

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-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.

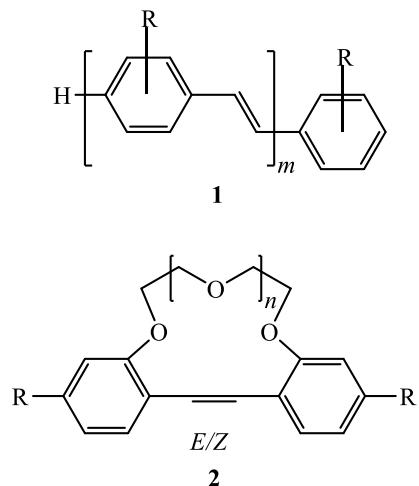
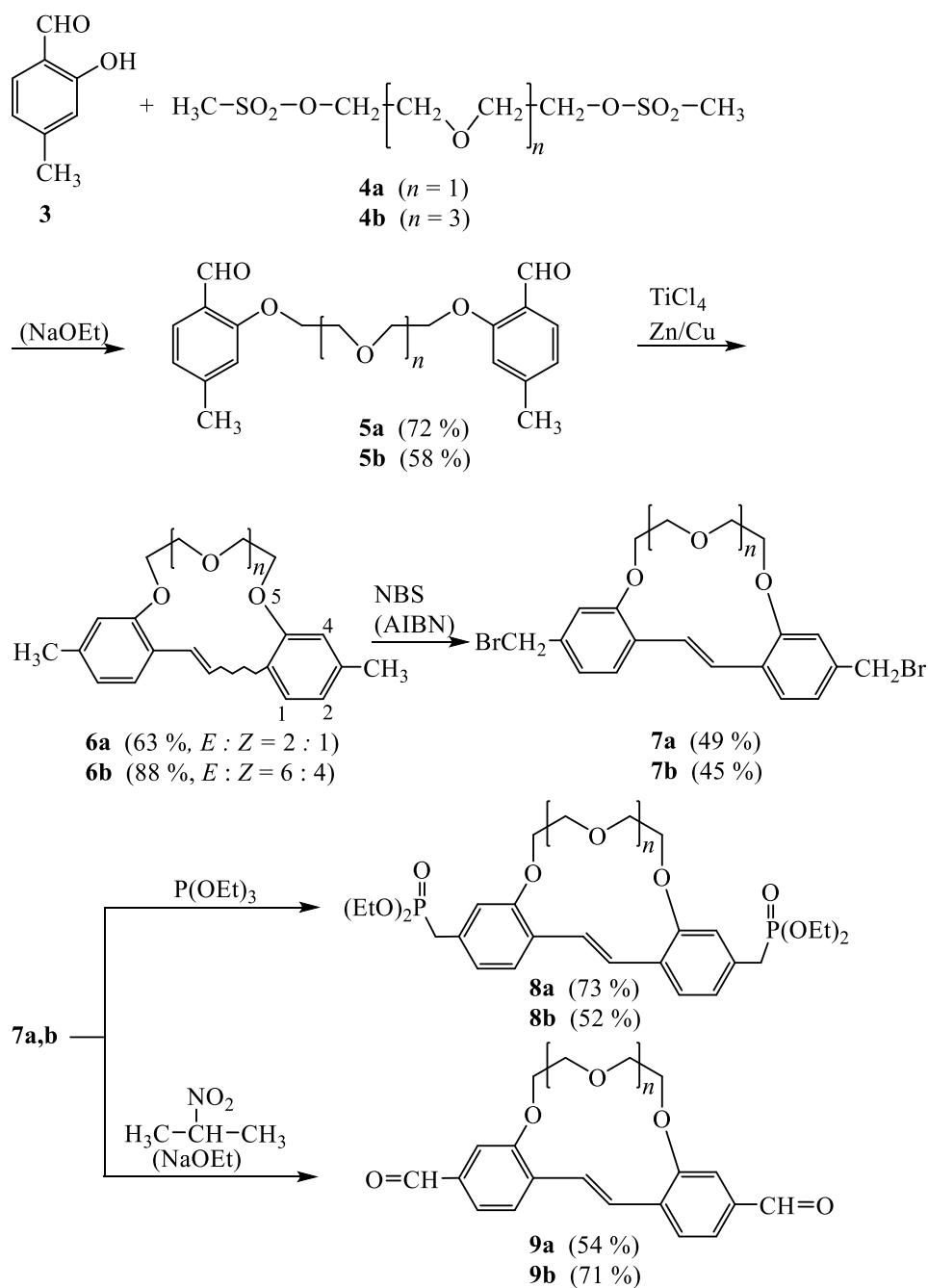


Figure 1. OPVs **1** ($m = 2,3,\dots$) and stilbene crowns **2** ($n = 1,2,3,\dots$).

