H-1, H-15). \(^13\text{C NMR (CDCl}_3\):} \delta 55.2 (\(\text{OCH}_3\)), 70.6, 71.4 (\(\text{OCH}_2\)), 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\(_\text{q}\)).MS (FD), \(m/z\) (%) = 546 (100) \([\text{M}^+\).UV/Vis (\(\text{CH}_2\text{Cl}_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\)) = 401 nm (56700 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{36}\)H\(_{44}\)O\(_5\) (546.7): C, 79.10; H, 6.27. Found: C, 79.20; H, 6.28.

\(\text{(E,E,E)-6,7,9,10,12,13,15,16-Octahydro-3,19-bis[2-(4-methoxy-phenyl)vinyl]-5,8,11,14,17-pentaoxa-dibenzo[a,e]cyclononadecene (17b)}\). Method a), yield: 837 mg (66%), mp 226–233 °C. \(^1\text{H NMR (CDCl}_3\):} \delta 3.68-3.72 (m, 8H, \(\text{OCH}_2\)), 3.82 (s, 6H, \(\text{OCH}_3\)), 4.02-4.09 (m, 4H, \(\text{OCH}_2\)), 4.22-4.30 (m, 4H, \(\text{OCH}_2\)), 6.88/7.44 (AA‘BB‘, 4H, aromat. H), 6.91/7.05 (AB, \(^3\text{J} 16.4\) Hz, 4H, olefin. H), 7.01 (s, 2H, H-4, H-18), 7.08 (d, \(^3\text{J} 7.3\) Hz, 2H, H-2, H-20), 7.38–7.43 (m, 2H, H-1, H-21), 7.42 (s, 2H, H-22, H-23). \(^13\text{C NMR (CDCl}_3\):} \delta 55.3 (\(\text{OCH}_3\)), 68.0, 70.0, 71.2, 71.7, (\(\text{OCH}_2\)), 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\(_\text{q}\)). MS (FD), \(m/z\) (%) = 634 (100) \([\text{M}^+\).UV/Vis (\(\text{CH}_2\text{Cl}_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\)) = 401 nm (54800 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{46}\)H\(_{48}\)O\(_7\) (634.8): C, 75.69; H, 6.67. Found: C, 74.91; H, 6.22 (incomplete combustion).