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.³³ 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 ($S_0 \rightarrow S_1$).

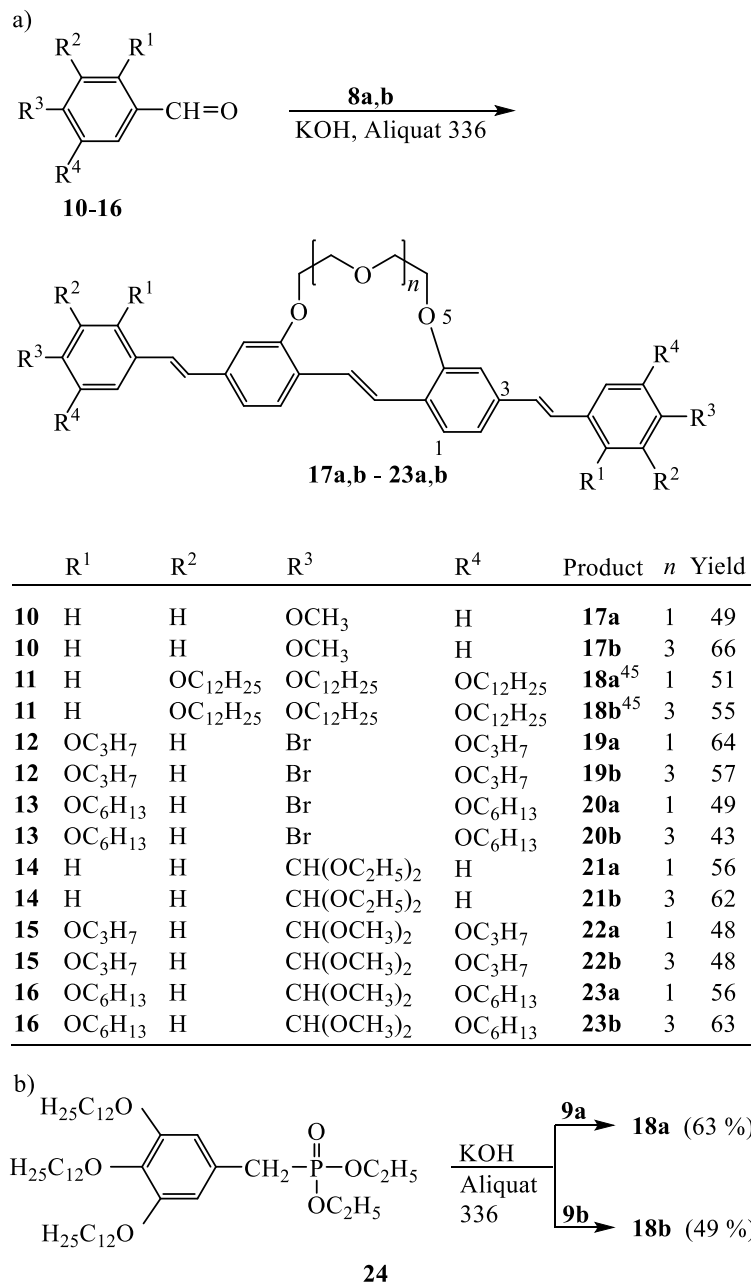
Results and Discussion

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.^{26,27} and improved by Merz et al.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 diphosphonates **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.