\(\text{(E,E,E)-6,7,9,10-Tetrahydro-3,13-bis[2-(3,4,5-triododecyloxyphenyl-phenyl)vinyl]-5,8,11-trioxa-dibenzo[a,e]cyclooctadecene (18a)}\). Method a), yield: 1620 mg (51%); method b), yield: 1003 mg (63%); mp 91 °C. \(^1\text{H NMR (CDCl}_3\):} \delta 0.84-0.90 (m, 18H, \(\text{CH}_3\)), 1.20-1.38 (m, 96H, \(\text{CH}_2\)), 1.40-1.50 (m, 12H, \(\text{CH}_2\)), 1.68-1.75 (m, 4H, \(\text{CH}_2\)), 1.75-1.84 (m, 8H, \(\text{CH}_2\)), 3.93-3.98 (m, 8H, \(\text{OCH}_2\)), 3.98-4.03 (m, 8H, \(\text{OCH}_2\)), 4.20-4.24 (m, 4H, \(\text{OCH}_2\)), 6.69 (s, 4H, aromat. H), 6.91/6.98 (AB, \(^3\text{J} 16.2\) Hz, 4H, olefin. H), 7.11 (s, 2H, H-4, H-12), 7.16 (d, \(^3\text{J} 8.1\) Hz, 2H, H-2, H-14), 7.46 (d, \(^3\text{J} 8.1\) Hz, 2H, H-1, H-15), 7.82 (s, 2H, H-16, H-17). \(^13\text{C NMR (CDCl}_3\):} \delta 14.0 (\(\text{CH}_3\)), 22.6, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.8 (\(\text{CH}_2\), partly superimposed), 69.3, 70.3, 70.9, 73.5 (\(\text{OCH}_2\)), 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\(_\text{q}\)). MS (FD), \(m/z\) (%) = 1592 (100) \([\text{M}^+\).UV/Vis (\(\text{CH}_2\text{Cl}_2\)): \(\lambda_{\text{max}}\) (\(\varepsilon\)) = 406 nm (55400 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{106}\)H\(_{174}\)O\(_9\) (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-pentaoxa-dibenzo[a,e]cyclonadecene (18b). Method a), yield: 1850 mg (55%); method b), yield: 825 mg (49%); mp 87 °C. 1H NMR (CDCl3): δ 0.84–0.91 (m, 18H, CH3), 1.20–1.39 (m, 96H, CH2), 1.42–1.51 (m, 12H, CH2), 1.69–1.76 (m, 4H, CH2), 1.76–1.85 (m, 8H, CH2), 3.69–3.73 (m, 4H, OCH2), 3.74–3.78 (m, 4H, OCH2), 3.93–3.98 (m, 4H, OCH2), 3.98–4.04 (m, 8H, OCH2), 4.04–4.08 (m, 4H, OCH2), 4.23–4.28 (m, 4H, OCH2), 6.70 (s, 4H, aromat. H), 6.92/6.98 (AB, 3J 16.3 Hz, 4H, olefin. H), 7.01 (s, 2H, H-4, H-18), 7.08 (d, 3J 7.8 Hz, H-2, H-20), 7.40 (d, 3J 7.8 Hz, H-2, H-1, H-21), 7.44 (s, 2H, H-22, H-23). 13C NMR (CDCl3): δ 14.0 (CH3), 22.6, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.3, 31.9 (CH2, partly superimposed), 67.9, 69.3, 70.0, 71.2, 71.7, 73.5 (OCH2), 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. Cq). MS (FD), m/z (%) = 1680 (100) [M]+; UV/Vis (CH2Cl2): λmax (ε) = 406 nm (59500 M–1cm–1). Anal. Calcd for C110H182O11 (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-trioxadibenzo[a,e]cycloptridecene (19a). Method a), yield: 1120 mg (64%), mp 188 °C. 1H NMR (CDCl3): δ 1.04–1.12 (m, 12H, CH2), 1.80–1.90 (m, 8H, CH2), 3.90–3.94 (m, 4H, OCH2), 3.94–3.96 (m, 4H, OCH2), 3.97–4.01 (m, 4H, OCH2), 4.20–4.25 (m, 4H, OCH2), 7.05/7.36 (AB, 3J 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, 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). 13C NMR (CDCl3): δ 10.5, 10.5 (CH3), 22.6, 22.6 (CH2), 70.2, 70.9, 71.2, 71.8 (OCH2), 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. Cq, partly superimposed). MS (FD), m/z (%) = 878, 876, 874 (100) [M]+; Br2 isotope pattern. UV/Vis (CH2Cl2): λmax (ε) = 412 nm (58300 M–1cm–1). Anal. Calcd for C46H52O2Br2 (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-pentaoxa-dibenzo[a,e]cyclonadecene (19b). Method a), yield: 1100 mg (57%). 1H NMR (CDCl3): δ 1.05–1.11 (m, 12H, CH3), 1.80–1.90 (m, 8H, CH2), 3.69–3.73 (m, 4H, OCH2), 3.73–3.77 (m, 4H, OCH2), 3.90–3.94 (m, 4H, OCH2), 3.94–4.02 (m, 4H, OCH2), 4.23–4.27 (m, 4H, OCH2), 7.01 (s, 2H, aromat. H), 7.07/7.36 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.07 (s, 2H, aromat. H), 7.11 (s, 2H, H-4, H-18), 7.12 (d, 3J 7.9 Hz, H-2, H-20), 7.42 (d, 3J 7.9 Hz, 2H, H-1, H-21), 7.45 (s, 2H, H-22, H-23). 13C NMR (CDCl3): δ 10.6, 10.6 (CH3), 22.7, 22.7 (CH2), 68.0, 70.0, 71.2, 71.3, 71.6, 71.9 (OCH2), 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. Cq). MS (FD), m/z (%) = 966, 964, 962 (100) [M]+; Br2 isotope pattern. UV/Vis (CH2Cl2): λmax (ε) = 412 nm (69900 M–1cm–1). Anal. Calcd for C50H50O6Br2 (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-trioxa-dibenzo[a,e]cyclotridecenc (20a). Method a), yield: 1023 mg (49%). $^1$H NMR (CDCl$_3$): $\delta$ 0.87-0.93 (m, 12H, CH$_3$), 1.25-1.40 (m, 16H, CH$_2$), 1.46-1.55 (m, 8H, CH$_2$), 1.78-1.86 (m, 8H, CH$_2$), 3.92-3.97 (m, 8H, OCH$_2$), 3.99-4.03 (m, 4H, OCH$_2$), 4.20-4.23 (m, 4H, OCH$_2$), 7.05/7.35 (AB, $^{3}J$ 16.4 Hz, 4H, olefin. H), 7.06 (s, 2H, aromat. H), 7.09 (s, 2H, aromat. H), 7.12 (s, 2H, H4, H-12), 7.19 (d, $^{3}J$ 8.0 Hz, 2H, H-2, H-14), 7.47 (d, $^{3}J$ 8.0 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H16, H-17). $^{13}$C NMR (CDCl$_3$): $\delta$ 13.9, 13.9 (CH$_3$), 22.5, 22.6, 25.6, 25.8, 29.5, 29.5, 31.5, 31.5 (CH$_2$), 69.6, 70.2, 70.3, 70.8 (OCH$_2$), 111.8, 115.1, 117.9, 121.2, 123.0, 126.2, 128.4 (aromat. and olefin. CH), 112.0, 126.6, 137.7, 149.9, 151.1, 157.1 (aromat. C$_{q}$, partly superimposed). MS (FD), $m/z$ (%) = 1042, 1044, 1046 (100) [M]$^+$, Br$_2$ isotope pattern. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) = 412 nm (67500 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{88}$H$_{76}$O$_7$Br$_2$ (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-trioxa-dibenzo[a,e]cyclotridecenc (20b). Method a), yield: 975 mg (43%), mp 120 °C. $^1$H NMR (CDCl$_3$): $\delta$ 0.84-0.96 (m, 12H, CH$_3$), 1.25-1.40 (m, 16H, CH$_2$), 1.45-1.58 (m, 8H, CH$_2$), 1.75-1.88 (m, 8H, CH$_2$), 3.67-3.78 (m, 8H, OCH$_2$), 3.90-4.00 (m, 4H, OCH$_2$), 4.00-4.09 (m, 8H, OCH$_2$), 4.20-4.29 (m, 4H, OCH$_2$), 7.01 (s, 2H, aromat. H), 7.06 (s, 2H, aromat. H), 7.07/7.35 (AB, $^{3}J$ 16.4 Hz, 4H, olefin. H), 7.10 (s, 2H, H-4, H-18), 7.13 (d, $^{3}J$ 7.9 Hz, 2H, 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$_3$): $\delta$ 14.0 (CH$_3$), 22.6, 25.7, 25.8, 29.3, 31.5 (CH$_2$, partly superimposed), 68.0, 69.7, 70.0, 70.4, 71.2, 71.7 (OCH$_2$), 110.2, 111.9, 118.0, 119.5, 123.1, 126.9, 129.0, 129.3 (aromat. and olefin. CH), 112.0, 126.7, 127.4, 137.8, 150.0, 151.2, 156.9 (aromat. C$_{q}$). MS (FD), $m/z$ (%) = 1130, 1132, 1134 (100) [M]$^+$, Br$_2$ isotope pattern. UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) = 412 nm (59100 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{62}$H$_{58}$O$_9$Br$_2$ (1133.2): C, 65.72; H, 7.47; Br, 14.10. Found: C, 65.83; H, 7.13; Br, 13.90.