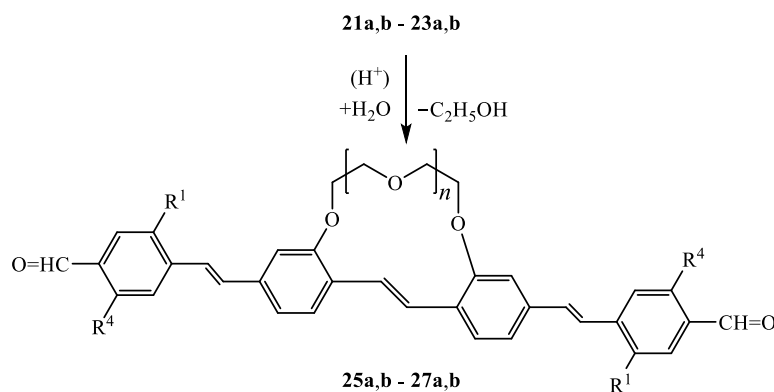
Twofold Wittig-Horner reactions of **8a,b** and the substituted benzaldehydes **10**³⁸, **11**³⁹, **12**⁴⁰, **13**⁴¹, **14**⁴², **15**⁴⁰, **16**⁴¹ led to an extension of the conjugated chain in the all-*trans* configured 4,4'-distyrylstilbenes **17a,b–23a,b**. Phase-transfer catalysis with Aliquat 336 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**^{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_{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).

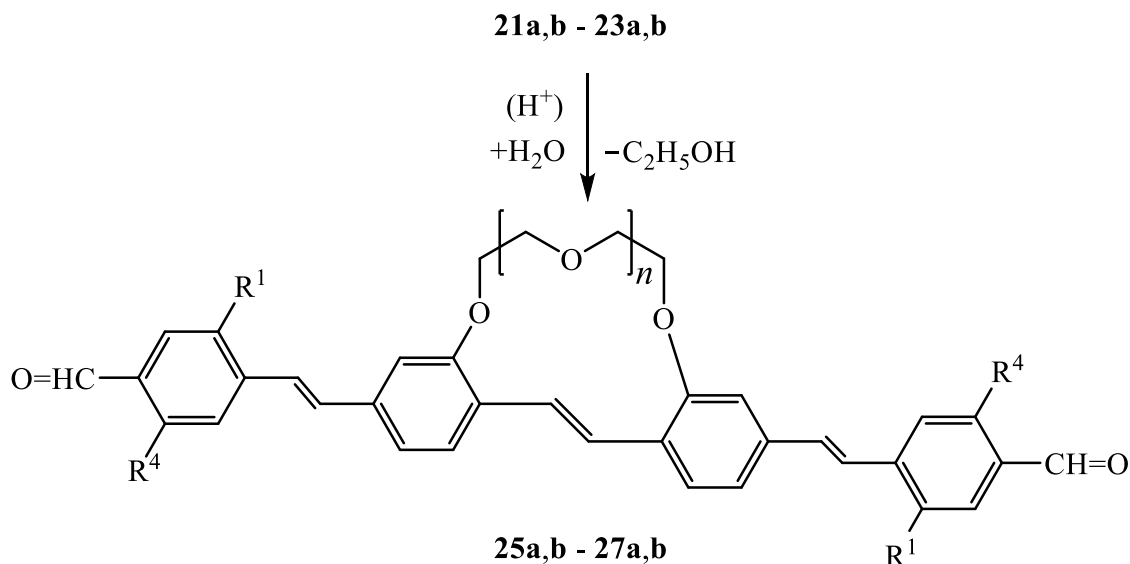


Product	R ¹	R ⁴	<i>n</i>	Yield [%]
25a	H	H	1	86
25b	H	H	3	86
26a	OC ₃ H ₇	OC ₃ H ₇	1	83
26b	OC ₃ H ₇	OC ₃ H ₇	3	89
27a	OC ₆ H ₁₃	OC ₆ H ₁₃	1	90
27b	OC ₆ H ₁₃	OC ₆ H ₁₃	3	93

Scheme 3. Cleavage of acetals **21a,b-23a,b**→**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.^{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**⁴⁸ and **29**⁴⁹ and reacted them with an excess amount of **9a,b** (Scheme 4). The portion, which was soluble in CH₂Cl₂, 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.



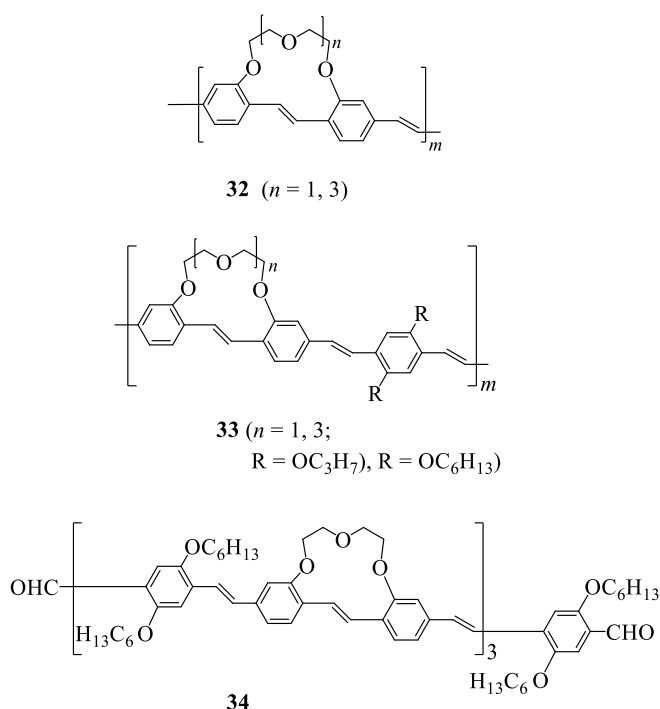
Product	R ¹	R ⁴	<i>n</i>	Yield [%]
25a	H	H	1	86
25b	H	H	3	86
26a	OC ₃ H ₇	OC ₃ H ₇	1	83
26b	OC ₃ H ₇	OC ₃ H ₇	3	89
27a	OC ₆ H ₁₃	OC ₆ H ₁₃	1	90
27b	OC ₆ H ₁₃	OC ₆ H ₁₃	3	93

Scheme 4. Synthesis of double stilbene crowns connected by a 1,4-divinylene-phenylene 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 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 $\text{C}_{140}\text{H}_{174}\text{O}_{19}$.

All monodisperse OPVs bearing crown ether units were characterized by their ^1H and ^{13}C NMR data and by MS spectra. Their electronic excitation resembles that of alkoxy substituted oligo(1,4-phenylenevinylene)s.^{16,50} The trimers **17–23** and **25–27** have in CH_2Cl_2 λ_{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.



Scheme 5. Higher OPVs containing (*E*)-stilbene crown ether structures.

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. ^1H 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-ethanediylloxy)]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. ^1H NMR (CDCl_3): δ 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): δ 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) $[\text{M}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5$ (342.4): C, 70.16; H, 6.41. Found: C, 70.06; H, 6.51.

2,2'-[Oxybis(2,1-ethanediylloxy-2,1-ethanediylloxy)]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. ^1H NMR (CDCl_3): δ 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): δ 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) $[\text{M}]^+$. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_7$ (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-trioxa-dibenzo[*a,e*]cyclotridecene (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_2CO_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

(%) 310 (100) $[M]^+$. Anal. Calcd for $C_{20}H_{22}O_3$ (310.4): C, 77.39; H, 7.14. Found: C, 77.31; H, 7.18.

The separation of the stereoisomers was possible by column chromatography (SiO_2 , CH_2Cl_2), but the next step could be made with the *E/Z* mixture as well.

(E)-6a: Colorless powder, mp 136 °C. 1H NMR ($CDCl_3$): δ 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, 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). ^{13}C NMR ($CDCl_3$): δ 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_2Cl_2): λ_{max} (ϵ) 328 nm (20100 $M^{-1}cm^{-1}$).

(Z)-6a: Oil. 1H NMR ($CDCl_3$): δ 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, 3J 7.6 Hz, 2H, H-1, H-15). ^{13}C NMR ($CDCl_3$): δ 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_2Cl_2): λ_{max} (ϵ) 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 $C_{24}H_{30}O_5$ (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_2Cl_2 . The organic phase was dried (Na_2SO_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. 1H NMR ($CDCl_3$): δ 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, 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). ^{13}C NMR ($CDCl_3$): δ 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_2Cl_2): λ_{max} (ϵ) 302 nm (7400 $M^{-1}cm^{-1}$).