(E,E,E)-3,13-Bis[2-(4-diethoxymethylphenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclotridecenc (21a). Method a), yield: 770 mg (56%), mp 204 °C. $^1$H NMR (CDCl$_3$): $\delta$ 1.23 (t, $^{3}J$ 7.4 Hz, 12H, CH$_3$), 3.49-3.66 (m, 8H, OCH$_2$CH$_3$), 3.91-3.98 (m, 4H, OCH$_2$), 4.20-4.25 (m, 4H, OCH$_2$), 5.50 (s, 2H, CH(OC$_2$H$_5$)$_2$), 7.05/7.09 (AB, $^{3}J$ 16.4 Hz, 4H, olefin. H), 7.13 (s, 2H, H-4, H-12), 7.18 (d, $^{3}J$ 8.2 Hz, 2H, H-2, H-14), 7.44/7.48 (AA'BB', 8H, aromat. H), 7.48 (d, $^{3}J$ 8.2 Hz, 2H, H-1, H-15), 7.84 (s, 2H, H-16, H-17). $^{13}$C NMR (CDCl$_3$): $\delta$ 15.2 (CH$_3$), 61.1 (OCH$_2$CH$_3$), 70.3, 71.0 (OCH$_2$), 101.4 (CH(OC$_2$H$_5$)$_2$), 115.2, 121.3, 126.3, 126.4, 127.3, 128.2, 128.4, 128.6 (aromat. and olefin. CH), 129.1, 137.4, 137.4, 138.7, 157.7 (aromat. C$_{q}$). MS (FD), $m/z$ (%) = 690 (100) [M]$^+$, UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$) = 399 nm (67300 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{44}$H$_{56}$O$_8$ (690.9): C, 76.49; H, 7.29. Found: C, 76.19; H, 7.01.
(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]cyclooctadecane (22a). Method a), yield: 830 mg (48%) yellow crystals, mp 112 °C. 1H NMR (CDCl3): δ 1.04-1.07 (m, 12H, CH3), 1.80-1.85 (m, 8H, CH2), 3.39 (s, 12H, OCH3), 3.95-3.99 (m, 12H, OCH2), 4.20-4.22 (m, 4H, OCH2), 5.62 (s, 2H, CH(OCH3)), 6.06/7.44 (AB, 16.3 Hz, 4H, olefin. H), 7.07 (s, 2H, aromat. H), 7.13 (s, 2H, H-4, H-12), 7.20 (d, 3J 8.1 Hz, 2H, H-2, H-14), 7.47 (d, 3J 8.0 Hz, 2H, H-1, H-15), 7.83 (s, 2H, H-16, H-17). 13C NMR (CDCl3): δ 10.7 (CH3), 22.8 (CH2), 54.1 (OCH3), 70.3, 70.9, 70.9, 71.1 (OCH2), 99.6 (CH(OCH3)), 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. Cα). MS (FD), m/z (%) = 866 (100) [M]+. UV (CH2Cl2): λmax (ε) = 411 nm (67000 M⁻¹cm⁻¹). Anal. Calcd for C52H66O11 (867.1): C, 72.02; 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]cyclononadecane (22b). Method a), yield: 920 mg (48%) yellow crystals, mp 251–265 °C. 1H NMR (CDCl3): δ 1.04-1.07 (m, 12H, CH3), 1.82-1.87 (m, 8H, CH2), 3.39 (s, 12H, OCH3), 3.70-3.77 (m, 8H, OCH2), 3.95-4.00 (m, 8H, OCH2), 4.02-4.07 (m, 4H, OCH2), 4.23-4.27 (m, 4H, OCH2), 5.62 (s, 2H, CH(OCH3)), 7.03 (s, 2H, H-4, H-18), 7.07/7.43 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.08, 7.08 (s, 4H, H-1, H-15), 7.12 (d, 3J 8.1 Hz, 2H, H-2, H-20), 7.41 (d, 3J 8.1 Hz, 2H, H-1, H-21), 7.44 (s, 2H, H-22, H-23). 13C NMR (CDCl3): δ 10.7 (CH3), 22.9 (CH2), 54.2 (OCH3), 68.0, 70.0, 71.0, 71.2, 71.3, 71.7 (OCH2), 99.7 (CH(OCH3)), 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. Cα). MS (FD), m/z (%) = 955 (100) [M]+. UV (CH2Cl2): λmax (ε) = 412 nm (69900 M⁻¹cm⁻¹). Anal. Calcd for C56H74O13 (955.2): C, 70.42; H, 7.81. Found: C, 69.97; H, 7.60.
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$_{90}$O$_{13}$ (1123.5): C, 72.70; H, 8.79. Found: C, 72.33; H, 8.39.