The filtered THF solution was evaporated and the residue dissolved in 300 mL of CH_2Cl_2 . The solution was washed twice with the same amount of H_2O and the dried organic phase (Na_2SO_4) 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 ($CDCl_3$): δ 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, 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). ^{13}C NMR ($CDCl_3$): δ 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 (CH₂Cl₂): 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]cyclotridecene (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 CCl₄ 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. ¹H 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, ³*J* 7.9 Hz, 2H, H-2, H-14), 7.42 (d, ³*J* 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. C_q). 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-dibenzo[a,e]cyclo-nonadecene (7b). Preparation according to **7a**. The heating was extended to 5 h. Recrystallization from diethylether/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**. ¹H 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, ³*J* 7.7 Hz, 2H, H-2, H-20), 7.35 (d, ³*J* 7.7 Hz, 2H, H-1, H-21), 7.37 (s, 2H, H-22, H-23). 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. C_q). 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]cyclo-tridecene-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 (CDCl₃): δ 1.24 (t, ³*J* 7.3 Hz, 12H, CH₃), 3.09 (d, ²*J* (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, ³*J* 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, ¹*J* (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. C_q). MS (FD), *m/z* (%) 582 (100) [M]⁺. Anal. Calcd for C₂₈H₄₀O₉P₂ (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-pentaoxa-dibenzo[a,e]cyclononadecene-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. C_q). 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. C_q), 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), 4.00-4.09 (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. C_q), 191.5 (CHO). MS (FD), *m/z* (%) = 426 (100) [M]⁺. Anal. Calcd for C₂₄H₂₆O₇ (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 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-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, OCH₃), 3.93-3.96 (m, 4H, OCH₂), 4.21-4.25 (m, 4H, OCH₂), 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), 7.82 (s, 2H, H-16, H-17). ¹³C NMR (CDCl₃): δ 55.2 (OCH₃), 70.6, 71.4 (OCH₂), 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_q). MS (FD), *m/z* (%) = 546 (100) [M]⁺. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 401 nm (56700 M⁻¹cm⁻¹). Anal. Calcd for C₃₆H₃₄O₅ (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-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, OCH₂), 3.82 (s, 6H, OCH₃), 4.02-4.09 (m, 4H, OCH₂), 4.22-4.30 (m, 4H, OCH₂), 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 (OCH₃), 68.0, 70.0, 71.2, 71.7, (OCH₂), 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_q). MS (FD), *m/z* (%) = 634 (100) [M]⁺. UV/Vis (CH₂Cl₂): λ_{max} (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-Tetrahydro-3,13-bis[2-(3,4,5-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, OCH₂), 3.98-4.03 (m, 8H, OCH₂), 4.20-4.24 (m, 4H, OCH₂), 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 (OCH₂), 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_q). MS (FD), *m/z* (%) = 1592 (100) [M]⁺. UV/Vis (CH₂Cl₂): λ_{max} (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-pentaoxa-dibenzo[*a,e*]cyclononadecene (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, 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). 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. C_q). MS (FD), *m/z* (%) = 1680 (100) [M]⁺. UV/Vis (CH₂Cl₂): λ_{max} (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-trioxa-dibenzo[*a,e*]cyclotridecene (19a). Method a), yield: 1120 mg (64%), mp 188 °C. ¹H NMR (CDCl₃): δ 1.04–1.12 (m, 12H, CH₃), 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, 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). 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. C_q, partly superimposed). MS (FD), *m/z* (%) = 878, 876, 874 (100) [M]⁺; Br₂ isotope pattern. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 412 nm (58300 M⁻¹cm⁻¹). Anal. Calcd for C₄₆H₅₂O₇Br₂ (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*]cyclononadecene (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), 3.98–4.02 (m, 4H, OCH₂), 4.02–4.07 (m, 4H, OCH₂), 4.23–4.27 (m, 4H, OCH₂), 7.01 (s, 2H, aromat. H), 7.07/7.36 (AB, ³*J* 16.4 Hz, 4H, olefin. H), 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). 