Preparation of the Dialehydes 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-trioxa-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
(E,E,E)-3,13-Bis[2-(4-formyl-2,5-dipropoxy-phenyl)vinyl]-6,7,9,10-tetrahydro-5,8,11-trioxa-dibenzo[a,e]cyclotridecene (26a). Orange crystals; yield: 129 g (83%); mp 168-176 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.07 (t, \(3J = 7.2\) Hz, 12H, CH\(_3\)), 1.82-1.92 (m, 8H, CH\(_2\)), 3.93-3.96 (m, 4H, OCH\(_2\)), 3.96 (t, \(3J = 7.3\) Hz, 4H, OCH\(_2\)), 4.06 (t, \(3J = 7.3\) Hz, 4H, OCH\(_2\)), 4.20-4.24 (m, 4H, OCH\(_2\)), 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). \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 10.6 (CH\(_3\)), 22.6, 22.7 (CH\(_2\)), 70.3, 70.8, 70.9, 71.0 (OCH\(_2\)), 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 (aromat. C\(_q\)), 189.0 (CHO). MS (FD), \(m/z\) (%) = 774 (100) [M]\(^+\). UV/Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}}\) (\(\epsilon\)) = 438 nm (58100 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{44}\)H\(_{38}\)O\(_7\) (630.5): C, 76.17; H, 6.07. Found: C, 76.53; H, 5.71.