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. C_q). MS (FD), *m/z* (%) = 966, 964, 962 (100) [M]⁺; Br₂ isotope pattern. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 412 nm (69900 M⁻¹cm⁻¹). Anal. Calcd for C₅₀H₆₀O₉Br₂ (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*]cyclotridecene (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, ³*J* 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, 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, 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, 128.1, 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]⁺, Br₂ isotope pattern. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 412 nm (67500 M⁻¹cm⁻¹). Anal. Calcd for C₅₈H₇₆O₇Br₂ (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-bromo-2,5-dihexyloxyphenyl)vinyl]-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-dibenzo[*a,e*]cyclononadecene (20b). Method a), yield: 975 mg (43%), mp 120 °C. ¹H NMR (CDCl₃): δ 0.84-0.96 (m, 12H, CH₃), 1.25-1.40 (m, 16H, CH₂), 1.45-1.58 (m, 8H, CH₂), 1.75-1.88 (m, 8H, CH₂), 3.67-3.78 (m, 8H, OCH₂), 3.90-4.00 (m, 4H, OCH₂), 4.00-4.09 (m, 8H, OCH₂), 4.20-4.29 (m, 4H, OCH₂), 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). ¹³C NMR (CDCl₃): δ 14.0 (CH₃), 22.6, 25.7, 25.8, 29.3, 31.5 (CH₂, partly superimposed), 68.0, 69.7, 70.0, 70.4, 71.2, 71.7 (OCH₂), 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]⁺, Br₂ isotope pattern. UV/Vis (CH₂Cl₂): λ_{max} (ε) = 412 nm (59100 M⁻¹cm⁻¹). Anal. Calcd for C₆₂H₈₄O₉Br₂ (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*]cyclotridecene (21a). Method a), yield: 770 mg (56%), mp 204 °C. ¹H NMR (CDCl₃): δ 1.23 (t, ³*J* 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(OC₂H₅)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). ¹³C NMR (CDCl₃): δ 15.2 (CH₃), 61.1 (OCH₂CH₃), 70.3, 71.0 (OCH₂), 101.4 (CH(OC₂H₅)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 (CH₂Cl₂): λ_{max} (ε) = 399 nm (67300 M⁻¹cm⁻¹). Anal. Calcd for C₄₄H₅₀O₇ (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. ^1H NMR (CDCl_3): δ 1.24 (t, 3J 7.4 Hz, 12H, CH_3), 3.46-3.67 (m, 8H, OCH_2CH_3), 3.67-3.79 (m, 8H, OCH_2), 4.01-4.10 (m, 4H, OCH_2), 4.22-4.30 (m, 4H, OCH_2), 5.50 (s, 2H, $\text{CH}(\text{OC}_2\text{H}_5)_2$), 7.03 (s, 2H, H-4, H-18), 7.08 (s, 4H, olefin. H), 7.11 (d, 3J 8.2 Hz, 2H, H-2, H-20), 7.42 (d, 3J 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_2CH_3), 68.1, 70.0, 71.3, 71.7 (OCH_2), 101.4 ($\text{CH}(\text{OC}_2\text{H}_5)_2$), 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_q). MS (FD), m/z (%) = 778 (100) $[\text{M}]^+$. UV (CH_2Cl_2): λ_{max} (ϵ) = 399 nm ($71400 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{O}_9$ (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*]cyclotridecene (22a). Method a), yield: 830 mg (48%) yellow crystals, mp 112 °C. ^1H 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, $\text{CH}(\text{OCH}_3)_2$), 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, 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). ^{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 ($\text{CH}(\text{OCH}_3)_2$), 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_q). MS (FD), m/z (%) = 866 (100) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 411 nm ($67000 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{52}\text{H}_{66}\text{O}_{11}$ (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-dipropoxy-phenyl)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. ^1H 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, $\text{CH}(\text{OCH}_3)_2$), 7.03 (s, 2H, H-4, H-18), 7.07/7.43 (AB, 3J 16.4 Hz, 4H, olefin. H), 7.08, 7.08 (2 s, 4H, aromat. H), 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). ^{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 ($\text{CH}(\text{OCH}_3)_2$), 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_q). MS (FD), m/z (%) = 955 (100) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 412 nm ($69900 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{56}\text{H}_{74}\text{O}_{13}$ (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*]cyclotridecene (23a). Method a), yield: 1160 mg (56%) yellow crystals, mp 93–96 °C. ^1H 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, $\text{CH}(\text{OCH}_3)_2$),

7.05/7.43 (AB, 3J 16.2 Hz, 4H, olefin. H), 7.07 (s, 4H, arom. 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 ($\text{CH}(\text{OCH}_3)_2$), 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 411 nm ($67100 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{64}\text{H}_{90}\text{O}_{11}$ (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. ^1H 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, $\text{CH}(\text{OCH}_3)_2$), 7.02 (s, 2H, H-4, H-18), 7.07, 7.08 (2s, 4H, arom. 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 ($\text{CH}(\text{OCH}_3)_2$), 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 411 nm ($62000 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{68}\text{H}_{98}\text{O}_{13}$ (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_2SO_4) and evaporated. A saturated solution of the residue in CH_2Cl_2 was then slowly dropped into a mixture of petroleum ether (bp 40-70 °C) and diethylether (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. ^1H 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, arom. 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 421 nm ($69300 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{O}_5$ (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. ^1H NMR (CD_2Cl_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, arom. H), 9.98 (s, 2H, CHO). ^{13}C NMR (CD_2Cl_2): 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. C_q), 191.8 (CHO). MS (FD), m/z (%) = 630 (100) [M]⁺. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 421 nm (55000 M⁻¹cm⁻¹). Anal. Calcd 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-trioxa-dibenzo[a,e]cyclotridecene (26a). Orange crystals; yield: 129 g (83%); mp 168-176 °C. ^1H NMR (CDCl_3): 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, arom. 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, arom. 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): 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. C_q), 189.0 (CHO). MS (FD), m/z (%) = 774 (100) [M]⁺. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 438 nm (58100 M⁻¹cm⁻¹). Anal. Calcd for C₄₈H₅₄O₉ (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 (CDCl_3): 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, arom. H), 7.21/7.45 (AB, 3J 16.2 Hz, 4H, olefin. H), 7.31 (s, 2H, arom. H), 7.39-7.51 (m, 2H, H-1, H-21), 7.47 (s, 2H, H-22, H-23). ^{13}C NMR (CDCl_3): δ 10.6, 10.5 (CH₃), 22.6 (CH₂), 68.0, 70.0, 70.7, 70.9, 71.2, 71.7 (OCH₂), 110.5, 110.5, 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: λ_{max} (ϵ) = 438 nm (70000 M⁻¹cm⁻¹). Anal. Calcd 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-trioxa-dibenzo[a,e]cyclotridecene (27a). Orange crystals; yield: 170 mg (90%); mp 99 °C. ^1H NMR (CDCl_3): δ 0.88-0.95 (m, 12H, CH₃), 1.30-1.40 (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, arom. 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, arom. 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): 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. C_q), 189.0 (CHO). MS (FD), m/z (%) = 943 (100) [M]⁺. UV/Vis: λ_{\max} (ϵ) = 438 nm (66400 M⁻¹cm⁻¹). Anal. Calcd 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, CH₃), 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, 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). 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. C_q), 189.0 (CHO). MS (FD), m/z (%) = 1031 (100) [M]⁺. UV/Vis: λ_{\max} (ϵ) = 438 nm (73900 M⁻¹cm⁻¹). Anal. Calcd for C₆₄H₈₆O₁₁ (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), diphosphonate **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, ³*J* = 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, 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). 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. C_q), 191.5 (CHO). MS (FD), m/z (%) = 946 (100) [M]⁺. UV/Vis (CH₂Cl₂): λ_{\max} (ϵ) = 447 nm (104300 M⁻¹cm⁻¹). Anal. Calcd 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, ³*J* = 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, 71.2, 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 443 nm ($111500 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{62}\text{H}_{70}\text{O}_{14}$ (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. ^1H 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, 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): 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 447 nm ($100900 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{60}\text{H}_{66}\text{O}_{10}$ (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. ^1H 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, 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): 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) $[\text{M}]^+$. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 443 nm ($108200 \text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd for $\text{C}_{68}\text{H}_{82}\text{O}_{14}$ (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), diphosphonate **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_2O for 3 d. After the addition of 50 mL of H_2O , 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. ^1H NMR (CD_2Cl_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): 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.

Acknowledgements

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

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