(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. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.08 (t, \(3J = 7.2\) Hz, 12H, CH\(_3\)), 1.75-1.95 (m, 8H, CH\(_2\)), 3.65-3.78 (m, 8H, OCH\(_2\)), 3.93-4.10 (m, 12H, OCH\(_2\)), 4.20-4.22 (m, 4H, OCH\(_2\)), 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). \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 10.6, 10.5 (CH\(_3\)), 22.6 (CH\(_2\)), 68.0, 70.0, 70.7, 70.9, 71.2, 71.7 (OCH\(_2\)), 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. C\(_q\)), 189.0 (CHO). MS (FD), \(m/z\) (%) = 862 (100) [M]\(^+\). UV/Vis: \(\lambda_{\text{max}}\) (\(\epsilon\)) = 438 nm (70000 M\(^{-1}\)cm\(^{-1}\)). Anal. Calcd for C\(_{52}\)H\(_{62}\)O\(_{11}\) (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-trioxa-dibenzo[a,e]cyclotridecene (27a). Orange crystals; yield: 170 mg (90%); mp 99 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.88-0.95 (m, 12H, CH\(_3\)), 130-1.40 (m, 16H, CH\(_2\)), 1.45-1.55 (m, 8H, CH\(_2\)), 1.80-1.88 (m, 8H, CH\(_2\)), 3.93-3.98 (m, 4H, OCH\(_2\)), 3.98-4.04 (m, 4H, OCH\(_2\)), 4.06-4.12 (m, 4H, OCH\(_2\)), 4.20-4.25 (m, 4H, CH\(_2\)), 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). \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 14.0 (CH\(_3\)), 22.6, 22.6, 25.8, 25.9, 29.2, 29.2, 31.5, 31.6 (CH\(_2\)), 69.3, 69.4, 70.3, 70.9 (OCH\(_2\)), 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. C), 189.0 (CHO). MS (FD), m/z (%): = 943 (100) [M]⁺. UV/Vis: \( \lambda_{\text{max}} (\varepsilon) = 438 \text{ nm} \). Anal. Calcd for C\text{60}H\text{78}O\text{9} (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. \(^1\)H NMR (CDCl\text{3}): \( \delta \) 0.81-0.95 (m, 12H, CH\text{2}), 1.25-1.40 (m, 16H, CH\text{2}), 1.40-1.60 (m, 8H, CH\text{2}), 1.75-1.95 (m, 8H, CH\text{2}), 3.66-3.77 (m, 8H, OCH\text{2}), 3.95-4.15 (m, 12H, OCH\text{2}), 4.20-4.30 (m, 4H, OCH\text{2}), 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, \( ^3\)J 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). \(^{13}\)C NMR (CDCl\text{3}): \( \delta \) 13.9, 14.0 (CH\text{3}), 22.5, 22.6, 25.7, 25.9, 29.2, 29.2, 31.5, 31.5 (CH\text{2}), 68.0, 69.2, 69.4, 69.9, 71.2, 71.7 (OCH\text{2}), 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. C), 189.0 (CHO). MS (FD), m/z (%): = 1031 (100) [M]⁺: UV/Vis: \( \lambda_{\text{max}} (\varepsilon) = 438 \text{ nm} \). Anal. Calcd for C\text{64}H\text{86}O\text{11} (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), diphasonate 28 or 29, (10.2 mmol), 85% KOH (50 m, 0.76 mmol), 0.50 g Aliquat 336, 0.5 mL of H\text{2}O and 100 mL of benzene were heated to reflux for 24 h. H\text{2}O (10 mL) was added and the organic phase separated and evaporated. The residue was treated with 5-10 mL of CH\text{2}Cl\text{2}. 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 CH\text{2}Cl\text{2} contained higher oligomers).

\((E,E,E,E)\)-PV-Tetramer 30a. Yield: 21 mg (11%) red solid, mp 275-280 °C. \(^1\)H NMR (CD\text{2}Cl\text{2}): \( \delta \) 1.14 (t, \( ^3\)J = 7.6 Hz, 6H, CH\text{3}), 1.87-1.95 (m, 4H, CH\text{2}), 3.92-4.10 (m, 12H, OCH\text{2}), 4.18-4.29 (m, 8H, OCH\text{2}), 7.13-7.25 (m, 6H, aromat. and olefin. H), 7.25-7.33 (d, \( ^3\)J 8.2 Hz, 2H, aromat. H), 7.49 (s, 2H, aromat. H), 7.53 (d, \( ^3\)J 16.2 Hz, 2H, olefin. H), 7.54 (d, \( ^3\)J 7.9 Hz, 2H, aromat. H), 7.57 (d, \( ^3\)J 7.9 Hz, 2H, aromat. H), 7.65 (d, \( ^3\)J 7.9 Hz, 2H, aromat. H), 7.79 (d, \( ^3\)J 16.7 Hz, 2H, olefin. H), 8.13 (d, \( ^3\)J 16.7 Hz, 2H, olefin. H), 9.93 (s, 2H, CHO). \(^{13}\)C NMR (CDCl\text{3}): \( \delta \) 11.0 (CH\text{3}), 23.3 (CH\text{2}), 70.4, 70.7, 71.1, 71.6, 71.8 (OCH\text{2}), 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. C), 191.5 (CHO). MS (FD), m/z (%): = 946 (100) [M]⁺: UV/Vis (CH\text{2}Cl\text{2}): \( \lambda_{\text{max}} (\varepsilon) = 447 \text{ nm} \). Anal. Calcd for C\text{60}H\text{66}O\text{10} (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. \(^1\)H NMR (CDCl\text{3}): \( \delta \) 1.12 (t, \( ^3\)J = 7.6 Hz, 6H, CH\text{3}), 1.82-2.00 (m, 4H, CH\text{2}), 3.63-3.79 (m, 16H, OCH\text{2}), 3.95-4.10 (m, 12H, OCH\text{2}), 4.20-4.32 (m, 8H, OCH\text{2}), 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$_3$): $\delta$ 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$_2$): $\lambda_{\text{max}}$ (\(\varepsilon\)) $= 443$ 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$_3$): $\delta$ 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, $^3J$ 6.4 Hz, 4H, OCH$_2$), 4.20-4.27 (m, 8H, OCH$_2$), 7.10/7.48 (AB, $^3J$ 16.4 Hz, 4H, olefin. H), 7.10 (s, 2H, aromat. H), 7.18 (s, 2H, aromat. H), 7.23-7.27 (m, 2H, aromat. H), 7.46 (s, 2H, aromat. H), 7.50 (d, $^3J$ 8.8 Hz, 2H, aromat. H), 7.53 (d, $^3J$ 8.2 Hz, 2H, aromat. H), 7.60 (d, $^3J$ 7.9 Hz, 2H, aromat. H), 7.72/8.16 (AB, $^3J$ 16.7 Hz, 4H, olefin. H), 9.94 (s, 2H, CHO). $^{13}$C NMR (CDCl$_3$): $\delta$ 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$_2$): $\lambda_{\text{max}}$ (\(\varepsilon\)) $= 447$ nm (100900 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{60}$H$_{66}$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$_3$): $\delta$ 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, $^3J$ = 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, $^3J$ 16.4 Hz, 4H, olefin. H), 7.11 (s, 2H, aromat. H), 7.15 (d, $^3J$ 8.2 Hz, 2H, aromat. H), 7.38 (s, 2H, aromat. H), 7.40 (d, $^3J$ 8.2 Hz, 2H, aromat. H), 7.42-7.46 (m, 2H, aromat. H), 7.48/7.57 (AB, $^3J$ 16.4 Hz, 4H, olefin. H), 7.60 (d, $^3J$ 7.8 Hz, 2H, aromat. H), 9.92 (s, 2H, CHO). $^{13}$C NMR (CDCl$_3$): $\delta$ 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$_2$): $\lambda_{\text{max}}$ (\(\varepsilon\)) $= 443$ 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), diphenonate 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$_2$): $\delta$ 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): λ_max (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.

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References

   http://dx.doi.org/10.1021/cr100052z, PMid:20583837
   http://dx.doi.org/10.1039/b609383c, PMid:17180218
   http://dx.doi.org/10.1002/anie.200461146, PMid:15846835
   http://dx.doi.org/10.1351/pac200476071409
   http://dx.doi.org/10.1039/b004407p
   http://dx.doi.org/10.1002/(SICI)1521-3773(19990517)38:10<1350::AID-ANIE1350>3.0.CO;2-6
   http://dx.doi.org/10.1007/3-540-49451-0_5
   http://dx.doi.org/10.1002/9783527603220
   http://dx.doi.org/10.1016/S0040-4039(00)87178-6
   http://dx.doi.org/10.1021/jo00183a026
   http://dx.doi.org/10.1002/jlac.199419941211
[http://dx.doi.org/10.1002/anie.199702781](http://dx.doi.org/10.1002/anie.199702781)

[http://dx.doi.org/10.1002/anie.19970611](http://dx.doi.org/10.1002/anie.19970611)

[http://dx.doi.org/10.1021/jo980920o](http://dx.doi.org/10.1021/jo980920o)

[http://dx.doi.org/10.1016/j.tet.2005.05.043](http://dx.doi.org/10.1016/j.tet.2005.05.043)

[http://dx.doi.org/10.1021/ja907711a](http://dx.doi.org/10.1021/ja907711a), PMid:19813746

[http://dx.doi.org/10.1016/j.catcom.2012.02.007](http://dx.doi.org/10.1016/j.catcom.2012.02.007)

[http://dx.doi.org/10.1139/v02-003](http://dx.doi.org/10.1139/v02-003)

[http://dx.doi.org/10.1016/j.tet.2009.07.028](http://dx.doi.org/10.1016/j.tet.2009.07.028)

38. Commercially available.

[http://dx.doi.org/10.1002/(SICI)1521-3897(199907)341:5<466::AID-PRAC466>3.0.CO;2-V](http://dx.doi.org/10.1002/(SICI)1521-3897(199907)341:5<466::AID-PRAC466>3.0.CO;2-V)

[http://dx.doi.org/10.1002/(SICI)1521-3897(199907)341:5<466::AID-PRAC466>3.0.CO;2-V](http://dx.doi.org/10.1002/(SICI)1521-3897(199907)341:5<466::AID-PRAC466>3.0.CO;2-V)

[http://dx.doi.org/10.1016/j.tet.2004.06.012](http://dx.doi.org/10.1016/j.tet.2004.06.012)

[http://dx.doi.org/10.1021/ol0060329](http://dx.doi.org/10.1021/ol0060329), PMid:10930260

[http://dx.doi.org/10.1016/S0040-4020(99)00823-6](http://dx.doi.org/10.1016/S0040-4020(99)00823-6)

[http://dx.doi.org/10.1002/ezoc.200900290](http://dx.doi.org/10.1002/ezoc.200900290)

[http://dx.doi.org/10.1002/ezoc.200701046](http://dx.doi.org/10.1002/ezoc.200701046)

[http://dx.doi.org/10.1021/ol061594z](http://dx.doi.org/10.1021/ol061594z), PMid:16928080
   http://dx.doi.org/10.1002/1099-0690(200206)2002:11<1745::AID-EJOC1745>3.0.CO;2-I
   http://dx.doi.org/10.1002/poc.811